VII. Mikroskopisk teori för supraledning

Vi har hittills betraktat grundläggande egenskaper hos supraledare och gjort oss en "makroskopisk" modell. Dvs. vi har betraktat elektronsystemet som ett stort korrelerat kondensat, för vilket vi kunnat teckna en vågfunktion. Men vi vet ej i detalj varför vi får detta kondensat (eller hur vi skall påverka dess uppkomst). För att lösa detta problem måste vi gå ned till mikroskopisk skala. Egentligen skulle vi betrakta varje elektron (ca 10^{23} st i ett makroskopiskt stycke) och införa växelverkningar med joner, gittersvängningar och alla andra elektroner och ev. övriga partiklar. Men detta är ett formidabelt evighetsjobb; för att få hanterliga uttryck måste vi ha en fiffig modell. Vi skall nu diskutera en sådan mikroskopisk modell, BCS-modellen. Först väljer vi emellertid ut några experimentella fakta, som skall vägleda oss i vårt modellval (dvs. med kunskap av vad vi vill ha vaskar vi fram vad som passar). Sedan betraktar vi två elektroner, som fattat tycke för varandra (attraktion). Detta tycke (vars natur vi diskuterar) utvidgar vi sedan till att gälla ett gigantiskt gruppäktenskap av korrelerade elektroner. Nu kan vi egentligen komma fram direkt till vår makroskopiska vågfunktion, men först studerar vi några av systemets egenskaper experimentellt. Sådana studier ger upphov till avsevärda teoretiska förfiningar.

VII.1 Egenskaper som leder till modellval

Låt oss först repetera några egenskaper som bidrager till en förståelse av supraledningens natur, till uppställandet av en mikroskopisk modell.

Kondensation, elektronpar

$p_s = 0$

$e^* = 2e$

Vi såg i Londons modell hur vi fick en kondensation av laddningsbärare till lägsta momenttillståndet. Mätning av kvantiserat flöde ger att laddningsbärarna har laddningen 2 x fria elektronladdningen.

Koherenslängd

$\xi_0 \approx 10^{-6}$ m

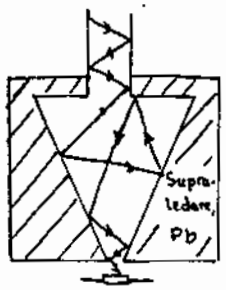
Ginzburg-Landaus och Pippards teorier ger en koherenslängd ξ. Uppskattningar av ytenergi i intermediära tillståndet gav $\xi_0 \approx 10^{-4}$ cm. Resistansen försvinner språngartat vid T_c, vilket tyder på att många elektroner, inom ett stort område, samverkar kollektivt. Superponerade skikt av supraledande och icke-supraledande filmer visar, att T_c hos supraledaren minskar, då supraledarens tjocklek $\lesssim \xi$. Heisenbergs osäkerhetsrelation ger även en utsträckning av elektronvågfunktionen. Hur?

Δ

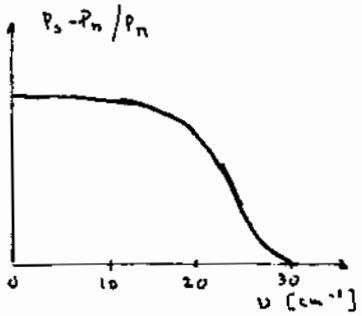
Energigap

Flera experiment indikerar ett energigap i excitationsspektrat från ett supraledande kondensat. Specifika värmet uppvisar ett exponentiellt temperaturberoende, $C_{el,s} \sim \exp(-1.44\, T_c/T)$ (jfr. temperaturberoendet hos halvledare). Värmeledningsförmågan i det supraledande tillståndet jämfört med den i det normala hos en ren metall visar ett liknande temperaturberoende. Mäter vi förlusterna vid högfrekvensstrålning mot en supraledare, finner vi en resistiv komponent vid höga frekvenser. Ju mer frekvensen ökar, ju större blir förlusterna. I det infraröda området är resistansen hos en supraledare lika med den i det normala tillståndet. I det optiska området har supraledaren samma egenskaper som motsvarande normal metall, de ser likadana ut. Låt oss studera strålning, som

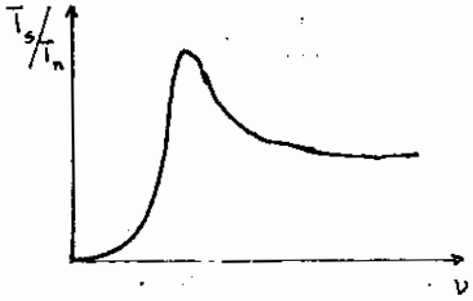
reflekteras i en supraledande "tratt" mot en strålningsdetektor och mäta den effekt som kommer fram till detektorn.



Förhållandet mellan ej absorberad energi i supraledande tillstånd jämfört med i normalt tillstånd har vidstående frekvensberoende:



Vi kan även mäta strålning som tränger genom en film och finner följande förhållande mellan transmitterad strålning i supraledande resp. normalt tillstånd:



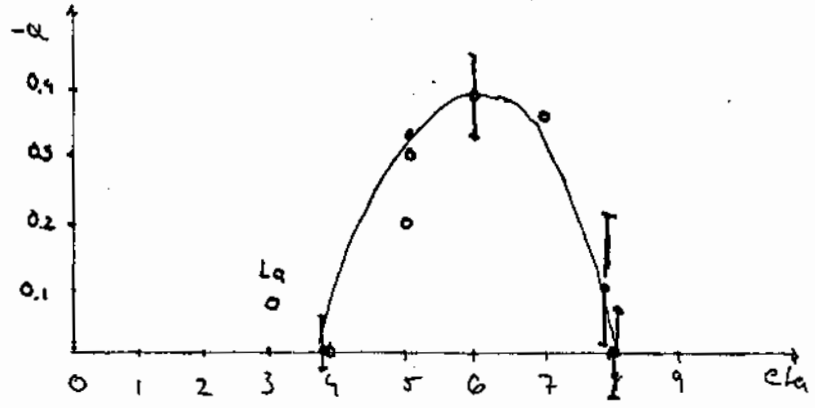
För Pb har rapporterats en s.k. "precursor", struktur vid lägre frekvenser. Detta tycks dock härstamma från experimentanordningen.

Tunneleffekter ger även gap, detta återkommer vi till senare

Isotopeffekt

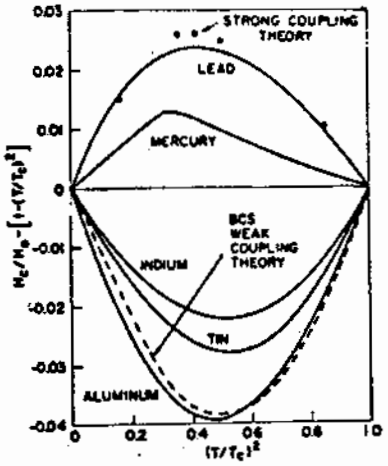
$T_c \sim \frac{1}{\sqrt{M}}$

Många supraledande grundämnen uppträder med flera isotopmassor, M. En bestämning av T_c för olika Hg-isotoper gav $T_c \sim 1/\sqrt{M}$ Många andra grundämnen har undersökts sedan dess - man finner $T_c \sim M^{\alpha}$, där α för de flesta icke-övergångsmetaller är -0.5. Undersöker man däremot övergångsmetaller finner man att α i allmänhet $\neq -0.5$. Man kan t.o.m. erhålla $\alpha = 0$.



Hur mäter man lämpligen T_c noggrannt för olika isotoper? Ett biresultat ger att H_{c0} också varierar med isotopmassan. Noggranna mätningar ger också att

$$H_c \neq H_{c0}\left(1-(T/T_c)^2\right)$$



Isotopeffekten, åtminstone i icke-övergångsmetaller, tyder på att fononer är inblandade i supraledning. Gittersvängningar har ju en frekvens $\omega \sim 1/\sqrt{M}$ (åtminstone i första approximationen). Ett annat tecken på att gittersvängningarna är betydelsefulla är faktumet att supraledare med höga T_c ofta är sådana ledare, som vid rumstemperatur har höga resistanser, dvs. en stark elektron-fonon-koppling.

VII.2 Strategi för modellval

Välj rätt
ψ
H
o. minimera
$\langle\psi|H|\psi\rangle$

Vi söker en modell för ett tillstånd, vars energi skiljer sig mycket litet från det normala tillståndets. Kondensationsenergin per elektron är inte större än 10^{-8} av den kinetiska energin, ε_F, för en typisk "fri" elektron i en normal metall. Vi söker en vågfunktion för detta tillstånd, ψ, samt motsvarande Hamiltonoperator för att söka det minsta egenvärdet, vi varierar således $\langle\psi|H|\psi\rangle$. För att ta hänsyn till den relativt lilla energiskillnaden mellan de normala och supraledande tillstånden bör ψ vara av sådan form att den redan innehålla växelverkningar i det normala tillståndet. Då behöver man endast betrakta en reducerad H-operator, som representerar skillnaden mellan de två tillstånden.

VII.3 Coopers problem - ett par

Vi skall nu försöka göra det troligt, att par av elektroner uppträder i supraledning (när vi mätte kvantiserat flöde fann vi en partikelladdning lika med dubbla elektronladdningen 2e, så vi känner oss kanske redan övertygade). Vår behandling blir ej fullständig (för en bättre behandling hänvisas till J.R. Schrieffer, "Theory of Superconductivity", Benjamin, 1964, eller G. Rickayzen, "Theory of Superconductivity", Interscience (1965)). Vi vet att många elektroner växelverkar inom ett koherensområde, men låt oss inte tänka på det utan betrakta ett enda elektronpar och bara ta hänsyn till växelverkningar mellan dessa två elektroner. Bakgrundselektroner deltar bara genom att blockera tillstånd under Fermiytan p.g.a. Pauliprincipen. Dvs. endast tillstånd med energin $\varepsilon_k > 0$ relativt Fermienergin är tillgängliga. Trots att kinetiska energin hos detta elektronpar tydligen är positiv relativt dubbla Fermienergin, skall vi se att totala energin, efter vi tagit hänsyn till en attraktiv potential, V, kan bli negativ, dvs. vi får ett stabilt tillstånd. Det ursprungliga grundtillståndet (det med alla tillstånd upp till E_F fyllda av elektroner) har blivit labilt och gett upphov till ett med parade elektroner vid Ferminivån.

Totala impulsen, $\hbar q$, och spinnet, S, hos paret är konstant även om parmedlemmarna sprids av växelverkan mellan dem. Vågfunktionen kan skrivas

$$\psi(r_1, r_2) = \varphi_q(\rho)\, e^{iq\cdot R}$$

där $\rho = r_1 - r_2$ och $R = (r_1 + r_2)/2$

Vågfunktionen är symmetrisk för S = 0 och antisymmetrisk om S = 1.

Låt oss först betrakta q = 0 och S = 0 (dvs. tillstånden $\mathbf{k}\uparrow$ och $-\mathbf{k}\downarrow$)

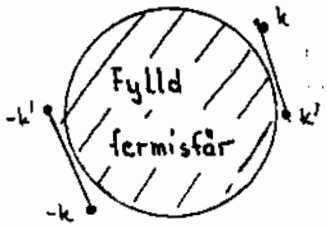
$$\psi(r_1, r_2) = \phi(s) = \sum_k a_k e^{i\mathbf{k}\cdot s} = \sum_k a_k e^{i\mathbf{k}\cdot r_1} e^{-i\mathbf{k}\cdot r_2}$$

där summan endast löper över tillstånd med $\varepsilon_k > 0$
Schrödingerekvationen:

$$(W - H_0)\psi = V\psi$$

$$(W - 2\varepsilon_k) a_k = \sum_{k'} V_{kk'} a_{k'}$$

där $V_{kk'} = \langle k, -k \mid V \mid k', -k' \rangle$ beskriver spridningen



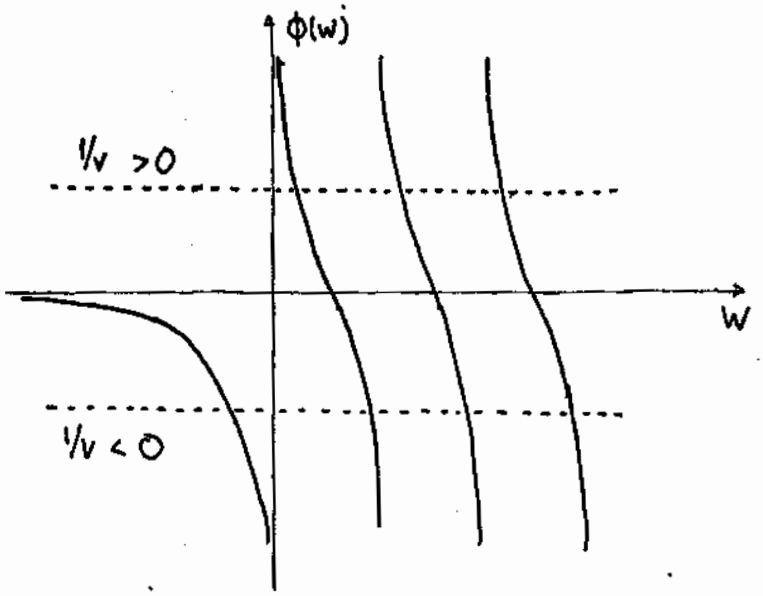
Antag nu, att $V_{kk'} = V$ $\quad 0 < \varepsilon_k, \varepsilon_{k'} < \hbar\omega_c$
$= 0$ $\quad$ för övrigt

$$(W - 2\varepsilon_k) a_k = V \sum_{k'(\varepsilon_{k'} < \hbar\omega_c)} a_{k'} = VC$$

$$a_k = VC/(W - 2\varepsilon_k) \quad ; \quad C = \sum_{k'(\varepsilon_{k'} < \hbar\omega_c)} VC/(W - 2\varepsilon_{k'})$$

$$\frac{1}{V} = \sum_{k'(\varepsilon_{k'} < \hbar\omega_c)} 1/(W - 2\varepsilon_{k'}) = \phi(W)$$

Om vi betraktar tillstånden i en stor, men ändlig, kristall så är ε_k medlemmar av ett diskret set, så att när W passerar genom $2\varepsilon_{k'}$ hoppar $\phi(W)$ från $-\infty$ till $+\infty$.



Egenvärdena W ges av skärningen mellan funktionen $\phi(W)$ och konstanta funktionen $1/V$.

Vi får ett egenvärde $W < 0$ för V negativ (dvs. attraktiv potential). Således kan vi få ett bundet tillstånd. Hur stor är bindningsenergin?

Gå nu över från summering till integrering:

$$\frac{1}{|V|} = \frac{N(0)}{2} \ln\left(\frac{|W|+2\omega_c}{|W|}\right)$$

eller $$|W| = 2\omega_c/(e^{2/N(0)|V|} - 1) \approx 2\omega_c e^{-2/N(0)|V|}$$

för $N(0)|V| \ll 1$ (svag koppling)

$N(0)$ är tillståndstätheten för en-elektrontillstånd för en spinnorientering i energiintervallet $0 < \varepsilon_k < \hbar\omega_c$. Vi antar att denna tillståndstäthet är konstant i intervallet.

Elektronpar $(p,\sigma;-p,-\sigma)$

Slutsats: Om en attraktiv växelverkan mellan två elektroner, existerar inom ett intervall kring Fermiytan, så är det energetiskt fördelaktigt för elektronerna att bilda ett par. Kondensationsenergin är dock liten, och det är lätt att excitera paret (inget energigap). Man kan visa, att bindningen blir starkast, om elektronerna i paret har motriktade, och till beloppet lika, impulser och spinn. Vågfunktionen för elektronparet har en utsträckning av $\xi_0 \approx 10^{-4}$ cm.

Vi har nu betraktat ett enstaka elektronpar. Men mellan kontrahenterna befinner sig miljontals andra elektroner, som växelverkar sinsemellan och med paret. Nästa steg skall bli att ta med växelverkningar mellan alla par. Detta görs i BCS-modellen (uppställd 1957 av Bardeen, Cooper och Schrieffer) som vi skall studera, men låt oss först diskutera hur man kan få en attraktiv kraft mellan två elektroner som övertrumfar den repulsiva Coulomb-kraften (ett annat sätt att säga detta är med en negativ dielektricitetskonstant i skärmningen av Coulombpotentialen).

VII.4 Attraktiv potential

Elektron-fonon-koppling

Vi behöver en attraktiv växelverkan, hur skall vi få den? Jo, vi påpekade tidigare att gittret hade viss inverkan på supraledning. Vi hade en isotopeffekt, $T_c \sim M^{-1/2} \sim \omega_D$ och vi såg att dåliga normala ledare (således med stark elektron-fonon-koppling) ofta var bra supraledare. Detta tyder på att vi har en elektron-fononkoppling vilket påpekades av Fröhlich.

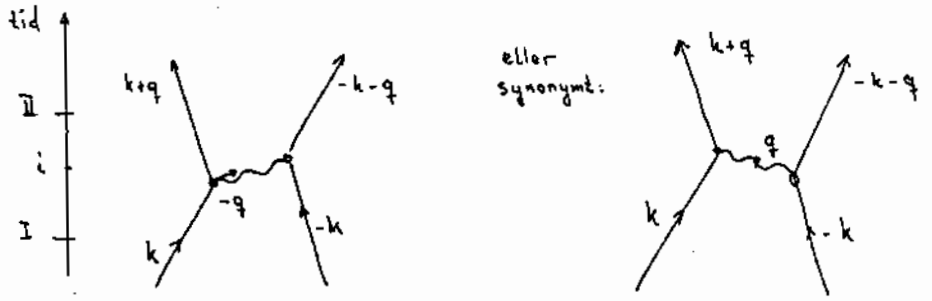
Fysikaliskt: rörlig elektron polariserar gitter. Då elektronen passerat genom gittret fås spår av positiv laddning längs dess bana. En andra elektron attraheras till detta område med överskott av positiv laddning, om detta spår ej har hunnit försvinna (retarderad växelverkan).

Bardeen och Pines fann att effektiva matriselementet för spridning av två elektroner med vågtalen k, k' till $k+q, k'-q$ genom utbyte av en fonon med impulsen $\hbar q$ är

$$\frac{2\hbar\omega_q |M_q|^2}{(\varepsilon_k - \varepsilon_{k+q})^2 - (\hbar\omega_q)^2}$$

där $\hbar\omega_q$ = fononens energi, ε_k en elektronenergi mätt från Fermienergin och M_q = matriselement för spridning av elektron mot fonon.

Härledning finns bl.a. i Ziman. Skisserar här kvantmekaniskt betraktelsesätt:



$E_I = 2\varepsilon_k$

$E_{II} = 2\varepsilon_{k'}$ $\qquad (k' = k+q)$

2 intermediära tillstånd: (både ε_k och ω_q är jämna funktioner)

$E_{i1} = \varepsilon_{k'} + \varepsilon_k + \hbar\omega_q$

$E_{i2} = \varepsilon_{k'} + \varepsilon_k + \hbar\omega_q$

till 2:a ordningens störningsräkning:

$$\langle I | H_{ex} | II \rangle = \sum_i \langle I | H_{el\text{-}ph} | i \rangle \tfrac{1}{2} \left(\frac{1}{E_I - E_i} + \frac{1}{E_{II} - E_i} \right) \langle i | H_{el\text{-}ph} | II \rangle =$$

$$= \frac{|M_q|^2}{\hbar} \left(\frac{1}{\omega - \omega_q} - \frac{1}{\omega + \omega_q} \right) =$$

$$= \frac{2|M_q|^2}{\hbar} \cdot \frac{\omega_q}{\omega^2 - \omega_q^2} \qquad \text{där } \hbar\omega = \varepsilon_{k'} - \varepsilon_k$$

Attraktiv växelverkan för $\omega < \omega_q$

för $\omega < \omega_q$ fås attraktion $\sim -\frac{2|M_q|^2}{\hbar\omega_q}$

$\omega > \omega_q$ " repulsion

Vidare har vi Coulombrepulsion mellan de två elektronerna: U_q

Vårt resulterande matriselement blir

$$-\frac{2|M_q|^2}{\hbar\omega_q} + U_q$$

(matriselementen är skärmade växelverkningar).

Ansätt konstant attraktiv växelverkan för $\omega < \omega_q$

I BCS-teorin ansätter man en genomsnittlig växelverkan för $\omega < \omega_q$:

$$-V = \left\langle -\frac{2|M_q|^2}{\hbar\omega_q} + U_q \right\rangle$$

VII.5. BCS-teorin

Bardeen, Cooper and Schrieffer formulerade 1957 en mikroskopisk modell för supraledning. Denna har helt accepterats och beskriver supraledningsegenskaperna i detalj. Modellen innehöll vissa förenklingar. Senare utvidgningar har behandlat mera komplicerade (och realistiska) approximationer, vilka vi återkommer till. BCS-modellen har också tillämpats med framgång i andra sammanhang, t ex för att beskriva mångpartikelfenomen i atomkärnor och suprafluiditet i ^{3}He.

För en behandling av BCS-modellen hänvisas till den artikel "The Microscopic Theory of Superconductivity-Verifications and Extensions" som ingår i föreläsningsanteckningarna. Mera utförliga behandlingar ges i ett flertal böcker och sammanfattningar. Bl a rekommenderas en artikel av M. Tinkham i "Low Temperature Physics" (de Witt et al, eds., Gordon & Breach, 1962) samt boken av J.R. Schrieffer, "Theory of Superconductivity". Här ges nu endast en summarisk översikt:

Utgångspunkter:

(i) Baserat på Coopers resultat antar man att det supraledande grundtillståndet är uppbyggt av elektronpar (med S=0 och totala impulsen den samma för varje par, noll för I=0).

(ii) Paren hålls samman av en attraktiv kraft mellan elektronerna. Attraktionen skulle, i princip, kunna orsakas av flera mekanismer, BCS betraktade en växelverkan mellan par genom ett utbyte av virtuella fononer vilka ger upphov till en överskärmning av Coulombrepulsionen.

(iii) F ö antogs alla andra växelverkningar vara desamma som i det icke-supraledande tillståndet. Detta innebär att man endast behöver beakta kinetiska energin relativt Fermihavet hos elektronerna samt den speciella växelverkanspotentialen - övriga egenskaper ligger inbakade i en-elektronvågfunktionerna.

Behandling:

När man således har ställt upp vågfunktion, ψ, och Hamiltonoperator, H, kan man skrida till verket och minimera energin $\langle\psi|H|\psi\rangle$.

BCS tillgrep viktiga

Approximationer:

(i) man släppte på kravet att antalet elektronpar skulle vara bevarat. Denna approximation kan jämföras med den stora kanoniska ensemblen i statistisk fysik

(ii) man antog en konstant attraktiv växelverkan inom ett energiområde, av storleksordningen Debyeenergin, runt Ferminivån.

Resultat:

- Även vid T=0 finns det elektroner med kinetisk energi större än E_F. Dock finns det också en bindningsenergi varför totala energin för det supraledande grundtillståndet är lägre än det normalas.
- För att exitera elektroner ur grundtillståndet fordras en minsta gapenergi.
- Energigapet är temperaturberoende och går mot noll då T går mot T_c.
- $2\Delta(0) \approx 3.53\ kT_c$
- $T_c \approx \theta_D \exp(-1/N(0)V)$
- Kondensationsenergin $\approx -\frac{1}{2}N(0)\Delta^2$

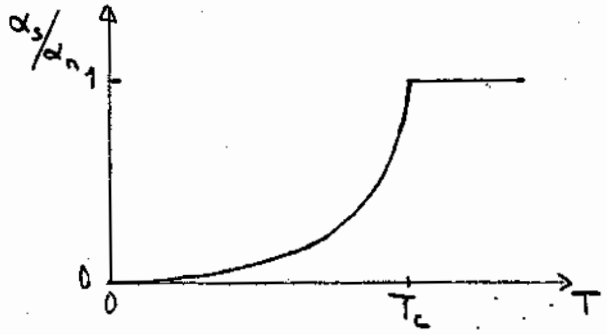
- En mängd egenskaper kunde beräknas. Speciellt bör nämnas olika typer av spridningseffekter där förekomsten av en elektron i tillståndet k är likvärdig med ett hål i -k (eftersom antalet par får varieral

- Man (Gorkov) kunde senare visa att Ginzburg-Landaus ekvationer följer av BCS-teorin, varför de (makroskopiska och fenomenologiska) koncept vi tidigare studerat innefattas i den mikroskopiska teorin.

Verifikationer:

Studera nu den nämnda artikeln, som diskuterar flera yttringar av koncepten elektronpar, energigap och attraktiv växelverkan, Vi skall snart behandla ett av ämnena - tunneleffekten - i större detalj.

Ytterligare en yttring av energigapet bör nämnas, nämligen ultraljudabsorption. Mätning av temperaturberoendet för denna absorption ger för supraledare relativt normal metall:



Kurvan stämmer väl överens med BCS-teorins uttryck:

$$\alpha_s/\alpha_n = 2 / (1+\exp(2\Delta(T)/kT))$$

Dock visar mätningar att resultatet beror på vilken kristallriktning man mäter absorptionen. Anisotropin i energigapet, dvs också $V_{kk'}$, kan bestämmas.

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The Microscopic Theory of Superconductivity—Verifications and Extensions

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Abstract

The microscopic theory of superconductivity—Verifications and extensions. T. Claeson and S. Lundqvist (Department of Physics, Chalmers University of Technology, Fack, S-402 20 Gothenburg, Sweden).
Physica Scripta, (Sweden) 10, 5–34, 1974.

The microscopic theory of superconductivity was formulated in 1957 by Bardeen, Cooper, and Schrieffer. In the BCS model, the ground state of super electrons is built up by pairs kept together by an attractive interaction. An exchange of phonons can give such an attraction. The electrons in the superconducting condensate are correlated within a macroscopic distance. To excite electrons, or break pairs, a certain gap energy is needed.

A number of experimental confirmations were discussed already in the original paper. The BCS theory initiated many experiments. Some of them provided a stimulus to logical extensions of the theory. These have mainly been concerned with a more realistic, energy- and momentum-dependent interaction than the original approximation. Lifetime aspects are also of importance.

In this short survey we describe the results of a few experiments that test the concepts of pairing, energy gap and phonon-mediated attraction. The main emphases are on the powerful tunneling method and the variation of the superconducting transition temperature with different physical and chemical parameters.

Contents

1. Preview

The microscopic theory of superconductivity was formulated 1957 in a famous paper by Bardeen, Cooper and Schrieffer [1]. It describes the superconducting ground state as built up by pairs of electrons, Cooper pairs, which mutually interact within a coherence distance of the order of a thousand atomic distances. An attractive interaction between electrons is required to form such pairs. An exchange of virtual phonons gives, on average, an attraction within a certain energy interval around the Fermi level, and this attraction may under certain circumstances dominate over the screened Coulomb repulsion. The correlated state possesses a small condensation energy in comparison with the non-superconductive one. In order to break a pair, to excite electrons out of the ground state, an energy greater than a minimal energy, the so-called gap energy, is required.

Already in the original paper, a number of experimental consequences of the theory were discussed. Connections to previous phenomenological theories were also drawn. The BCS theory initiated a number of experimental investigations of its different aspects. Some of these have stimulated certain extensions of the theory, although still within its main assumptions. One has, for example, introduced a more realistic potential than the original approximation and taken into account the finite lifetime of Cooper pairs as well as of excitations. In particular the restriction to weak electron-phonon coupling has been relaxed and the case of strong coupling has been thoroughly investigated. The more sophisticated calculations agree with experimental values to within one part in a hundred. This accuracy is considerably better than for most other electronic properties of condensed matter.

The fact that electrons appear coupled in pairs in a superconductor is amply documented. Observations of quantized magnetic flux and a number of verifications of the many facets of the Josephson effect can be mentioned. Scattering experiments, such as damping of ultrasound and infrared radiation or relaxation of nuclear spins, show correlation effects, i.e. that the pairs consist of electrons of equal but oppositely directed momenta and spins. The limited lifetime of a pair is demonstrated by the effect of fluctuations at the superconducting transition and by proximity effects between superconductors and non-superconductors.

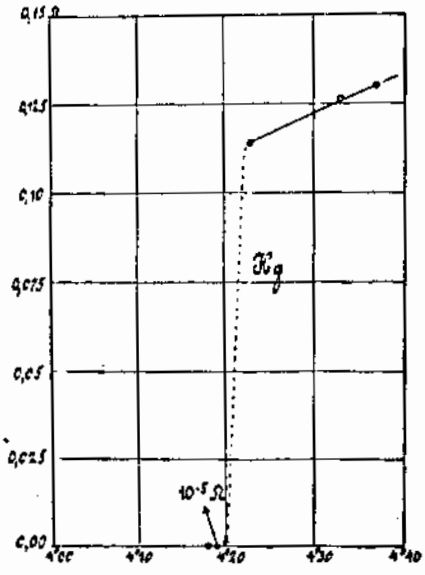


Fig. 1. The electrical resistance of several metals drops discontinuously at a material dependent critical temperature, T_c. The diagram shows Kamerlingh-Onnes' results on mercury. (From Ref. 2.)

The connection between the attractive interaction and lattice vibrations, phonons, was early established by the so-called isotope effect and later direct identification of structure due to phonons in tunneling curves. Other attractive interactions than the one mediated by phonons have been suggested and, in principle, they are possible, but at present there is no conclusive experimental evidence for any other coupling causing superconductivity.

A condensation energy of the right size has been registered. It is only a very small part (about 10^{-6}) of the total energy of the electronic system in the metal. The thermodynamic properties of a superconductor are well accounted for by the theory.

A great number of superconducting properties are characterized by the existence of an energy gap in the excitation spectrum. The gap can be studied, for example, through electron tunneling into a superconductor or the temperature dependence of ultrasonic attenuation, specific heat, heat conductivity or Knight shift in NMR. Small deviations between the original theory and experiments have been noted. As these discrepancies have been emphasized and sometimes have been used as an evidence against the validity of the theory, we will treat these aspects in a little greater detail than most other phenomena. Most of the differences can indeed be explained if one uses a more realistic, directionally and frequency dependent attraction than the original BCS approximation. Other discrepancies have subsequently been explained by measurements carried out under better or more univocal experimental conditions.

In this survey, we wish to concentrate mainly on experiments that measure how the superconducting transition temperature is related to different physical parameters and upon results obtained by the tunneling technique which is the most powerful technique for the study of superconductors. It has been developed (both experimentally and theoretically) to such a precision that it can measure not only properties specific to the superconducting state, but also "normal state" properties. The limited scope of this review is, of course, dependent upon a desire to make it short and comprehensive but also upon the interests of the authors. Our choice gives a chance to demonstrate how a theory can be expanded, yet remain within its fundamental assumptions, guided by a strong interaction with new significant experiments.

As far as we know, there are no experimental data that conclusively oppose the microscopic theory of superconductivity built upon the work by Bardeen, Cooper and Schrieffer from 1957. One should note that even the original BCS approximation gives a complete theory of the phenomenon of superconductivity for a weak coupling, isotropic superconductor. It is highly remarkable that such a relatively simple model with only one parameter can explain so many aspects of the complicated phenomenon of superconductivity.

2. Historical review

Superconductivity was discovered 1911 by Kamerlingh-Onnes [2] (Fig. 1). The superconducting state is characterized, as the name tells us, by its lack of electrical resistance. It appears in a number of metals [3] for subcritical values of temperature, magnetic field and electrical current density (Fig. 2). Magnetic flux is furthermore expelled from the superconductor so that the flux density inside it is zero—the so-called Meissner effect [4]. The difference in free energy between the superconducting and the non-superconducting states—the condensation energy—is small. It is of the order of 10^{-6} of the other contributions to the electron energy. The transition into the superconducting state is, in the absence of external fields, of second order, which means that there is a continuous decrease to zero at T_c of some sort of order parameter.

Of course, to explain this spectacular phenomenon was a challenge. Yet it resisted the many theories that were proposed during almost fifty years. Something was always missing. Becker's theory [5] for a perfect conductor could not explain the Meissner effect. The brothers F. and H. London [6] treated the electrodynamic properties of a superconductor phenomenologically with great success—their concept of the superconductor as a macroscopic quantum state of electrons has been of great importance. Pippard [7] modified their local response by introducing a coherence length. A two-fluid model, separating the ground state electrons and excited electrons into parts, was presented by Gorter and Casimir [8]. Ginzburg and Landau [9] published in 1950 a theory which was founded upon a theory by Landau [10] about phase transitions of second order. An order parameter, of macroscopic scale, which grows continuously as the temperature is lowered below the transition point, was introduced. This phenomenological theory has been very successful, and it explains, for example, how the so-called type II superconductivity appears.

But these models do not give any atomistic explanation of the superconducting state or why it is formed, why some elements become superconducting at relatively high temperatures while others remain "normal" down to the lowest temperature obtained, why the resistance actually disappears, why the condensation energy is so small, or why there is an exponential dependence in the specific heat of a superconductor at low temperatures.

An important step towards a microscopic theory was taken by the theoretical prediction of the isotope effect by Fröhlich [11] and the independent experimental discovery of Maxwell and Reynolds et al. [12, 13]. This demonstrated that the phenomenon of superconductivity was related to the interaction between the electrons and the phonons. Fröhlich [11], Bardeen [14], Bardeen and Pines [15] and others attempted to formulate a microscopic theory of superconductivity based upon the electron-phonon interaction, but with little success.

The work of Cooper [16] in 1956 is a landmark on the

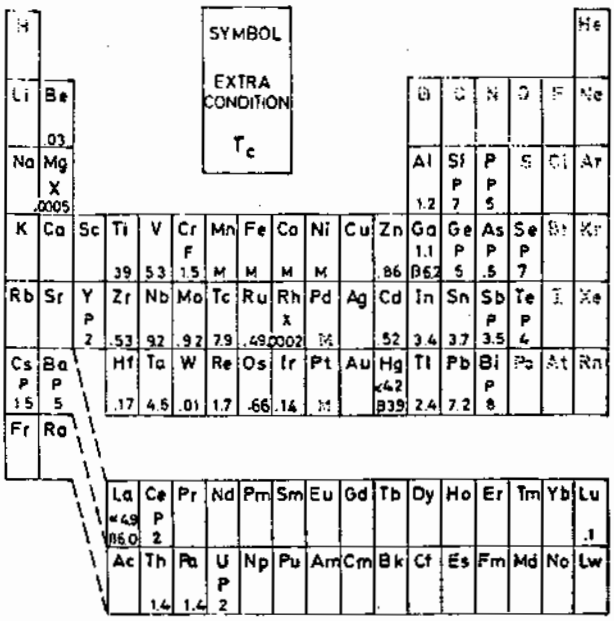


Fig. 2. Superconducting transition temperatures of different elements are given. *P* denotes that the metal is superconducting under pressure only (or in some cases in the form of an amorphous film). *X* indicates that the estimated value is extrapolated from T_c for binary alloys. *F* is a sputtered, disordered film. A magnetic metal is denoted by *M*, while a nearly magnetic one is symbolized by a dotted *M*. Dotted chemical symbols are non-metals (some of the usually non-metallic elements are marked as metals, they become metallic and superconducting under pressure).

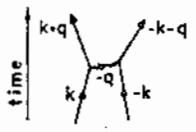


Fig. 3. Two electrons, in states k and k' are scattered to states $k+q$ and $k'-q$ by the exchange of a virtual phonon (the process occurs rapidly; due to the uncertainty principle, energy needs not to be conserved, hence the name virtual process). In the BCS model bound pairs, Cooper pairs, $(k\uparrow, -k\downarrow)$ and $(k+q\uparrow, -k-q\downarrow)$ are formed. The binding is strongest when the electrons have opposite but in magnitude equal momenta and spins.

way towards a microscopic theory. He showed that even the weakest attraction between two electrons excited slightly from the Fermi sea leads to an instability towards pair formation. A new ground state of lower energy is formed, where bound pairs of electrons with opposite, but equal, momenta and spins play an important role. Cooper's independent pairs gave no energy gap in the excitation spectrum, however.

3. The Bardeen–Cooper–Schrieffer theory

Based upon Cooper's important contribution, Bardeen, Cooper and Schrieffer presented their theory for superconductivity in 1957 [1]. Their work gives a microscopic theory of superconductivity. It explains why superconductivity occurs, how the wave function which describes the superconducting condensate is constructed, and which properties this state possesses. We shall give a brief discussion of the theory here and refer the reader to any main text for a more detailed presentation. The reader who wants to skip the sometimes technical description of the theory can pass on to the resumé in section 3.5.

3.1. *Starting points which in retrospect seem most relevant*

From previous experimental and theoretical works, one knew that an acceptable theory had to explain a number of properties, among which we can mention the following

that the superconducting state is a macroscopic quantum state where the wavefunction describing the condensate is of long range and is "stiff" against applied magnetic fields; a macroscopic extension of the state leads in the London model to a total momentum of zero;

that the current–field relations are non-local within a coherence distance of the order of 10^{-6} m in a pure superconductor;

that the state can be described by an order parameter that goes smoothly towards zero as the critical temperature T_c is approached;

that the free energy difference between the superconductive and the non-superconductive states is very small. It is several orders of magnitude smaller than the accuracy one has in calculating the total electron energy of the system. A reasonable choice of the part that separates a superconductor from a "normal" metal has to be made;

that an energy gap exists of the order of $k_B T_c$ in the excitation spectrum of electrons; and

that the electron–phonon interaction is important for the occurrence of superconductivity and for the magnitude of T_c.

3.2. *Main assumptions*

(*a*) The superconductive ground state is formed by pairs in singlet, time-reversed states. The total momentum of each pair is the same and equal to zero for the state with no current.

(*b*) An attractive force acts between electrons in pairs for electron energies within a certain interval of the Fermi energy, E_F. BCS assumed it consisted of an attractive part resulting from an exchange of virtual phonons and a repulsive part from the screened Coulomb interaction. If the resultant force is attractive within the energy interval considered, pairing and superconductivity results. As a first approximation, BCS ignored the directional and energy dependence of the interaction and chose it attractive and constant within an interval $\hbar\omega_c$ from E_F, otherwise zero. With the electron–phonon interaction as the attractive part, the cut-off energy is the Debye energy, $\omega_c = \omega_D$.

(*c*) Except for the pairing, all other microscopic properties of the superconducting state are assumed to be the same as those of the non-superconducting one in the same metal.

3.3. *Outline of intermediate steps*

The BCS theory provides the theoretical framework for handling a state of electrons in which a macroscopic number of pairs interact and move in a correlated way. The wave function of the state, ψ, is built up by pair states and a model Hamiltonian is introduced which contains an attractive interaction potential. After giving expression for ψ and H, we are going to minimize the expectation value $\langle\psi|H|\psi\rangle$ of the energy. The formal treatment is greatly simplified by introducing creation and annihilation operators $c^+_{k,\sigma}$ and $c_{k,\sigma}$ that create or destroy particles with a momentum $\hbar k$ and spin σ.

Consider a state described by

$$|\psi\rangle = \sum_i a_i |\psi_i\rangle$$

where for example

$$|\psi_i\rangle = |\underset{1\uparrow}{1}\ \underset{1\downarrow}{1}\ \underset{2\uparrow}{1}\ \underset{2\downarrow}{0} \ldots \underset{k\uparrow}{1}\ \underset{k\downarrow}{0} \ldots \underset{k\uparrow}{0}\ \underset{k\downarrow}{1} \ldots\rangle$$

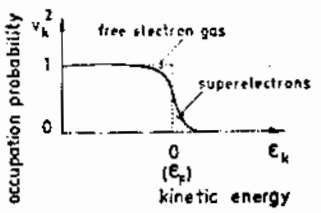


Fig. 4. The probability of finding a state occupied is plotted against kinetic energy of the state for a free Fermi gas (i.e. no interactions) and for the superconducting ground state at $T=0$. (Energy is counted from the Fermi energy.) For the free Fermi gas, all states with energy less than the Fermi energy are occupied, and none with $\varepsilon_k > 0$. In the superconducting ground state, on the other hand, electrons with wave numbers $|k| > k_F$ participate in Cooper pairs. Although the kinetic energies of such electrons are higher than ε_F, the interaction energy from the phonon exchange lowers the energy of the system to a level lower than the one of the non-interacting electron gas.

which can be written

$$|\psi_1\rangle = c_{1\uparrow}^+ c_{1\downarrow}^+ c_{2\uparrow}^+ \cdot 1 \cdot \ldots c_{k\uparrow}^+ \cdot 1 \ldots 1 \cdot c_{k'\downarrow}^+ \ldots |0\rangle$$

where $|0\rangle$ is the vacuum state.

The interaction potential expressed in these operators is:

$$V(r_1, r_2) = \tfrac{1}{2} \sum_{\substack{k,k',q \\ \sigma,\sigma'}} V(q)\, c_{k+q,\sigma}^+ c_{k'-q,\sigma'}^+ c_{k',\sigma'} c_{k,\sigma}$$

The terms in the potential can be interpreted as scattering processes in which two electrons in the states k, σ and k', σ' are scattered to $k+q$, σ and $k'-q$, σ' by an exchange of a phonon q (Fig. 3). We neglect the diagonal terms of $\langle\psi|H|\psi\rangle$, which are the same in the superconducting and normal states, and concentrate upon the non-diagonal elements which contain the new effects. As $|\psi\rangle$ is a superposition of different electron configurations, alternating signs for $\langle\psi|V|\psi\rangle$ are found as the occupation number of electron states is changed (this is a direct consequence of Fermi statistics). These terms tend to add up to approximately zero unless one makes a particular selection of configurations.

BCS assumed that the ground state could be expressed solely in the form of superimposed electron pairs $(k\uparrow, -k\downarrow)$. All the electron configurations, the superposition of which form the ground state, will differ by even occupation numbers, and each matrix element $\langle\psi|H|\psi\rangle$ will have the same sign. All the contributions from the interaction will then add up to a sizeable energy contribution.

Pairing assumption, wave function approximation. At $T=0$K all electrons form pairs

$$\Phi_N = A\Phi(r_1 - r_2)\Phi(r_3 - r_4) \ldots \Phi(r_{N-1} - r_N)(1\uparrow)(2\downarrow) \ldots (N\text{-}1\uparrow)(N\downarrow)$$

where A is an antisymmetrization operator and $\Phi(r_i - r_j)$ is the wave function for a pair of electrons at r_i and r_j. In terms of creation operators in momentum space, an equivalent form is

$$\Phi_N = \sum_{k_1 \ldots k_{N/2}} g_{k_1} \cdots g_{k_{N/2}} c_{k_1\uparrow}^+ c_{-k_1\downarrow}^+ \cdots c_{k_{N/2}\uparrow}^+ c_{-k_{N/2}\downarrow}^+ |0\rangle$$

This is a function which is difficult to handle. The calculations will be much simpler if we use instead:

$$|\psi\rangle = c \prod_k (1 + g_k c_{k\uparrow}^+ c_{-k\downarrow}^+)|0\rangle$$

This wave function does not correspond to a fixed number of particles but to a superposition of the form $|\psi\rangle = \Sigma \lambda_N \Phi_N$. However, the coefficients λ_N are sizeable only for $N \approx \langle N\rangle$. The deviation in the particle number from the mean value, $\Delta N/\langle N\rangle$, goes as $1/\sqrt{\langle N\rangle}$, which means that for large systems, it is negligible. The situation is similar to the difference between the grand canonical and canonical ensembles. The wave function approximation is very important for the successful solution of the many-body problem, and we will see how simple the calculations become with this function.

We now introduce operators which create and annihilate pairs:

$$b_k^+ = c_{k\uparrow}^+ c_{-k\downarrow}^+$$

$$b_k = c_{-k\downarrow} c_{k\uparrow}$$

In terms of these we have

$$|\psi\rangle = \prod_k (u_k + v_k b_k^+)|0\rangle$$

where $v_k/u_k = g_k$; $u_k^2 + v_k^2 = 1$.

The Hamiltonian can now be written

$$H = 2\sum_k \varepsilon_k b_k^+ b_k + \sum_{kk'} V_{kk'} b_{k'}^+ b_k$$

where the first term denotes the kinetic energy of the free electrons, while the second term contains the interaction, i.e. the potential energy.

The ground state. The stable state is the one in which the expectation value of the total energy

$$W = \langle\psi|H|\psi\rangle = \ldots = 2\sum_k \varepsilon_k v_k^2 + \sum_{kk'} u_k v_k u_{k'} v_{k'} V_{kk'}$$

is a minimum.

Minimize W with respect to the parameters u_k and v_k. As these are not independent, we write

$$u_k = \sin\theta_k$$

$$v_k = \cos\theta_k$$

and minimize W with respect to θ_k.

The minimal W is obtained for

$$v_k^2 = \frac{1}{2}\left[1 - \frac{\varepsilon_k}{(\Delta_k^2 + \varepsilon_k^2)^{\frac{1}{2}}}\right]$$

where we have introduced

$$\Delta_k = -\sum_{k'} V_{kk'} u_{k'} v_{k'}$$

If we set $E_k = (\Delta_k^2 + \varepsilon_k^2)^{\frac{1}{2}}$ (we will soon show that this is the excitation energy for a quasiparticle out of the ground state), the ground state parameters are:

$$v_k^2 = \frac{1}{2}\left[1 - \frac{\varepsilon_k}{E_k}\right]$$

$$u_k^2 = \frac{1}{2}\left[1 + \frac{\varepsilon_k}{E_k}\right]$$

As shown in Fig. 4, the ground state at $T=0$ is not, as in a free Fermi gas, built up solely by electrons with kinetic energies less than the Fermi energy. There is a finite probability to find paired electrons with kinetic energies higher than the Fermi level. For these the interaction energy lowers the total energy such that a condensed state with an energy lower than the non-interacting gas is obtained.

Approximation in choice of attractive potential. BCS assumed that the electron-electron interaction (the scattering potential) was attractive when the energy exchange between the two electrons, $\hbar\omega$, was less than a cut-off value, $\hbar\omega_c$. In particular they were considering an attraction mediated by an exchange of virtual phonons. Then ω_c is of the order of the Debye frequency, ω_D. As a first approximation, they chose:

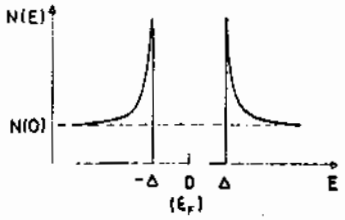


Fig. 5. The density of states per unit energy for one-electron excitations out of the superconducting ground state. Note that the energy is counted from the Fermi energy. Superelectrons are condensed into a bound state such that it costs an energy greater than a gap value, 2Δ, to break a pair and excite two electrons. No states are available within the interval $(-\Delta, \Delta)$.

$$V_{kk'} = -V \quad \text{for } |\varepsilon_k|, |\varepsilon_{k'}| \leq \hbar\omega_c$$
$$= 0 \qquad \text{otherwise}$$

The parameter, Δ_k, behaves similarly:

$$\Delta_k = \Delta \quad |\varepsilon_k|, |\varepsilon_{k'}| \leq \hbar\omega_c$$
$$= 0 \quad \text{otherwise}$$

The expression defining the latter parameter:

$$\Delta = \Delta_k = -\sum_{k'} V_{kk'} u_{k'} v_{k'} = -\sum_{k'} V_{kk'} \tfrac{1}{2}\left(1 - \left(\frac{\varepsilon_{k'}}{E_{k'}}\right)^2\right)^{\frac{1}{2}}$$
$$= -\sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2E_{k'}} = \frac{V\Delta}{2}\sum_{k'}\frac{1}{E_{k'}} = V\Delta N(0)\int_0^{\hbar\omega_c}\frac{d\varepsilon}{(\varepsilon^2+\Delta^2)^{\frac{1}{2}}}$$

where, in the last step, we integrate instead of sum. $N(0)$, the density of electron states at the Fermi energy, is introduced in that step (the energy ε_k is always counted from ε_F, as in Landau's theory for Fermi liquids).

The final expression for Δ becomes:

$$\Delta = \frac{\hbar\omega_c}{\sinh(1/N(0)V)} \approx 2\hbar\omega_c e^{-1/N(0)V}$$

where the last step is valid in the weak coupling limit ($N(0)V \ll 1$).

What is Δ? The simplest type of excitation is one where we add a particle $(k_1, \uparrow)$ (or subtract one with $(-k_1, \downarrow)$, which leads to the same excitation as we do not conserve the number of particles).

$$\psi_{k_1} = c^+_{k_1\uparrow}\prod_{k\neq k_1}(u_k + v_k b^+_k)|0\rangle$$

The excitation energy

$$\Delta W = \langle\psi_{k_1}|H|\psi_{k_1}\rangle - \langle\psi|H|\psi\rangle = \ldots = E_{k_1} = (\Delta^2+\varepsilon^2_{k_1})^{\frac{1}{2}}$$

Hence the smallest excitation energy is equal to Δ. There is a gap in the spectrum which has to be exceeded as illustrated in Fig. 5. To break a pair, i.e. to form the two excitations $(k_1, \uparrow)$ and $(-k_1, \downarrow)$, costs an energy of 2Δ.

The density of states for the excitations:

$$N(E) = \frac{dN}{dE} = \frac{dN}{d\varepsilon}\cdot\frac{d\varepsilon}{dE} = \frac{N(0)}{dE/d\varepsilon} = \begin{cases} N(0)\dfrac{|E|}{(E^2-\Delta^2)^{\frac{1}{2}}} & \text{for } E \geq \Delta \\ 0 & E < \Delta \end{cases}$$

Condensation energy. The condensation energy, $W = W_s - W_n = \ldots = -\tfrac{1}{2}N(0)\Delta^2(1-e^{-2/N(0)V}) \approx -\tfrac{1}{2}N(0)\Delta^2$

This value is of the right order of magnitude. Not all, but of the order of $N(0)\cdot\Delta$ electrons, each with the condensation energy equal to the gap value Δ, contribute to a lowering of the total energy.

We can equate with the condensation energy one finds from expelling the magnetic field (i.e. the Meissner effect). A zero flux density ($B = 0$) within the superconductor can be regarded as resulting from an induced magnetization, M, that cancels the flux density due to the applied magnetic field, $M = -H$. Then as $dW = \mu_0 M\cdot dH$ (where μ_0 is the vacuum permeability):

$$W = \mu_0\int_0^{H_c} M\cdot dH = -\tfrac{1}{2}\mu_0 H_c^2 = -\tfrac{1}{2}N(0)\Delta^2$$

i.e. $H_c \propto \Delta \propto \omega_c \propto (\text{ionic mass})^{-\frac{1}{2}}$ if the attraction is mediated by phonons.

Non-zero temperature. At a non-zero temperature, one must also take into account thermally excited electrons. These contribute not only to the kinetic energy of the system but also to the potential energy, as they block possible states for pairs. If a state $(k\uparrow)$ is already occupied the pair $(k\uparrow, -k\downarrow)$ has to be excluded, which raises the total energy.

Denote the part of the states occupied by thermal excitations with $f_k(T)$, yet to be determined. Then we write:

$$\text{K.E.} = 2\sum_k |\varepsilon_k|[f_k + (1-2f_k)v_k^2]$$

$$\text{P.E.} = \sum_{kk'} V_{kk'} u_k u_{k'} v_k v_{k'} (1-2f_k)(1-2f_{k'})$$

The factor $(1-2f_k)$ has to be taken into account, since a thermal excitation blocks the pair if either of its two electron states is occupied!

Besides the kinetic and potential energy contributions, we must add the entropy term, i.e. the contribution due to the disorder introduced by the thermal excitations, to the free energy.

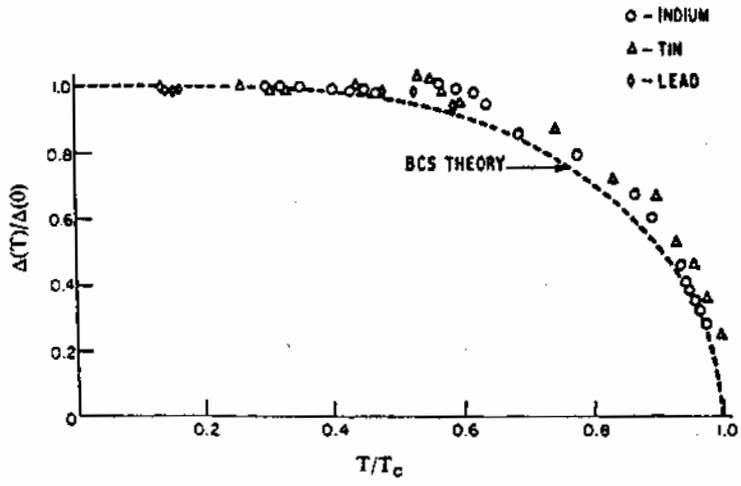


Fig. 6. The gap parameter, $\Delta(T)$, decreases with increasing temperature and becomes zero at $T = T_c$. The dashed line is the solution of the gap equation, while the points are experimental points determined by the tunneling technique. (From Giaever and Megerle [17].)

$$TS = 2k_B T \sum_k [f_k \ln f_k + (1 - f_k) \ln (1 - f_k)]$$

$$F = K.E. + P.E. - TS$$

Minimizing F with respect to the parameters u_k, v_k gives:

$$\Delta_k(T) = \sum_{k'} V_{kk'} u_{k'} v_{k'} (1 - 2f_{k'})$$

which shows that the energy gap parameter is decreased when $T \neq 0$. But what is f_k? Minimize F with respect to f_k and you will get:

$$f_k = \frac{1}{e^{E_k/k_B T} + 1} = f(E_k)$$

i.e. a Fermi distribution function for excitations, k, with energy

$$E_k = (\varepsilon_k^2 + \Delta_k^2(T))^{\frac{1}{2}}$$

Temperature-dependent energy gap. As done previously, we substitute expressions for u_k, v_k, and f_k into Δ_k with the same approximation for the interaction as used before and after integration, instead of summation,

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_c} \frac{\tanh [(\varepsilon^2 + \Delta^2(T))^{\frac{1}{2}}/2k_B T]}{(\varepsilon^2 + \Delta^2(T))^{\frac{1}{2}}} d\varepsilon$$

$\Delta(T)$ can be calculated numerically, and the result is given in Fig. 6.

Transition temperature. As evident from Fig. 6, $\Delta(T)$ goes to zero as the superconducting transition temperature, T_c, is approached from below. Then

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_c} \frac{\tanh (\varepsilon/2k_B T_c)}{\varepsilon} d\varepsilon$$

which can be solved

$$k_B T_c \approx 1.14 \hbar\omega_c e^{-1/N(0)V}$$

With an electron–phonon interaction, the natural choice of a cut-off energy is the Debye energy $\hbar\omega_D = k_B \theta_D$. Then

$$T_c \approx \theta_D e^{-1/N(0)V}$$

which is the most quoted result of the BCS theory.

By coupling the expressions for $\Delta(0)$ and T_c, we find that the energy gap at $T = 0$, $2\Delta(0) = 3.53\, k_B T_c$.

3.4. *Dirty superconductors*

T_c is surprisingly insensitive to non-magnetic impurities and to disorder. Even in quench-condensed, amorphous, films where the electron mean free path is diminished to the order of an atomic distance, T_c is not changed dramatically. In such "dirty" metals the scattering lifetime is so short that the energy uncertainty is several orders of magnitude larger than, for example, the gap energy. The momentum k is no longer a good quantum number.

Anderson [18] showed that if time-reversed wave functions, which already contain the scattering (a superposition of scattered Bloch waves), are used, the BCS formalism can be applied using these electron states and an interaction averaged over the Fermi surface.

3.5. *Resumé of results*

Based upon Cooper's observation that the Fermi sea of electrons became unstable against pair formation if the electrons interacted attractively two-by-two, BCS built a theory of interacting pairs at the Fermi level. These condense into a ground state separated from the unpaired ground state by a condensation energy of $-\frac{1}{2}N(0).1^2$. Due to the correlation between the pairs, it costs a finite energy, a gap energy of 2Δ, to break a pair and create two excitations. The density of excited states goes as $N(0) \cdot |E|/(E^2 - \Delta^2)^{\frac{1}{2}}$. Δ is a function of temperature, $\Delta(T)$. At $T = 0$, $2\Delta(0) \approx 3.53\, k_B T_c$. As T is increased, $\Delta(T)$ first decreases slowly, but as more thermally excited electrons block possible pair states, it decreases rapidly at higher T and is zero at $T = T_c$.

The members of a pair are separated by a relatively large coherence distance. Within the extension of the pair wave function there are many other pairs. They all interact and move with the same center of mass momentum. At current transport each pair carries the momentum P, i.e. its wave function has a wave length of h/P. The phases of the different pair functions are all the same. If there should exist a voltage difference, V, between two ends of a superconductor, a pair would gain an energy of $2eV$ by traversing, and in time a phase shift $(2eVt/\hbar)$ would develop between pairs at the two ends. Rather than go to a higher energy state, that the breakdown of the pair phase-locking would imply, the superconductor carries the current without a voltage drop. Only when the kinetic energy from the center-of-mass movement is so large, that is suffices to break up the pair, will a finite resistance appear.

4. Verification of the theory; further developments initiated by experiments

Even in the original paper, BCS discussed a number of experimental consequences of the theory. Most experimental facts were in good or reasonable accord with the theory. The model also initiated many experimental investigations of its properties. If one is particularly satisfied with a theory that gives precise predictions that fit later experiments or that, within its scope, can explain new effects, then the BCS theory is such an example.

We will concentrate here upon points that either give a good and simple verification of different aspects of the theory, or have raised objections against the BCS theory. We will try to show how these objections have led to natural developments of the theory; developments that show there is no doubt about the general correctness of the microscopic theory of superconductivity. Our treatment can be divided into three main parts, namely:

(*a*) the pairing concept, the basic idea which leads to the superconducting state;

(*b*) the energy gap, which is the property of the state which most type of experiments, in one way or another, ultimately test; and

(*c*) the attractive potential which is needed to form pairs. BCS applied a simple approximation for this attraction, and some of the later developments of the theory have been centered around the problem to study more realistic models of the interaction.

4.1. *Pairs.*

The pairing concept is one of the very cornerstones in the microscopic theory of superconductivity. We can have superconductivity without an energy gap and other attractive mechanisms than the electron–phonon interaction have been proposed, but the existence of Cooper pairs has rarely been questioned [19]. Several experiments can only be explained by the so-called coherence effects, i.e. that the scattering of an electron from state $k\uparrow$ to $k'\uparrow$ due to the pairing, also depends upon the occupancy of states $-k\downarrow$ and $-k'\downarrow$. The explanations of the temperature

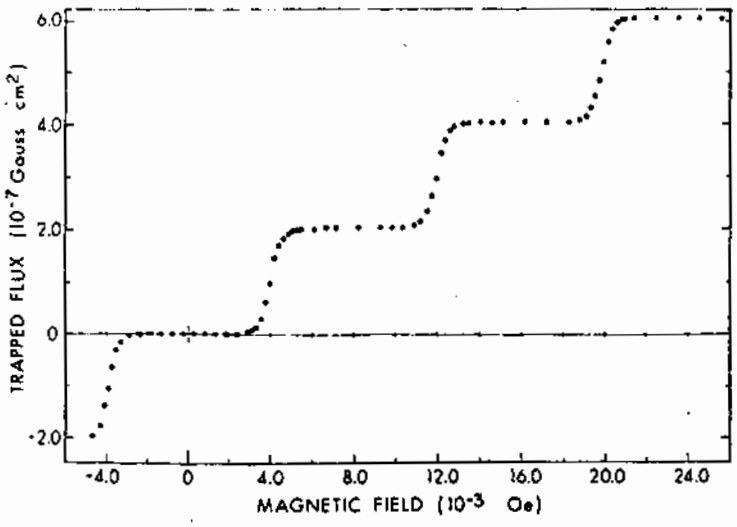


Fig. 7. By cooling a cylinder through its T_c within an applied magnetic field, flux is trapped. This trapped flux is quantized in units of $\Phi_0 = h/2e$ as the diagram above (from Goodman et al. [24]) shows.

dependence of the ultrasonic attenuation and the absorption of electromagnetic (infra-red) radiation build upon electrons with opposite (but to absolute value equal) momenta, while the temperature dependence of the spin relaxation time needs electrons with opposite spins. We choose not to treat these aspects here, but refer the reader to the literature treating this field [20]. Instead we shall briefly describe the first, dramatic, experiments that really tell us that the charge carrier in a superconductor has the same charge as two free electrons. We think of the detection of quantized flux within a superconducting ring. Josephson experiments have shown that exactly 2 electrons form a pair without any corrections due to possible higher order interactions, which would experimentally show up as a dependence on the material.

Because of the interaction between pairs, these move in a correlated way such that the center of mass motion of all pairs is the same. The state can then be described by an effective wave function. We get a natural connection to the earlier phenomenological theories of London and of Ginzburg and Landau. The Cooper pairs have a considerable extension in space and have a long life-time. They can penetrate into a metal in close contact with the superconductor or through a thin insulating barrier between two superconductors and still act as bound pairs although the attractive interaction is not present in the new environment. The two phenomena are named proximity and Josephson effects respectively. Through thermal fluctuations, it is possible for two electrons to form a pair with a short life-time at a temperature well above T_c under certain circumstances. In the following sections we will treat these properties while pair-breaking interactions will be treated at a later stage in section 4.3.

4.1.1. *Quantized flux.* F. London pointed out, in a foot-note to his book on superconductivity [21], that the magnetic flux enclosed within a superconducting ring could not take on any value but only an integral number of a quantized flux unit. To motivate the equations, London had to assume that the wave function that describes the superconducting condensate was rigid, i.e. not disturbed by the application of a magnetic field ($H < H_c$). The BCS theory could justify and explain the stiffness of the wave function and also why twice the electron charge and not only the single electron charge appeared in the expression for the flux quantum.

The electrons in the ground state appear as pairs, each with the same total momentum. The wave function corresponding to a single pair has a large extension. Hence it couples strongly to other pair functions that occupy the same region—the phases of all pair functions are correlated and all of them, i.e. the whole condensate can be described by one macroscopic wave function $\psi(r,t) = \sqrt{\varrho(r,t)}e^{i\varphi(r,t)}$, where ϱ is the super-electron density and φ is the phase.

For a particle of mass m^* and charge q, that moves in a vector potential A, the total momentum is a sum of the kinetic part m^*v and the electromagnetic contribution qA. As the momentum operator is $-i\hbar\nabla$, we can write:

$$v = (1/m^*)\,\mathrm{Re}\,\{\psi^*(-i\hbar\nabla - qA)\psi\}$$

The electrical current density for the state ψ is:

$$j = (\varrho q/m^*)(\hbar\nabla\varphi - qA)$$

By introducing the penetration depth (for a magnetic field)

$$\lambda \equiv (m^*/\varrho q^2\mu)^{\frac{1}{2}}$$

where μ is the magnetic permeability, we can write one of London's equations:

$$\nabla\varphi = (q/\hbar)(\mu\lambda^2 j + A)$$

If we integrate this phase gradient along a closed curve within a singly connected superconductor, we get zero. With a multiply connected region (for example a superconductor with a hole), the requirement of uniqueness of the wave function leads to the condition that the integral must be a multiple of 2π, thus

$$\oint \nabla\varphi = n \cdot 2\pi = (q/\hbar)\left(\oint \mu\lambda^2 j \cdot \mathrm{d}l + \oint A \cdot \mathrm{d}l\right)$$

If we now choose a superconducting ring thicker than a penetration depth (screening currents and penetrating magnetic fields are confined to such a region), we can set j in the first term above equal to zero. Hence by using Stokes theorem

$$\oint A \cdot \mathrm{d}l = \int_S (\nabla \times A)\,\mathrm{d}S = \Phi = n(h/q) = n\Phi_0$$

The magnetic flux within the ring is quantized in units of $\Phi_0 = h/q$. This fact was confirmed by two different groups [22, 23] in 1961. They found that $q = -2e$. The value of the quantized flux ($h/2e = 2.07 \times 10^{-15}$ Vs (2.07×10^{-7} Gcm²)) has later been verified [24] within $\pm\frac{1}{2}$%. Soon after the first experiments, a number of theoretical papers [25] dealing with fluxoid quanti-

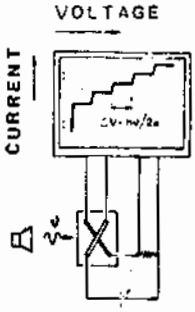


Fig. 8. A Josephson element, which is irradiated by a high frequency (r) field, displays current steps in its I–V curve. The steps are separated by a well defined voltage, $\Delta V = h\nu/2e$. Very accurate measurements of the ratio (Planck's constant/electronic charge) have been done. Conversely, it is possible to keep a voltage standard utilizing the a.c. Josephson effect (or even define electrical units in the form of frequency).

zation related the factor of 2 in the charge carrier to the pairing in superconductors.

If one fabricates a superconducting cylinder thinner than the penetration depth, screening currents will flow within the entire superconducting shell, and its transition temperature will be affected. It will be a periodic function of the enclosed flux [26]. Also here the periodicity is in $h/2e$.

4.1.2. *Is the pair really a pair?—The Josephson-effect.* The Josephson effect [27] has given us a tool to study if a pair is composed of exactly two electrons or not. This is no trivial question, as one might think of many body effects giving rise to an effective mass, or other combinations than pairs that might add up to the same total momentum.

To first describe what the Josephson effect is, we return to the wave function for the superelectrons. All these electrons move in a correlated fashion through the metal. The superconducting condensate can be described by one wave function $\psi = \sqrt{\varrho_0}e^{i\varphi(r,t)}$. If we regard two pieces of a superconductor, we know that if the two parts are well separated, the two electron systems are uncorrelated. On the other hand, if they are brought into metallic contact with each other, all the superelectrons in both of them can be described by one and the same wave function. Somewhere in between the two extreme cases, for a small separation between the two superconductors, the two electron systems will couple to each other. However, they do not need to be described by the same wave function. There may exist a phase difference, $\Delta\varphi(r, t)$, between the two superelectron wave functions.

Due to tunneling of electrons, the region between the two superconductors, whether it consists of vacuum, a thin insulator, a non-superconducting metal layer or even a superconductor of small dimensions, will act as a weak superconductor. Pairs, and not only single electrons, can tunnel through the weak link. A current can flow without an electric potential across the link. However, the critical current density is much smaller than the one in a usual superconductor (of the order of 10^{-6}; that is why the link is said to be a weak superconductor). Furthermore, the maximal current is a periodic function of the phase difference between the superconductors, $i_1 = i_0 \sin \Delta\varphi(r, t)$.

This phase difference is affected by the vector potential associated with electro-magnetic fields. The gradient of the phase difference is proportional to the magnetic flux density. The critical value of the Josephson current is thus a periodic function of the magnetic flux in the weak link. The period is, as you might have guessed already, the quantized value $\Phi_0 = h/2e$. So it is possible with this method to determine the flux quantum. With superconducting quantum interference devices (SQUID), i.e. in principle a superconducting loop interrupted by two interfering links [29], the sensitivity increases as the flux within the area enclosed by the loop is measured (and not only the flux in the weak link).

Yet there is another, more accurate way to determine the relation between Plancks constant and the charge carried by a pair, namely by the a.c. Josephson effect [27]. The d.c. Josephson effect, just treated, relies upon the spatial phase derivative's dependence on the magnetic field. We now turn to the scalar potential. It turns out that the time derivative of the phase difference is proportional to the electric potential across the weak link or, which is the same, the difference in chemical potentials between the two superconductors, thus

$$\frac{\mathrm{d}}{\mathrm{d}t}(\Delta\varphi(r, t)) = 2eV/\hbar$$

If V is a d.c. potential, the phase difference varies linearly with time. The Josephson current $i_1 = i_0 \sin \omega t = i_0 \sin (2eV_0 t/\hbar)$ is an a.c. current with a frequency of about 500 MHz per μV applied bias voltage. Radiation from microwave frequencies to infrared ones can be obtained [30]. If we, instead, superpose a high frequency a.c. voltage upon the d.c. bias, we get a frequency modulated Josephson current,

$$i_1 = i_0 \sin\left[2eV_0 t/\hbar + (2eV_1/\hbar)\int \cos \omega_1 t\,\mathrm{d}t\right],$$

an expression which can be expanded into Bessel functions. Another way to express this is to say that the externally applied radiation is mixed with the one generated in the Josephson link by the d.c. bias. Oscillations of sum and difference frequencies occur, and d.c. current spikes result each time the internal frequency equals a multiple of the external frequency, $2eV_0/h = n\nu$ (cf. Fig. 8).

By measuring the voltage difference between a large number of current steps, Langenberg and followers [31] have determined the ratio $2e/h$ with a very high accuracy, much higher than the one for the individual values of e and h. The uncertainty as regards the US legal volt is only 0.1 ppm, but on the other hand, that voltage standard has an uncertainty of more than 1 ppm compared with the absolute volt. (The maintained volt can be better defined by a frequency through the Josephson effect than by ordinary Weston cells if one assigns a fixed ratio of $2e/h$. As a matter of fact, the US legal volt is now based upon such determinations.)

By combining values of $2e/h$ with those of differently measured ones of e and h (the value determined by superconductivity is by far the most accurate one), we can establish to what degree the pair is really composed of two electrons. However, we can do even better by pure superconductive tunneling. If the effective number of electrons in a pair differs from the number 2, the difference should be material dependent, such that the number in lead, for example, is not the same as the one in tin. However, Clarke [32] has found no difference in voltage between the same order of step in two irradiated Josephson links of different materials. The pair charge was found to be the same within a limit of one part of 10^9 in lead, tin, and indium.

Complex many body interactions in normal metals and superconductors evidently do not give any observable renormalization of the effective charge of the electrons in a Cooper pair. It is believed that the charge of the Cooper pair is twice the free

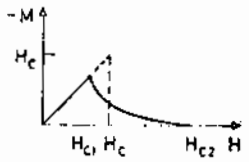


Fig. 9. Here we display a superconductor's response to an applied magnetic field, H, in the form of its magnetization (defined by $B = \mu(H + M)$. The dashed line denotes the behaviour of a type I superconductor (usually a pure metal: geometrical demagnetization effects have been neglected). The flux density, B, is zero until a critical field H_c is reached. In a type II superconductor (full line), on the other hand, the field is completely expelled to a field H_{c1}. At that field a number of flux lines penetrate the superconductor, and the magnetic flux is only partly expelled. Superconductivity persists until a field H_{c2} (which can be much greater than H_{c1} and the thermodynamical critical field H_c).

electron value to an accuracy of 1 part in 10^7. But is the situation the same for the electronic mass? It is well known that corrections from band effects and phonon renormalization, for example, can give a sizeable contribution to the effective electron mass in a metal. However, it should be pointed out, that the concept of "effective mass" does not apply to the inertial properties of electrons in metals. It is used to describe the electronic dynamic properties in the presence of external fields, when these are not corrected for local electric or magnetic fields. For convenience, the effects from crystal fields are treated as a correction to the electron mass instead of as corrections to the external field.

If a superconducting cylindrical ring, part of which is described to form a weak link, is rotated, a current will flow. Due to the weak link, the current is periodic, and the period contains, besides the circumvented area, the factor m/h. The value of m has been determined [33] to be twice the free electron mass although the effective mass of tin, which was used in the experiment, is 1.1 m_e. As it is difficult to measure an area precisely, the present accuracy is not better than 0.04%. However, more accurate experiments are planned [33]. The relativistic corrections to the electron mass in a superconductor is expected to be of the order of 10 ppm [34].

The Josephson effects beautifully illustrate the properties of the superconducting ground state wave function. The motion of pairs is correlated so that they all move in phase. The correlation extends over "miles of dirty lead wire" as Bardeen expressed himself. The phase $\varphi(r, t)$ is the interesting part to study. In a weak link, where the pair density is low, it can be modulated by external fields, enabling us to study quantum effects in a macroscopic scale. Several excellent reviews of the Josephson effect and its applications exist [35].

4.1.3. *Order parameter. The Ginzburg–Landau theory.* When the BCS theory first appeared, it was not clear as to how wide a class of superconductors it applied. There were a number of superconductors—at the time, all alloys—which did not possess the simple magnetization behaviour discussed in the introduction, namely one in which the magnetization $M(H)$ dropped to normal value at a critical field $H_c(T)$. Instead the magnetization changed rapidly with increasing field at a value H_{c_1} ($< H_c$) but the superconductor continued to be diamagnetic (relatively the non-superconducting metal) until some higher field H_{c_2} (see Fig. 9). Furthermore the ratio H_{c_2}/H_{c_1} varied from superconductor to superconductor. It could even be changed in a given superconductor by heat treatment or cold working. Few scientists in the West would at the time (1958) believe that the BCS theory could explain that behaviour.

In Russia, however, the phenomenological theory of Ginzburg and Landau [9] had already had great success in explaining the so-called intermediate state behaviour. This work was extended in 1957 by Abrikosov [36] who showed how the complex magnetization behaviour of a type II superconductor could be understood in terms of a new solution of the Ginzburg–Landau equations.

We have already introduced a macroscopic wave function which describes the superconducting state. The strong correlations between different pairs makes it possible to introduce a macroscopic wave function to describe the whole system in a manner anticipated already by London. Ginzburg and Landau [9] also introduced an effective wave function, which they called an order parameter ψ, which characterizes the "degree of superconductivity", in their phenomenological theory of 1950 [37]. The density of the superconducting condensate is proportional to $|\psi|^2$. Close to the critical temperature or at high magnetic fields, where $|\psi|$ is small, the free energy can be expanded in powers of $|\psi|^2$ following the theory for phase transitions developed by Landau.

$$g_{s_0} = g_{n_0} + \alpha|\psi|^2 + (\beta/2)|\psi|^4 + \ldots$$

Where g_{n_0} is the free energy per unit volume of the normal state, α and β are parameters, and ψ is assumed not to vary in space.

If $\psi(r)$ varies in space one has to add a kinetic energy term proportional to $(\nabla\psi)^2$. This term must be modified if one applies a vector potential $A(r)$ (such that the magnetic field strength $H = \nabla \times A$). Then we know that the momentum transforms like

$$P = -i\hbar\nabla \to -i\hbar\nabla - qA$$

where q is an effective charge which will turn out to be twice the electronic charge.

The free energy becomes to leading terms in $|\psi|^2$:

$$G_s = G_n + \int d^3r\{\alpha|\psi|^2 + (\beta/2)|\psi|^4 + (1/2m^*)|(-i\hbar\nabla - qA)\psi|^2 + (\mu/2)|H|^2\}$$

The first terms in the integral represent the lowering in the free energy due to a higher degree of order in the condensate, the last one is due to the field energy caused by the distortion of the magnetic field, while the middle term describes the increase of the kinetic energy from diamagnetically induced currents and from extra "wiggles" in the wave function.

A variation of the free energy with respect to ψ, ψ^* and A gives the stable configuration. One obtains the two so-called Ginzburg–Landau equations:

$$\alpha\psi + \beta|\psi|^2\psi + (1/2m^*)(-i\hbar\nabla - qA)^2\psi = 0 \qquad \text{(G.L.1)}$$

$$j_s = \nabla \times H = (q/2m^*)[\psi^*(-i\hbar\nabla - qA)\psi + \psi(i\hbar\nabla - qA)\psi^*] = -(iq\hbar/2m^*)(\psi^*\nabla\psi - \psi\nabla\psi^*) - (q^2/m^*)\psi^*\psi A \qquad \text{(G.L.2)}$$

Two characteristic lengths are deduced from the equations. A disturbance from the equilibrium state ψ_0 dies off with a characteristic length $\xi = (\hbar^2/2m^*|\alpha|)^{\frac{1}{2}}$. This is the coherence distance.

An applied magnetic field penetrates a distance λ into the superconductor. λ, the London penetration depth, obtains a value of

$$\lambda = (\mu q^2\psi_0^2/m^*)^{-1/2}$$

where the equilibrium density $\psi_0^2 = -\alpha/\beta$.

ξ and λ have both a temperature dependence of $(T_c - T)^{-\frac{1}{2}}$.

Fig. 10. Magnetic field penetrates a type II superconductor (e.g. an alloy or a thin film) in the form of flux lines. Each flux line carries one flux unit ($\Phi_0 = h/2e$), and the flux lines repel each other such that a lattice of flux lines is formed. Triangular as well as square arrangements are possible. This picture is an electron microscope replica of a film of small magnetic particles evaporated upon a type II superconductor kept in a magnetic field. The magnetic particles are attracted by the flux lines peeping out of the surface and condense in a two-dimentional lattice. The lattice, of course, contains defects. As the lattice constant can easily be changed (by varying the external field) and as forces can be applied upon the flux lines by sending a current through the film ($F \sim B \times I$), the influence upon the lattice defects can be studied in a fundamental way. The picture is taken from Seeger [40].

High field superconductivity. We shall now consider a superconductor in a strong magnetic field. At sufficiently high fields the metal is normal and the field penetrates evenly across the sample. If the field is decreased, superconductivity is nucleated at a critical field $H = H_{c_2}$. This is generally not the thermodynamic critical field H_c. It can be larger as well as smaller.

The result, which was obtained by Abrikosov [36], follows from the Ginzburg–Landau theory, and one gets the numerical result

$$H_{c_2} = \sqrt{2}\kappa H_c = \Phi_0/2\pi\xi^2\mu$$

$\Phi_0 = h/2e$ is the quantized flux unit, as usual.

$\kappa = \lambda/\xi = 1/\sqrt{2}$ marks a border line, a separation between so-called Type I (low κ) and Type II (high κ) superconductors. For $\kappa < 1/\sqrt{2}$, the critical magnetic field is smaller than the thermodynamic one. This results in supercooling—the magnetic field must be decreased to a lower value for the superconducting state to reappear than the value where it was lost at increasing field.

$\kappa > 1/\sqrt{2}$ is a case of great technological importance. In superconducting alloys, large values of κ can be found. The β–W compounds that have high T_c's also possess large values of H_{c_2}.

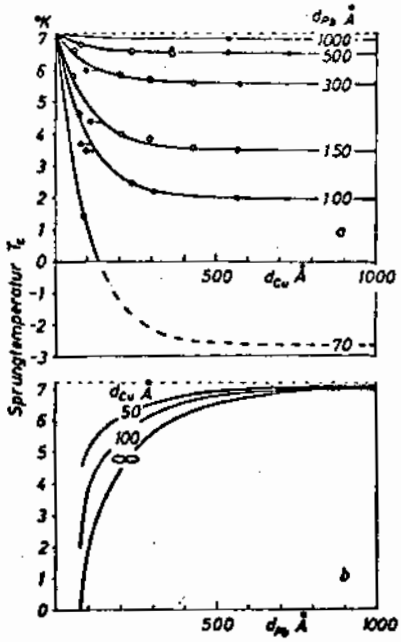


Fig. 11. If two thin films (one of which is superconducting and one is normal) are kept in metallic contact with each other, the "sandwich" will have a T_c different from the superconducting film. The T_c of the superconducting film will be depressed and superconductivity may be induced in the otherwise non-superconducting film. The T_c of the layered package will depend upon film thickness and materials. This is shown in the diagrams above, where T_c as a function of the thicknesses of the superconducting, d_{Pb}, and normal, d_{Cu}, films is displayed. The effect is often called the proximity effect. (From Hilsch [43].)

A critical magnetic flux density of 42 Vs/m² (420 kG) has been estimated [38] for Nb_3 (Al, Ge).

In type II superconductors a correlated state nucleates at $H < H_{c_2}$. It does not show any electrical resistance, but a complete Meissner expulsion of the magnetic field is not recovered until the field has been decreased to $H_{c_1} < H_c$ as shown in Fig. 9.

As the magnetic field, H, is increased above H_{c_1}, it starts to penetrate a type II superconductor. The magnetic flux is not evenly distributed, but penetrates the superconductor in the form of flux lines, each containing one unit of the flux quantum, Φ_0. In such a flux line, the superconducting order parameter increases from zero at the center to its full value within the coherence length, while the magnetic field penetrates the area around the flux line within the penetration depth. The flux lines repel each other. The energetically stable state is the one where the flux lines form a lattice (Fig. 10). The latter is often of triangular symmetry [39, 40] and the lattice constant is determined by the magnetic field strength.

The Ginzburg–Landau theory, and its extensions, has been very successful in describing the high field properties of superconductors. But it is no microscopic theory. Gorkov [41] showed in a series of papers that it is possible to derive the Ginzburg–Landau equations from the microscopic BCS-theory. He finds that the Ginzburg–Landau wave function ψ is proportional to the local value of the energy gap parameter. So the Ginzburg–Landau theory has a firm basis and conversely, its success in describing high field properties can be included in the impressive amount of facts that support the BCS-theory.

4.1.4. *Extension of pairs in space—proximity effect.* We already remarked that the superconducting order parameter varies over a coherence length within the cross section of a flux line in type

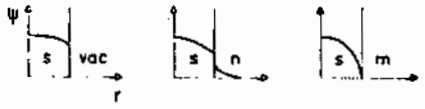


Fig. 12. This is a schematic picture of the superconducting order parameter close to the boundary between a superconductor and (*a*) vacuum; (*b*) a normal metal (or a superconductor with a lower T_c); and (*c*) a magnetic metal.

II superconductors. The flux line cross section can be described as an area of non-superconducting material. What happens if we place a normal metal in contact with a superconductor? The order parameter in the superconductor is depressed close to the boundary, and extends into the normal metal (at least if the latter is not magnetic). Electron pairs leak into the normal metal and it will become a superconductor. On the other hand, the attraction between the electrons in a pair decreases, and the pairs will be broken. Hence the superconducting transition temperature will be decreased in a sandwich composed of a superconducting thin film in direct contact with a non-superconducting (or with a film that will superconduct at a lower temperature) [42]. The situation is illustrated in Figs. 11 and 12.

If the superconductor is much thicker than a coherence length, its T_c will not be affected by the proximity of another film. A magnetic over-layer has a much more profound effect upon T_c than a non-magnetic one.

4.1.5. *Extension of pairs in time-fluctuations.* If one measures the transition into the superconducting state at T_c, one normally observes a very sharp transition in a pure bulk metal. However, if one goes to small dimensions, to more or less two-dimensional films or one-dimensional filaments, the transition is broadened [44]. The resistance starts to decrease at temperatures which in the extreme cases can be of the order of several times T_c. The conductivity above T_c is increased by a term with a temperature dependence $(T-T_c)^{-\gamma}$, where $\gamma = 2-(\text{dimensionality})/2$, i.e. $\gamma = 1$ for a two-dimensional film, the most investigated case (cf. Fig. 13).

We can compare the situation with the one in magnetic materials above the Curie temperature. Critical spin fluctuations, paramagnons, exist there. Here, Cooper pairs, i.e. fluctuations in the order parameter, are formed above T_c. They have a short,

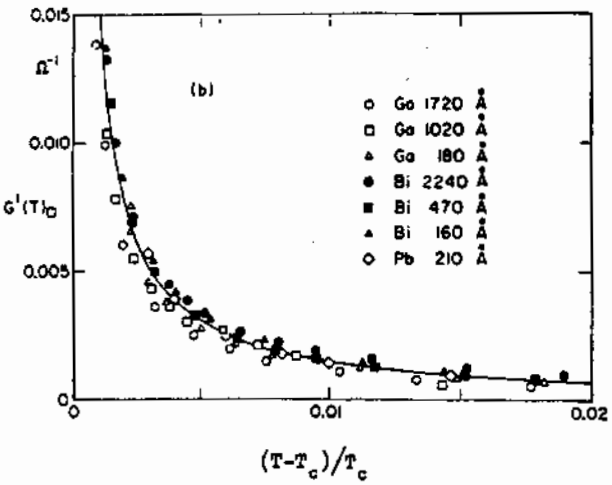


Fig. 13. The extra conductivity (relative to temperature) due to fluctuations, i.e. Cooper pairs with short, temperature dependent lifetimes, in thin disordered films. (From Glover [44].)

temperature-dependent life-time, during which they contribute to the conductivity. The situation was first explained by Aslamazov and Larkin [45].

The susceptibility also shows a diamagnetic contribution above T_c in disordered thin films or layered structures. Geballe and coworkers [46] have detected a starting transition at 35 K (an order of magnitude larger than T_c) in layered compounds, consisting of about 6 Å thick metallic layers separated by organic molecules of varying thickness. Heeger's group at Univ. of Pennsylvania have recently made organic layer compounds, in which the metallic conductivity increases considerably at low temperature [47]. In a few samples it is roughly 500 times larger at about 60 K than at room temperature. Alas, the compound then transforms into an insulator. The behaviour was interpreted as a fluctuation contribution above T_c—the strong attraction needed to give such a high T_c was supposedly mediated by soft phonon modes at the metal–insulator transition (see Sec. 6).

4.2. *Energy gap*

The BCS theory implies an energy gap in the excitation spectrum for single electrons. An energy larger than the gap value is needed to excite quasiparticles out of the superconducting ground state. For energies less than this value no states exist. Above the gap the following expression for the density of excited states is obtained:

$$N_s(E) = N(0)\frac{|E|}{\sqrt{E^2-\Delta^2}}$$

(cf. Fig. 5). $N(0)$ is the "normal" electronic density of states at the Fermi energy. Energies are counted from this level.

The energy gap is one of the most striking results of the BCS theory. There are many ways to show its existence experimentally. As mentioned, specific heat measurements at low temperatures indicate the presence of an energy gap. Several scattering experiments, like acoustic attenuation, also base their interpretation upon interactions with excited quasiparticles. As the number of these excitations is equal to an energy integral over the density of excited states multiplied by a Fermi factor, there is a gap dependence.

The most elegant method to show the existence of a gap is probably the one of electron tunneling into a superconductor. We choose to present the results of this type of experiment in greater detail than other verifications. It is easy to understand, because it tests a central result of the theory. Furthermore, it gives small deviations from the original theory that in some minds have given rise to skepticism, but these have on the other hand inspired the further development of the theory to a degree of accuracy that surpasses almost any other theory of a solid state property.

Compilations of experimental values of the energy gaps in different materials are given in Ref. [48].

4.2.1. *Tunneling.* When hearing about the energy gap in superconductors, Giaever [49] extended his previous work on tunneling in metals to the case of superconductors. The tunnel effect is about as old as quantum mechanics. If two conductors are separated by a thin insulating layer, there is a finite probability that electrons will penetrate the forbidden area. They will "tunnel" from one conductor to the other.

If we apply a simple-minded golden rule argument, the current

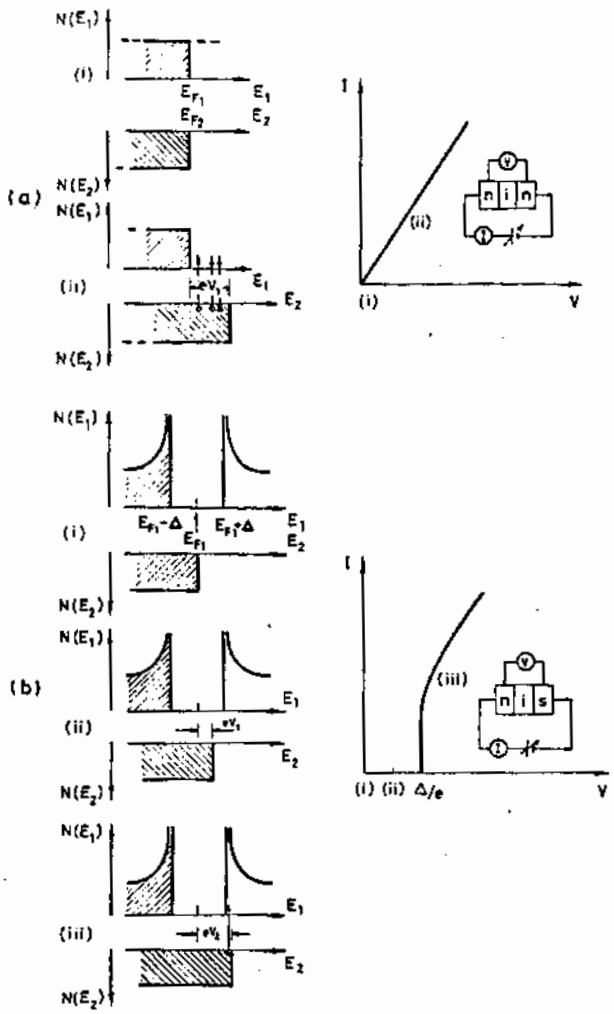


Fig. 14. A tunnel current can arise when a voltage is applied between two conductors separated by an insulating barrier. In case (*a*) both metals are normal (i.e. non-superconducting). With no external potential between metals (1) and (2), the chemical potentials of these two metals adjust such that the Fermi energies, E_{F_1} and E_{F_2}, coincide. When a potential is applied there is a higher probability for electrons to penetrate the forbidden insulator from the metal with the lower potential to the one with the higher than vice versa. For small voltages, I is proportional to V. (*b*) One of the metals is a superconductor. This implies that if we increase the electrical potential with a value $V < \Delta/e$, there will be no available states in the superconductor (1) to receive electrons tunneling from the normal metal (2). When $V = \Delta/e$ a sudden current increase is registered, as there is a large number of available states in the superconductor at corresponding energy to receive electrons. The diagrams are drawn for $T = 0$. For finite temperatures, the I–V curve of (b) is smeared.

between two conductors, 1 and 2, biased with the voltage V relative each other can be written:

$$I = A \int_{-\infty}^{\infty} |M|^2 N_1(E) N_2(E+eV)[f(E) - f(E+eV)]\,dE$$

where M is the matrix element for transitions between states of equal energies in the two metals, $N_1(E)$ and $N_2(E)$ are the electronic density of states at energy E, $f(E)$ is the Fermi function $(1/(1 + \exp(E/k_B T))$, and A is a constant.

Between two "normal" conductors one obtains at low voltages

$$I_{nn} = C_n V$$

which is experimentally verified [50].

If one of the conductors is a superconductor

$$I_{sn}(V) = C_n \int_{-\infty}^{\infty} N_s(E)[f(E) - f(E + eV)]\,dE$$

At $T = 0$, I_{sn} jumps from zero to a finite value at $eV = \Delta$, the voltage derivative becomes

$$\left(\frac{dI}{dV}\right)_{T=0} = C_n' N_s(eV)$$

so it is possible to directly get a picture of the density of states of the excitations. The procedure is illustrated in Fig. 14.

The simple model used by Giaever and Megerle [17] was criticized for its simplifying assumptions. A more satisfactory treatment in the one-electron approximation shows that no density of states effects would be seen in experiments [51]. But the clear picture of the density of states was still there. This paradox was resolved by Bardeen who showed that a many-body treatment gives a tunnel current, which reflects the quasi-particle density of states [52]. Later calculations have shown that band structure effects also show up in one-electron models [53]. For an excellent account of single particle tunneling in superconductors, see Ref. [54].

Josephson [27] extended studies of the microscopic tunneling theory to tunneling of pairs. As we have already mentioned in section 4.1.2. his effects beautifully illustrate the occurrence of Cooper pairs. Although there are features in Josephson tunneling that are of relevance to a discussion of energy gaps, we will not treat these here.

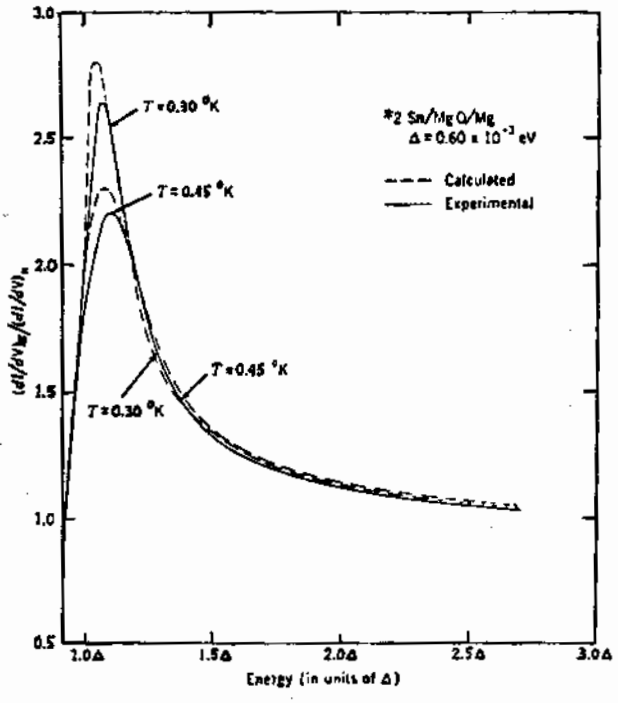


Fig. 15. This is one of Giaever's first curves of dI/dV (in the superconducting state normalized to the one of the normal state) vs. V for superconductor (Sn) to normal metal (Mg) tunneling [55]. The dashed curves are conductances calculated from the BCS theory for two different temperatures (thermal broadening due to the Fermi factor). Note the correspondence between theoretical and experimental curves.

Table I. *Measured values of* $2\Delta(0)/k_B T_c$
CS value in weak coupling limit is 3.53

uper- on- uctor	Tunneling	Ref.	Ultrasonic attenua- tion	Ref.	Infrared absorp- tion	Ref.	Thermo- dynamic
l	2.8–3.6	56	3.7±0.3	58	3.37	59*a*	3.51
	3.37±0.1	57					
d	3.2	59*b*					3.52
ia	3.63–3.94	60*a*	3.5–3.9	62			3.51
	3.47–3.70	60*b*					
	2.9–3.5	61					
lg	4.6±0.1	63			4.6±0.2	64	4.10
n	3.63±0.1	17			4.1±0.2	64	3.67
	3.45±0.07	57			3.9±0.3	65	
a	3.2	66			2.85±0.25	68	3.60
	3.7	67					
Pb	3.84±0.06	69	3.4–3.6	71*a*	2.8±0.3	64	3.67
	3.59–4.02	70	3.52±0.02	71*b*	3.81±0.06	72	
Sb	4.38±0.01	73	4.1±0.2	76	4.1±0.2	64	3.97
	3.80–4.65	74			4.37±0.1	77	
	3.70–4.45	75					
Se	3.35–3.91	78	2.9–3.5	79			3.11
In	3.46±0.1	17	3.1–3.8	81	3.5	83	3.58
	3.51±0.18	69	3.2–3.8	82	3.6±0.2	64	
	3.1–4.3	80			3.3±0.2	65	
Ta	3.6±0.1	69	3.5±0.1	84	3	64	3.58
Th	3.47	85					3.66
Tl	3.57±0.05	86	3.8–4.0	87			3.71
			3.7–3.9	88			
V	3.4	89	3.1–3.4	90	3.4±0.2	64	3.34
			3.5±0.1	84			
Zn	3.2±0.1	91					3.46

The thermodynamical ratios were calculated from $\mu_0 H_c^2/2 = N(0)\Delta^2/2$, utilizing the "free" electron relationship for the specific heat coefficient, $\gamma = 2\pi^2 N(0) k_B^2/3$. Values for T_c, H_c and γ are taken from Ref. 3.
Where a range of values is given, these usually refer to measurements in everal crystal directions in a single crystal.

4.2.2. *Temperature dependence of the energy gap.* An example of Giaever's results is given for tunneling into superconducting Sn in Fig. 15. The dashed lines are conductances computed from the BCS theory while the full lines are experimental curves. Due to he Fermi factor in the expression for the tunnel current, the dI/dV curves are broadened at finite temperature.

The energy gap parameter, $\Delta(T)$, is dependent upon temperature. The more thermally excited quasiparticles there are, the smaller is the fraction of unbroken pairs and the smaller the energy gap.

From tunneling experiments it is possible to determine the energy gap as a function of temperature, and a comparison between this function and the BCS relation is given in Fig. 6.

4.2.3. *The relation between the zero temperature energy gap* $2\Delta(0)$ *and the critical temperature* T_c. The original BCS theory, with its simplifying assumptions of an isotropic, average interaction potential and well defined electronic states, gives for the ratio between the energy gap at $T = 0$ and the transition temperature, $2\Delta(0)/k_B T_c$, a value of 3.53. Experimentally, one notes considerable deviations from this value (see Table I). Larger as well as smaller values have been reported. For example for Pb average ratios between 4.29–4.38 have been reported, for Hg 4.6, while corresponding ratios as small as 3.2 have been measured for Cd and Zn. As these deviations have, at times, led to a criticism of the theory, we will show here that they can be satisfactorily explained.

Values of $2\Delta(0)/k_B T_c$ smaller than 3.53 can be explained by anisotropies or by inhomogenities in the films. The directionally dependent interaction potential $V_{kk'}$ for scattering of pairs from states $\pm k$ to $\pm k'$ was approximated by an isotropic potential V. This evidently is an approximation. The phonon dispersion relations depend upon the direction of the waves. The Fermi surface for electrons is also anisotropic. In reality we have then a highly anisotropic potential that gives rise to different energy gaps in different crystal directions. A measurement of the energy gap in a single crystal depends upon the crystal surface chosen. Thin films are polycrystalline and one usually measures an average value. The critical temperature, on the other hand, corresponds to the maximal gap value. As an average value generally is smaller than a maximum, it is not surprising that values less than 3.53 are registered.

But for some metals, and in particular Pb and Hg, values larger than 3.53 appear. Why? The answer is related to the fact that quasi-electrons are no longer well defined when there is a strong coupling between electrons and phonons; they are damped. One has to take into account lifetime effects [92–95]. We will treat these aspects later in the part dealing with strong coupling superconductors; let us for the time being relate a few of the results.

$\Delta(0)$ is measured at, or rather extrapolated to, $T = 0$. For $T \neq 0$ thermal phonons are excited. In a metal with a strong electron–phonon coupling (and hence a low Debye temperature) particularly many phonons are excited. These contribute to the damping of quasi-electrons [96], and $\Delta(T)$ decreases more than $\Delta(0)$ [96, 97]. Then also T_c (from $\Delta(T_c) = 0$) decreases more than $\Delta(0)$ and it is plausible that $2\Delta(0)/k_B T_c > 3.53$. For Pb, Hg and Al values of 4.33–4.40, 4.8, and 3.5 resp. have been calculated [98]. The agreement with the experiment is very good. Similar calculations have also been performed for Sn and In [99]. The value 3.5 for Al implies that the theory goes into the normal BCS theory for weak coupling, which it should do. In disordered films [100–104] one often observes $2\Delta(0)/k_B T_c > 3.53$. This is in accord with the argument above, as more vibrational states are excited at lower frequencies in these than in ordered films.

4.2.4. *Anisotropies, multiple energy gaps, fine structure.* We have just mentioned that in a single crystal one has to take into account the directional dependence of the interaction. Even in a certain direction there can be more than one gap due to electrons

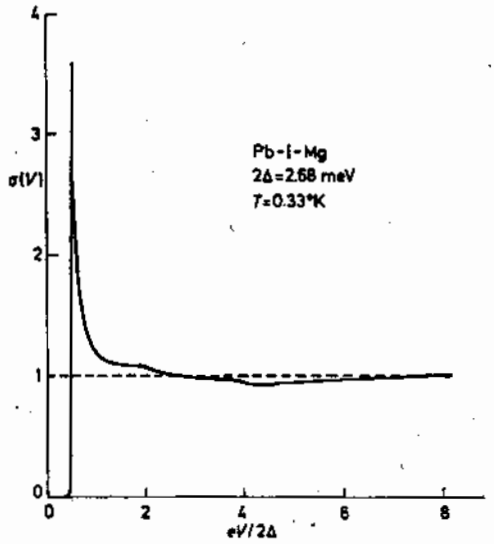


Fig. 16. Normalized conductance vs. energy for a Mg–MgO–Pb junction. Note that the curve deviates from a smooth, unstructured, curve at energies well above the gap energy. The curve is taken from Giaever et al. [55].

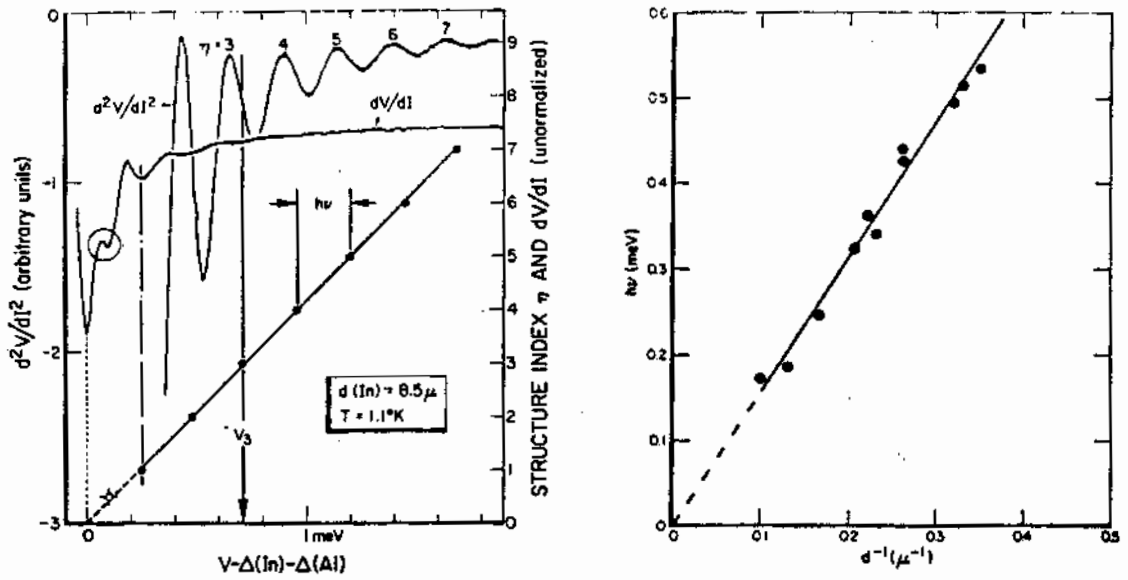


Fig. 17. The left diagram displays the first and second derivatives of an *I–V* curve taken with an Al–AlO_x–In/Ag junction. The indium film is relatively thick. The observed structure became stronger when a thin layer of silver was evaporated on top of the 8.5 μm thick indium film. The peaks are separated by an energy $h\nu$, and the diagram to the right shows the variation of this oscillation period with film thickness. The data of the right diagram are taken upon thick Pb films. (From Tomasch [112].)

in different Brillouin zones. More than one energy gap has been detected by tunneling into a thick film [69, 105]. The effect disappears, as expected, if disorder is introduced, for example as the film is made thin or at alloying (it remains, though, to surprisingly high impurity contents [106, 107]). A dirty superconductor is more ideal, more isotropic, than a pure one.

Zavaritskii [80] performed tunneling experiments upon single crystals of tin, and he found energy gaps falling in a range of ±20% of the average value. Experiments with single crystals of Nb [70], Pb [74, 75], Ga [61], and Re [78] have also been made (cf. Table I). The results have been compared with those of theoretical works [108–110]. Some details are still not solved; details that are connected to the tunneling process and selection rules regarding the directional dependence of the injected electrons.

Do tunneling data hide more secrets—more deviations from the theory? There do exist structures in experimental tunneling curves that are not present in the original BCS density of excited states. One of the oldest examples is given in Fig. 16. We will now discuss how structure can be obtained even from the original model if one regards the dual (electron-hole) nature of the excitations or correlations between tunneled particles. By making more realistic, but at the same time considerably much more complex, assumptions, we shall later indicate how the microscopic theory can be developed into such a detailed state that there is an excellent agreement between theoretical and experimental "fine structure".

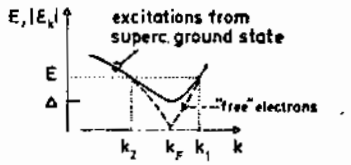


Fig. 18. The degenerate nature of an excitation with energy E is indicated by this figure. When $E>\Delta$ two states, with wavenumbers smaller or larger than the Fermi wave number, have the same energy. The Tomasch effect is explained as an interference appearing as the difference in wave number times the film thickness equals a factor of 2π.

4.2.5. *Tomasch effect.* Oscillations in the effective density of states of thick (of the order of μm) superconducting films were observed by Tomasch [111, 112]. The effect was particularly strong as electrons were tunneled into films where the opposite side was covered by a thin non-superconducting film. The period of the oscillations was a function of the inverse film thickness as shown in Fig. 17.

The appearance of these oscillations is a good verification of the BCS model. McMillan and Andersson [113] explained them as a geometrical resonance effect caused by interference between electron and hole-like excitations. The excited quasi-particles are degenerate as indicated in Fig. 18. Counted from the Fermi energy, the quasi-particle kinetic energy can be written

$$\pm(E^2-\Delta^2)^{\frac{1}{2}} = \varepsilon_k = \hbar^2k^2/2m - \hbar^2k_F^2/2m$$

$$= (\hbar^2/2m)(k+k_F)(k-k_F) \approx (\hbar^2k_F/m)(k-k_F)$$

$$\text{so } k_{1,2} = k_F \pm (E^2-\Delta^2)^{\frac{1}{2}}/\hbar v_F$$

An injected quasi-particle of energy E can be considered as a superposition of electron- and hole-like wave functions with different wave numbers as shown above. As the particle traverses the film there will be a phase difference between the two components. When it arrives at the opposite side it can change character as the gap function is disturbed at the surface (particularly so with a "normal" film on top). A constructive interference between the two wave functions results if the phase difference is a multiple of 2π, i.e. $n\cdot 2\pi = d|k_1 - k_2|$, where d is the film thickness.

Resonance appear at

$$E_n = eV_n = \pm\sqrt{\Delta^2 + (nh v_F/2d)^2}$$

The relationship is experimentally well documented [112]. By measuring in different crystal directions it is possible to determine the directional dependence of the Fermi velocity [75].

4.2.6. *Photon and phonon stimulated tunneling.* Imagine a tunnel junction biased at a voltage less than the gap value. What happens

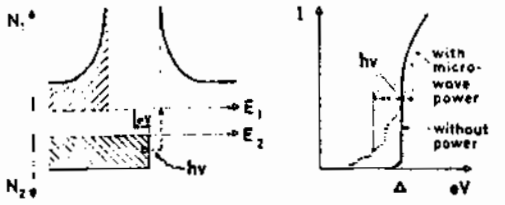


Fig. 19. Photons or phonons can stimulate tunneling. If these are of frequency ν, tunneling can occur against the huge density of states at Δ each time the applied voltage $V=(\Delta \pm n\cdot h\nu)/e$, and current steps are obtained at these voltages. [Cf. 117.]

when such an element is irradiated by photons or phonons; The current through it can increase. We can distinguish between two cases, namely the energy of the radiation quanta, $h\nu$, being larger or smaller than the energy gap 2Δ.

For large frequencies, $h\nu$ larger than 2Δ, the incident photons or phonons will break Cooper pairs and create two excitations above the energy gap. These can tunnel through the barrier and give an excess current. As a matter of fact we have got a detector for high frequency radiation [114, 115].

If a tunnel junction is irradiated by photons or phonons of energy $h\nu$ less than 2Δ, such quasi-particles can assist tunneling whenever the tunneled electron energy differs from Δ by a multiple of $\pm h\nu$ [116]. The electron can either absorb or emit (stimulated emission) one or several photons or phonons of energy $h\nu$. Photon- or phonon-assisted tunneling is illustrated in Fig. 19. A mechanism of stimulated emission of phonons has also been invoked to explain extra structure in ultra thin, patchy films [117].

Photons and phonons are also generated in a superconducting tunnel junction [115]. Electrical power is dissipated in the junction as current is passed at finite voltage. It is delivered to the surroundings, mainly in form of phonons to the refrigerator. Single electrons that have been injected in a superconductor will recombine into Cooper pairs. They will do so by sending out photons or phonons. The phonon process is by far the most probable one. The recombination mostly occurs in two steps—first the excitation relaxes into a state just above the energy gap (where there is a high density of states), and then two electrons will recombine into a pair. Relaxation phonons form a continuous energy spectrum extending from 0 to $eV-\Delta$, while the recombination phonons have an energy of 2Δ [118].

Phonons in a narrow band of frequencies can be generated. The spectrum from a Sn/I/Sn junction was found to be almost monochromatic ($\nu \approx 2\Delta/h$), and the power output is sizeable. Large power can be obtained by applying a heat pulse to a superconductor (Dynes and Narayanamurti [116]). The black body phonon radiation excites electrons and these will relax and recombine. Due to the two step process, there will be a frequency cut-off at $2\Delta/h$, the emitted density being peaked at that frequency. Usable recombination phonon frequencies range from about 10^{11}–10^{12} Hz depending upon material. A narrow band generator in this interval is hard to obtain by other techniques.

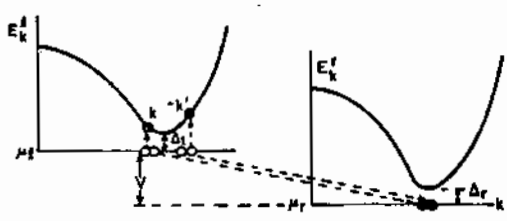


Fig. 20. Multiparticle tunneling is illustrated in this schematic picture. Two excited electrons from two Cooper pairs tunnel across the insulator and recombine in a second superconductor into a new Cooper pair. The process will give a very small current contribution at a voltage of Δ/e. The contribution is small, as two independent electrons will tunnel with a probability of the square of the tunneling matrix. It is a completely different process than the Josephson tunneling, which involves two electrons tunneling as a pair. The tunneling in the latter case is in first order and will occur already at zero bias. (Courtesy by J. W. Wilkins.)

4.2.7. *Multiparticle tunneling.* Hitherto we have regarded tunneling of independent particles. What happens if two single electrons tunnel at the same time in a correlated fashion? For example if both of the members of the Cooper pair tunnel simultaneously to form two quasi-electrons in the second superconductor, or vice versa (cf. Fig. 20). This is a situation which is unique for a superconductor, in normal metal tunneling there is no correlation between the tunneled particles. Mathematically we can say, we have to go to second order in the square of the tunneling matrix when we do our integration to get the tunnel current. Calculations were done by Schrieffer and Wilkins [119, 120], and they found a finite current contribution coming at $eV \sim \Delta$ in agreement with an experiment by Taylor and Burstein [121]. Two-particle tunneling has also been claimed to be seen in a recent work [122].

Excess currents at voltages equal to subharmonics $2\Delta/n$, where n is larger than 2, has also been reported [121]. These contributions have been interpreted in even higher orders than two of the tunneling matrix square. But such an interpretation must fail for large n. Excess currents have been noted [123] for up to 11 subharmonics, and clearly an eleventh order in the tunneling matrix must be an extremely small tunneling probability. The situation is complex experimentally too [124]. In order to get a sizeable contribution from the second order process, the matrix element must not be too small, i.e. the barrier has to be thin. At thin barriers there can be Josephson current contributions, and there is a great risk that metallic shorts will appear. By shining light upon a CdS barrier separating two Sn films, Giaever and Zeller [125] were able to vary the "effective barrier thickness". The subharmonic structure, they observed, varied more like M^3 than like M^4 (where M is the tunneling matrix element). This is in contrast to what one would expect from multi-particle tunneling. So one is left with the conclusion that if such tunneling really has been observed, it must have been under very favourable circumstances.

4.3. *The attractive interaction*

To form Cooper pairs, there must exist an attractive interaction between electrons close to the Fermi level. BCS applied such an interaction within a certain energy interval of the order of a Debye energy arguing that this interaction was caused by an exchange of virtual phonons. Popularly we can say that a negatively charged electron attracts positive ions as it moves through the lattice and hence leaves a track of positive charge behind it. As the ions are much heavier than the electrons, it takes a considerable time, measured in the time scale of electrons, for the lattice vibration to die out. If a second electron meanwhile arrives to the track, it will feel an attraction.

Bardeen and Pines [15] had found the effective matrix element, for the scattering of two electrons with wave numbers k and k' to $k+q$ and $k'-q$ respectively through an exchange of a phonon, q, to be

$$\frac{2\hbar\omega_q |M_q|^2}{(\varepsilon_k - \varepsilon_{k+q})^2 - (\hbar\omega_q)^2}$$

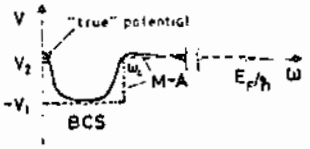


Fig. 21. BCS applied a potential which was attractive, $-V_1$ for $0<\omega<\omega_c$ and zero otherwise (dotted curve). This is certainly an approximation for the real ("true") potential, which is known to be attractive in a certain frequency region and repulsive in other regions. The Coulomb contribution is not cut off at a relatively low frequency (of the order of the Debye frequency) but rather on the scale of $E_F/\hbar$. A better approximation is the one applied by Morel and Anderson (*M–A*, dashed curve, $V=-V_1$ for $0<\omega<\omega_c$, $V=+V_2$ for $\hbar\omega_c<\hbar\omega<E_F$ and $V=0$ otherwise.

where $\hbar\omega_q$ is the phonon energy, ε_k the electron energy counted from the Fermi energy, and M_q the matrix element for the scattering of an electron against a phonon.

Evidently, the interaction is attractive (negative) for excitation energies $\hbar\omega=|\varepsilon_k-\varepsilon_{k+q}|<\hbar\omega_q$. For larger frequencies, the lattice does not react fast enough, and the interaction becomes repulsive (cf. a driven oscillator where a phase shift of 180 degrees appears when the driving frequency exceeds the resonance frequency of the oscillator).

Opposed to the phonon mediated attraction is the repulsive, screened Coulomb interaction, $U_q(q)=4\pi e^2/q^2\varepsilon(q,\omega)$. The most important transitions are those for which $|\varepsilon_k-\varepsilon_{k+q}|<\hbar\omega_q$. The resulting interaction potential for these frequencies is:

$$-\frac{2|M_q|^2}{\hbar\omega_q}+U_q$$

The criterion for superconductivity becomes

$$-V=\left\langle-\frac{2|M_q|^2}{\hbar\omega_q}+U_q\right\rangle_{av}<0$$

An indication of the importance of the electron–phonon coupling for the occurrence of superconductivity is the fact, that the superconductors with high T_c are usually those metals that display a relatively high resistivity at room temperature. At that temperature the largest contribution to the electron scattering cross section stems from phonons. An example is Pb, which has a relatively high room temperature resistance and a T_c of 7.2 K, while the good conductors Ag, Au and Cu do not superconduct even in the millidegree range.

4.3.1. *Isotope effect.* One of the strongest indications of the importance of the electron-phonon coupling is given by the so-called isotope effect. One can measure T_c as a function of atomic mass for elements with several isotopes. The earliest measurements [12, 13] of 1950 gave $T_c\propto M^{-\beta}$, where $\beta=\frac{1}{2}$. This value supported the model that Fröhlich [11] independently presented at the same time. He, and independently Bardeen [14], suggested the importance of the electron–phonon coupling to the occurrence of superconductivity.

The BCS expression for the transition temperature, $T_c\approx\theta_D e^{-1/N(0)V}$ contains $T_c\propto\theta_D\propto M^{-\frac{1}{2}}$ in agreement with the earliest experiments on Sn and Hg [12, 13]. But is the relation universal? Measurements on other elements gave $\beta\neq\frac{1}{2}$, and for certain transition elements even $\beta\approx 0$, as shown in Table II. The deviation from $\beta=\frac{1}{2}$ has been invoked as an argument against the BCS model and the electron–phonon coupling, but theoretical calculations with a more realistic interaction potential do give $\beta<\frac{1}{2}$. In the original BCS model, the interaction potential was approximated by a negative, constant value up to $\hbar\omega_D$ and zero otherwise. Evidently this is an approximation. We have just argued that the electron–phonon interaction is repulsive for $\omega>\omega_D$ and furthermore it is not correct to cut off the Coulomb repulsion at ω_D. It dies off much less rapidly, rather on the scale of the Fermi energy. A better approximation of the potential is given by the curve marked M – A in Fig. 21, where the electron-phonon interaction is put equal to $-V_1$ up to $k_B\theta_D$, but where the Coulomb repulsion, V_2, acts up to E_F. Such an approximation was introduced by Bogoliubov et al. [141] and later motivated by Morel and Anderson [126]. It gives the same type of expression for T_c as the BCS first approximation, but with another value of the effective interaction potential:

$$V=V_1-V_2/\{1+N(0)V_2\ln(E_F/k_B\theta_D)\}$$

A differentiation of the expression for T_c with respect to mass (which is contained in θ_D) gives:

$$\beta=\frac{1}{2}\left\{1-\frac{1}{(N(0)V)^2}\left[\frac{N(0)V_2}{1+N(0)V_2\ln(E_F/k_B\theta_D)}\right]\right\}\approx\frac{1}{2}\left[1-\frac{0.01}{(N(0)V)^2}\right]$$

Garland [127] has carried the calculations one step further by introducing more parameters describing the interaction potential. McMillan [142] derived an expression for T_c in transition metals from the theory of strong coupling superconductors (we will present it in a later part). From this theory, values of β can also be obtained that are in good accord with experimental values.

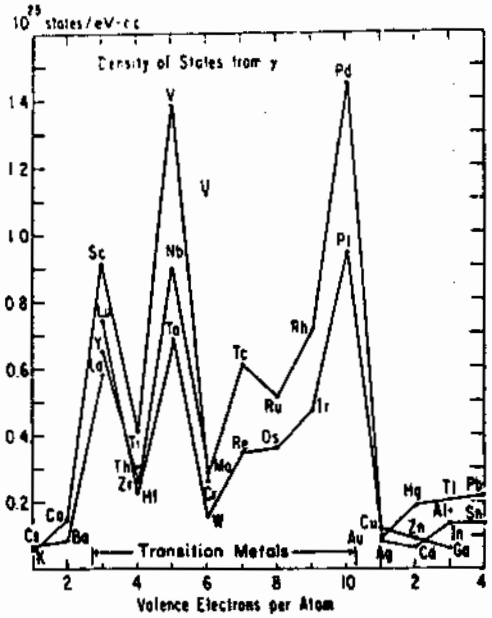
In Table II, experimental and theoretical values of β are given. It is clear that the values compare favourably even in the rather rough approximations given. Only uranium displays a value which deviates completely from theoretical estimates. At a pressure of 11 kbar a negative value of the exponent is measured. However, it should be emphasized that the metallurgical problems regarding U isotopes are not negligible and that the data for T_c display a large scatter. It is, furthermore, not impossible to obtain a positive isotope effect with an electron–phonon coupling if the electronic density of states if sharply peaked within $k_B\theta_D$ of E_F [143].

4.3.2. *Phonon structure in tunneling.* The success of the theory of strong-coupling superconductors, and in particular its duplication of phonon-induced structure in tunneling curves taken on

Table II. *The isotope effect*

Experimental values for β, obtained from $T_c\sim M^{-\beta}$, are compared with theoretical values by Morel and Anderson [126] and by Garland [127]

Superconductor	T_c [K]	β_{exp}	β_{MA}	β_G	Ref.
BCS		0.5			1
Cd	0.52	0.5±0.1			128
		0.32	0.34	0.385±0.025	129
Hg	4.15	0.50±0.03	0.46	0.48±0.005	13
Mo	0.92	0.35			130
	0.90	0.37±0.09	0.3	0.35±0.08	131
Os	0.66	0.23±0.02	0.25	0.23±0.10	132
Pb	7.19	0.48±0.01	0.47	0.485±0.005	133
Re	1.70	0.39±0.01	0.41	0.36±0.05	134
Ru	0.49	0.00±0.05	0.35	0.07±0.15	132
Sn	3.72	0.47±0.02	0.42	0.455±0.01	12, 134*a–b*
Tl	2.39	0.5±0.1	0.43	0.48±0.02	135
α – U	≈2.1	−2.2±0.2			136
γ – U	≈2.1	0.40±0.01	0.42		137
Zn	0.86	0.5			138
		0.3	0.25	0.415±0.015	139
Zr	0.53	0.00±0.15	0.30	0.15±0.17	140



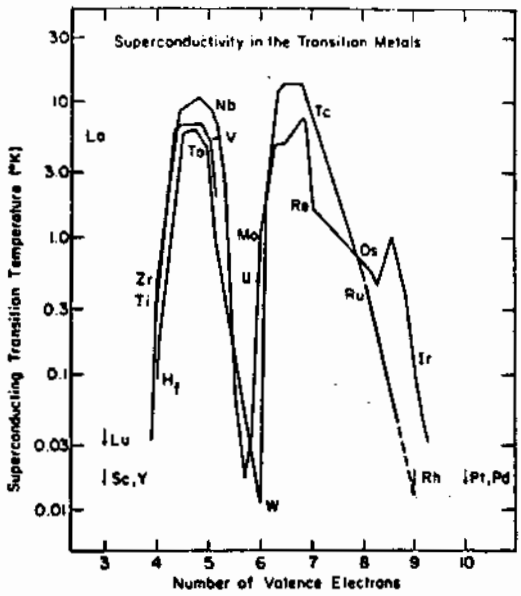


Fig. 22. The density of electron states at the Fermi energy, $N(0)$, varies periodically with the number of electrons per atom in the transition metal series. High values of T_c are obtained for elements that have a high $N(0)$ except at either ends of the transition metal series (and except magnetic elements). In the central part of a transition series, T_c obeys Matthias' rules [176]. The diagram originates from Jensen [175a].

superconductors with a sizeable electron–phonon coupling, leaves no doubt of the importance of the electron–phonon mechanism for a great number of superconductors [94, 95, 144]. There is a one-to-one correspondence between peaks and critical points in the phonon density of states and detailed structure in tunneling characteristics. Of the elements, phonon-induced tunneling deviations have been seen in the strong and intermediately strong superconductors like Pb [73, 144], Hg [145], La [67], In [146], Tl [146, 147], Sn [148], Nb [67], Ta [67, 149], V [150], amorphous Bi [151], and amorphous Ga [151] but also traces in a weak coupling superconductor like Al [152]. The phonon density of states can be mapped as a function of energy by a deconvolution of tunneling curves [73, 144]. The phonon distribution has also been studied in a great number of alloys and intermediate compounds like Pb-Bi [153, 154], Pb-Tl [106, 154–156], Pb-Tl-Bi [157], Pb-In [158–162], Bi-Tl [156], In-Tl [163] In_2Bi [164], Nb_3Sn [165], and amorphous Pb alloys [166].

We will return to this phenomenon and discuss the strong coupling theory in section 4.4.

4.3.3. *Electron structure effects.* A large number of investigations have been made concerning the dependence of T_c upon the composition in a binary alloy [3]. The results have often been interpreted in terms of the BCS model. By varying the number of electrons per atom by alloying, one has tried to study the energy dependence of $N(0)$ through its effect upon T_c. Merriam [167] has related kinks in T_c vs. composition curves to Brillouin zone–Fermi surface interactions occurring when an expanding Fermi surface touches a Brillouin zone face. Similar relations between the electron structure and T_c have also been suggested by other authors [168–170].

A survey of the crystal structure dependence of T_c is given by Matthias et al. [171]. Structural order–disorder transformations (superstructure) occurring in an alloy as the temperature is varied can influence T_c through all the parameters contained in the BCS formula for T_c [172, 173].

4.3.4. *Transition metals.* In the expression for T_c there is an exponential dependence of $1/N(0)V$. If the resulting interaction strength V did not differ too much from element to element, one would expect to obtain high values for T_c whenever the density of states at E_F, $N(0)$, is high. In the transition metals, the narrow d-band gives a high $N(0)$. But T_c is not as high as $N(0)$ would imply [174]. It is true that there is a periodic variation in T_c among the transition metals similar to the one of $N(0)$ [175] in the central part of the transition metal series (cf. Fig. 22), but V is much smaller than for non-transition metals as seen in Fig. 23.

This is not too surprising. The d-electrons in transition metals tend to be more localized around the ionic cores than the s- and p-electrons in a non-transition metal, i.e. they spend a larger part of the time in the vicinity of the core and a shorter time as free conduction electrons. If two d-electrons are in the same unit cell, they will be kept together by the ionic potential and experience a strong Coulomb repulsion. Other electrons will, as usual, screen this interaction, but it is still sizeable.

Not only is V small in transition metals; it is also dependent on $N(0)$. Bucher et al. [177] found that $N(0)V_{ph} = a \cdot N(0)/[1 + b \cdot N(0)]$. Such a relation can be explained by renormalization effects [174]. In the central region of the transition series ($4 \leq Z \leq 7$ where Z is the valence) T_c is in reasonable agreement with the model based upon strong coupling between electrons and phonons.

In the late (noble) transition metals, T_c does not at all follow the trend given by $N(0)$. For example, T_c decreases as Ir is added to Os while the specific heat γ (proportional to a renormalized $N(0)$) increases [174, 178–180]. The density of states is close to a maximum for Pd and Pt as shown in Fig. 22, but these metals do not superconduct. The magnetic susceptibility also increases rapidly as the ends of the 4d- and 3d-series are approached. The general trend of T_c, γ, and χ in fcc late transition metals is shown in Fig. 24.

The behaviour was initially thought to support a hypothesis that coupling other than the electron–phonon one caused super-

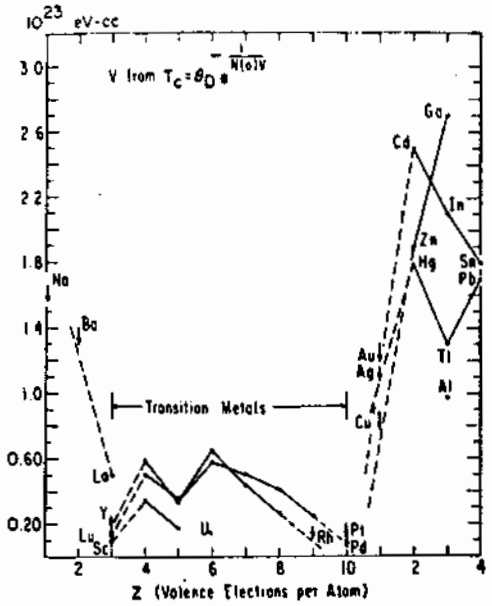


Fig. 23. The interaction strength V (as defined by $T_c = \theta_D e^{-1/N(0)V}$, varies from element to element. It is particularly low for the transition metals that possess a high density of states originating from *d*-electrons. The figure is taken from Jensen [175a].

conductivity in transition metals [181]. However, one should be aware of the strong increase in magnetic susceptibility for alloys close to the ends of the transition series. These are becoming almost ferromagnetic. It has been proposed [182] that long-lived spin fluctuations (paramagnons) exist in metals like Pd. Then a repulsive interaction due to the spin polarization, V_{spin} has to be added. In a Cooper-pair the electrons have opposite spin directions. Evidently a spin fluctuation, where the spins tend to align parallel in space, oppose the pair formation.

4.3.5. *Magnetic impurities.* Magnetic impurities in a superconductor will also break pairs, that is if a localized magnetic moment exists [183]. Generally, when impurities are dissolved in a superconductor, T_c first decreases as the concentration increases. This is due to an averaging of the interaction and the gap parameter in all directions—the metal becomes more isotropic [18]. After the initial decrease, T_c can continue to decrease or increase depending upon valence of the impurity etc. If the impurity is magnetic, on the other hand, T_c decreases for all concentrations,

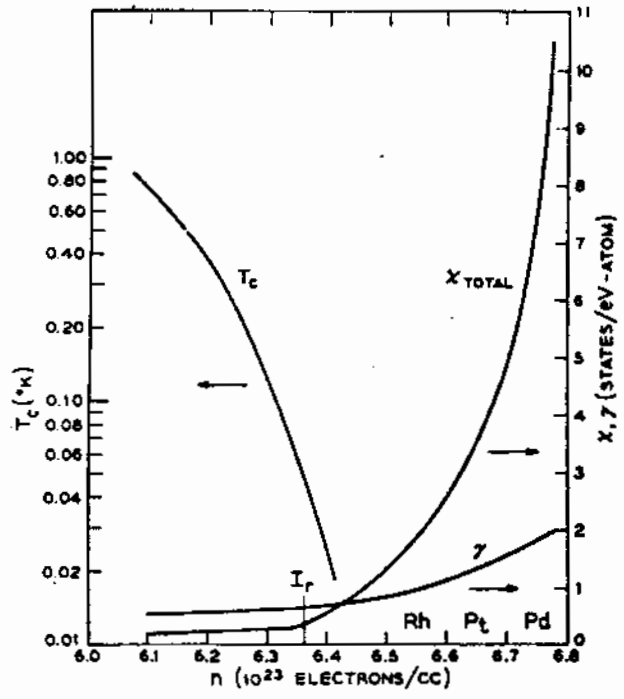
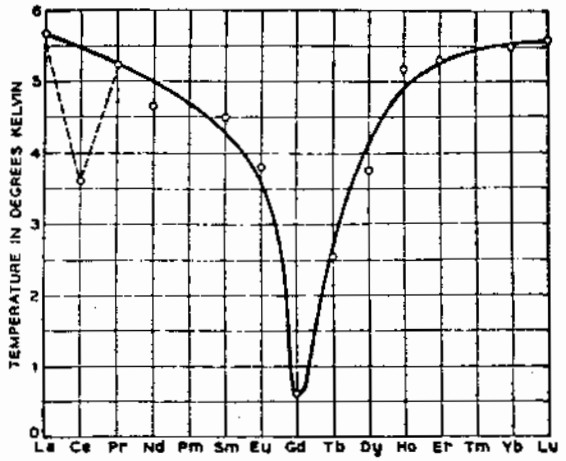


Fig. 24. The superconducting transition temperature, T_c, the electronic contribution to the specific heat, γ, and the magnetic susceptibility, χ, as functions of the number of valence electrons per unit volume of fcc alloys close to the end of the 4*d* and 5*d* transition metal series. T_c decreases although the density of states, $N(0)$, increases, but at the same time χ increases much more rapidly than expected from an increase of $N(0)$. This indicates some type of magnetic interaction. (Reprinted from Ref. [174], p. 756 by courtesy of Marcel Dekker, Inc.)



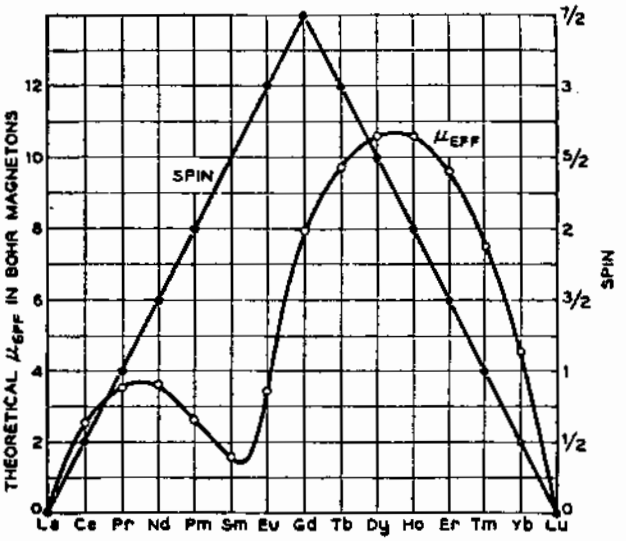


Fig. 25. T_c is depressed as 1 at. % of different magnetic rare earth impurities are dissolved in La. The depression correlates better with the spin number of the impurity element than with the magnetic moment of the dissolved magnetic impurity. (From Matthias et al. [171].)

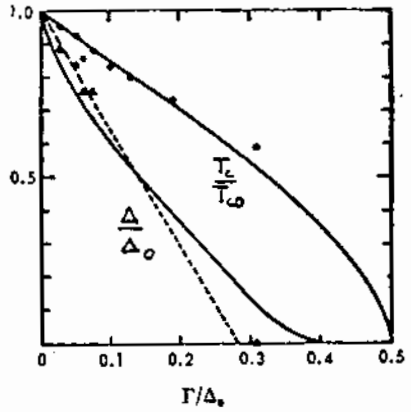


Fig. 26. T_c is depressed as the concentration of impurities with a localized spin is dissolved in a superconductor and is zero at a critical concentration c_{crit}. The half energy gap, Δ, decreases even more rapidly and disappears at a concentration of 0.91 c_{crit}. Superconductivity exists without an energy gap in the excitation spectrum. T_c and Δ in the figure are normalized to the values found in the pure superconductor, T_{c0} and Δ_0. (From Skalski et al. [188].)

and the depression is large. Less than 0.01 %Fe in Mo suffices to depress T_c completely [184], and for Mn in Zn a value of $dT_c/dc \approx -315$ K/at.% has been measured [185].

We mentioned that the impurity must possess a localized magnetic moment in order to affect T_c. For example, Fe, Co, Ru, or Rh dissolved in Ti do not cause any lowering of T_c—it is, on the contrary, increased [186]. These solutions do not give any localized magnetic moments as measured by their susceptibilities. But is it the local moment or the spin of the impurity that is of greatest importance? Fig. 25 shows that T_c for La with 1 at.% of different rare earth impurities correlates best with the spin of the impurity element.

Abrikosov and Gorkov [187] formulated a theory for superconductors with magnetic impurities. Such a theory can lead to superconductivity without an energy gap, which at first sight seems to contradict our model, as we have previously emphasized the gap. They assumed that each impurity spin, S, is localized and coupled to the conduction electron spin, σ, by an exhange interaction $JS\cdot\sigma$. Hence an electron spin can flip and the time reversal symmetry (opposite momenta and spins) of a pair is broken, i.e. the life-time, τ, of a pair becomes finite. An energy smearing, $\Gamma \sim \hbar/\tau$, introduces states within the energy gap.

A Green function treatment of the problem gave the formula

$$\ln(T_{c0}/T_c) = \psi(\tfrac{1}{2} + \hbar/2\pi k_B T_c \tau) - \psi(\tfrac{1}{2})$$

where T_{c0} is the transition temperature of the pure material and ψ is the logarithmic derivative of the gamma function.

For low impurity concentrations, the expression can be expanded and one obtains a linear decrease in T_c with concentration. The whole expression is shown in Fig. 26. At a critical concentration, c_{cr}, $T_c = 0$. For most systems, the experimentally determined T_c vs. concentration curves agree reasonably with the theory up to a concentration of about 0.7 c_{cr}. (corresponding to $T_c/T_{c0} \approx 0.5$). The experimental values follow the theoretical predictions by A–G to concentrations close to c_{cr} in very few systems, notably (La, Gd)Al_2 [189] and ThGd [190]. In the majority of systems there is a definite departure from the A–G theoretical curve [183, 191]. Magnetism is a complicated phenomenon, the details of which are not fully understood. A magnetic impurity atom dissolved in a metallic matrix can have a long-lived local moment, it can act as a non-magnetic resonant d- or f-state or as a fluctuating localized spin. The model by Abrikosov and Gorkov applies to the well defined localized moment, but even here one finds complications. Crystal fields often lift the Zeeman degeneracy of the ground state of rare earth ions (often used as magnetic impurities) in metals. The depression of T_c in superconductors with such impurities with partially filled 4f shells should reflect these splittings, particularly if the latter are of the order of kT_{c0}.

Another complicating factor is the scattering associated with the so-called Kondo effect [192]. The Abrikosov–Gorkov theory considers scattering of conduction electrons against impurity spins only to order J^2. The Kondo effect, however, arises from higher order terms in J. The effect might affect superconducting properties as profoundly as it does normal state properties like the resistivity. A physical interpretation of the effect is that the impurity spins tend to be compensated by the conduction electron spins below a characteristic temperature T_K; the degree of compensation increases smoothly with lowered temperature. The energy of this "quasi-bound" state is of the order of $k_B T_K$. If this energy is of the same order of magnitude as the binding energy of a Cooper pair, $k_B T_{c0}$, the superconducting properties are expected to be strongly affected. The depression of T_c with increasing amount of impurities will be very large.

From the study of the temperature dependence of the spinflip

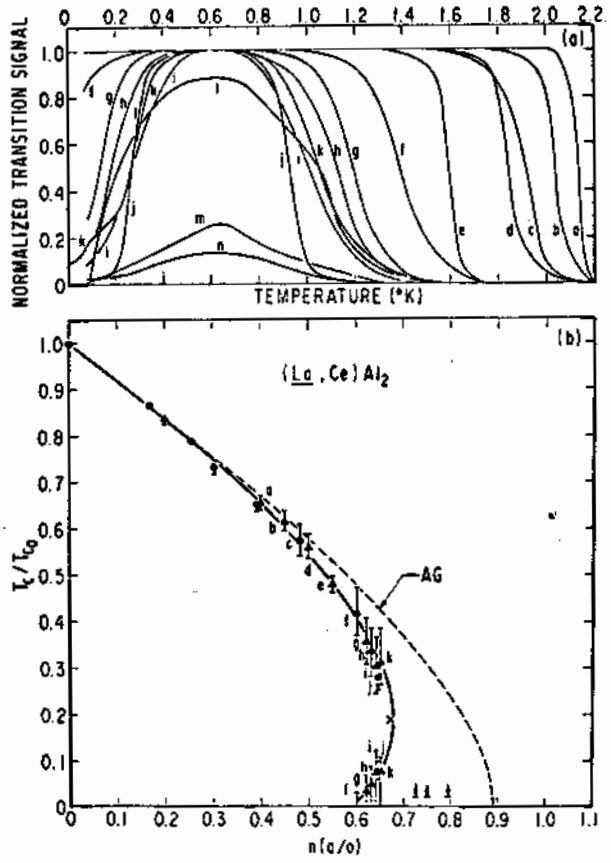


Fig. 27. The superconducting transition temperature, T_c, as a function of impurity concentration when Ce is substituted for La in $LaAl_2$. Note that within a certain compositional range, a sample that once has become a superconductor at T_c regains its normal state as a still lower temperature is reached (Fig. from Maple et al. [195]). The behaviour is due to an increased pair breaking around a so-called Kondo temperature according to Ref. [193].

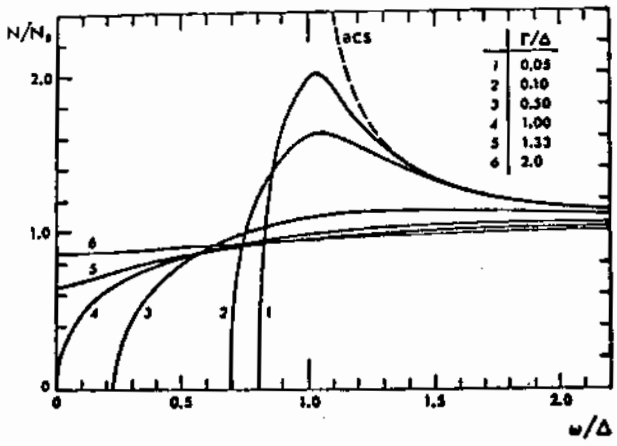


Fig. 28. The density of states for excitations from the superconducting ground state is displayed for several values of the pair breaking strength, Γ. As Γ is increased towards the half energy gap value Δ, more and more states are introduced in the gap, and at $\Gamma/\Delta = 1$ the superconductor is gapless. As there still is a depletion of states close to the Fermi energy ($\omega = 0$), the superconducting state is the stable one. (From Reif and Woolf [196].)

scattering (the degree of compensation of the impurity spin), some rather unusual variations of T_c vs. impurity concentration were recently proposed [193]. The pair breaking parameter will increase as T is lowered towards T_K, exhibiting a maximum at $T \approx T_K$. When the Abrikosov–Gorkov expression is evaluated with this varying Γ, one obtains three solutions for $T_c(c)$ in a certain range of concentration, c. As the temperature is lowered, an alloy in the pertinent concentration range first becomes superconducting at a temperature T_{c1}. However, as the temperature is lowered further, towards T_K, the pair breaking strength increases and superconductivity is lost at T_{c2}. The sample should then remain normal to a much lower temperature T_{c3} ($< T_K$) where it again becomes superconducting. Experiments that seem to confirm these ideas have been reported by Riblet and Winzer [194] and by Maple and Huber [195]. An example of the latter group's results is given in Fig. 27.

4.3.6. *Gapless superconductivity.* The most notable result of the calculations by Abrikosov–Gorkov [187], is that the energy gap is depressed more than T_c for a certain impurity concentration. The gap is zero already at an impurity content of 0.91 c_{cr}. There is a concentration range, $0.91\, c_{cr} < c < c_{cr}$, where superconductivity exists without an energy gap (cf. Fig. 26). The density of states for excitations out of the ground state is shown for several values of the pair breaking strength $\Gamma = \hbar/\tau$ in Fig. 28.

We have previously emphasized the importance of the energy gap, which is measured in so many experiments. However, superconductivity persists even when there is no gap in the excitation spectrum. A gapless superconductor displays a Meissner effect and an infinite conductivity. It is the existence of pair correlations rather than an energy gap that characterizes the superconducting state.

Experimental verifications of an energy gap decreasing faster than T_c as magnetic impurities were added to a metal, were first given by Reif and Woolf [196]. They performed tunneling experiments at 0.3 K on films quench-condensed upon a cold substrate in order to fabricate forced solutions (magnetic impurities are often difficult to dissolve in superconductors, particularly in Pb that was chosen as a solvent due to its high T_c). States that started to fill the gap smeared the tunneling curves considerably compared with those expected from the BCS theory with a pair-breaking potential included. For PbGd, tunnel curves and energy gaps agreed with expectations from the theory by Abrikosov and Gorkov. When paramagnetic d-transition metal atoms were dissolved (PbMn and InFe), tunneling curves were more smeared than what would be expected from the decrease in T_c. The pair-breaking was stronger. As the exchange interaction for 3*d*-electron solutes is strong, the deviations from the theory may be caused by a Kondo type scattering. Tunneling on LaCe films also indicate more states in the gap than expected from A–G theory [197]. Far infrared absorption measurements on quenched films gave similar conclusions as the tunneling experiments [198]. Specific heat measurements on bulk LaGd alloys verify the gapless behaviour [199]. Critical field measurements on ThGd alloys agree with the A–G theory within 0.5% [200], while results on ZnMn alloys indicate Kondo type contributions ($T_K \approx 0.2$ K). Thermal conductivity measurements on ThGd agree reasonably with the A–G theory [201].

4.3.7. *Other pair breaking effects.* It is not only magnetic impurities that break pairs and cause gapless superconductivity [202, 203]. Other mechanisms that can break the time reversal symmetry of pair members are: a magnetic field applied parallel to a thin film; Pauli paramagnetism; or a uniform current through a thin film. Interactions that break the time reversal symmetry are not needed, a spatial variation of the order parameter (in cases where the order parameter is small) can also give superconductivity without an energy gap. Examples of the latter case are a type II superconductor close to H_{c3}, a superconducting surface sheath in high magnetic fields (close to a critical field $H_{c3} \approx 1.7\, H_{c2}$), and the proximity effect in a metallic contact between a superconductor and a normal metal.

Experimental evidence for an energy gap decreasing faster than T_c and for the filling up of the energy gap in the excitation spectrum from the superconducting ground state have also been found by tunneling for these pair-breaking mechanisms [204–210]. Depairing effects in a surface sheath and in a metallic contact have also been studied by microwave resistance measurements [211].

4.3.8. *Superconductivity contra magnetism.* We have already emphasized that superconductivity and magnetism are competing phenomena. One involves a pairing of spins with opposite directions in momentum space, while in the other one, spins are aligned parallel or antiparallel in ordinary space. The majority of the metallic elements that have been found not to superconduct at the low temperatures obtained as yet, are those that have already become magnetic. T_c becomes immeasurably small even when the ends of the 4*d*- and 5*d*-transition regions are approached; the metals in those regions are almost magnetic with long-lived spin fluctuations.

Is there any possibility for superconductivity to exist at the same time as ferromagnetism? In certain alloy systems, like rare earth metals dissolved in La or Y, superconductivity appears at low impurity contents, while a dilute ferromagnetism is found at higher concentrations as shown in Fig. 29. But what happens in the region in between. Do the curves for the superconducting transition temperature and the Curie temperature respectively extrapolate in such a way that a superconducting and a weakly ferromagnetic state coexist? Theoretical results indicate the possibility [213], but it is difficult to perform conclusive measurements in this region. However, a systematic investigation by

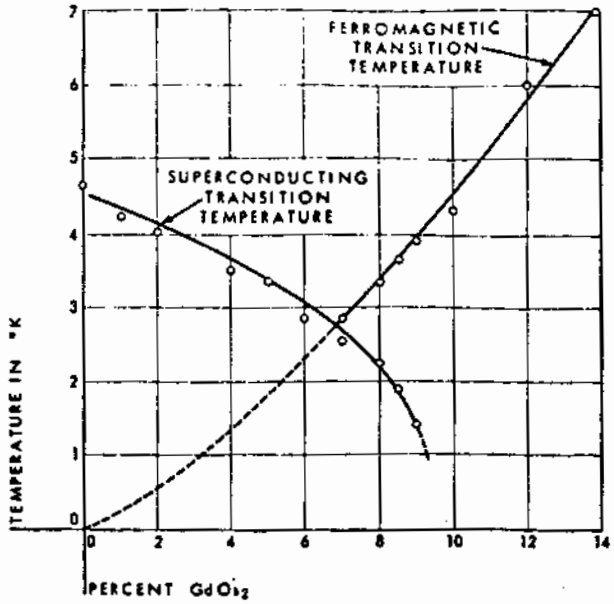


Fig. 29. Superconductivity and ferromagnetism usually do not go together. In certain alloy systems, however, a dilute type of ferromagnetism might co-exist with superconductivity as indicated by this figure where T_0 and the Curie temperature θ_0 are plotted against concentration. The figure stems from Matthias [212].

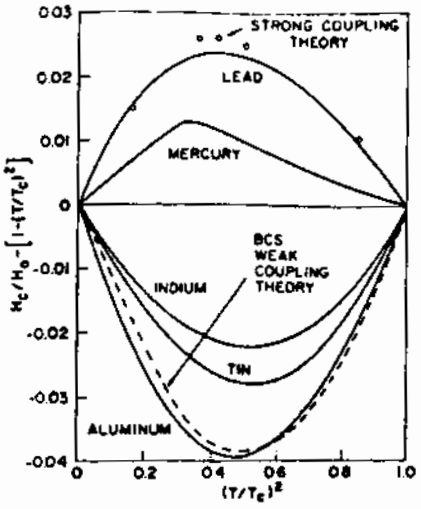


Fig. 30. The normalized critical magnetic field does not quite show a parabolic dependence upon temperature. Full lines are experimentally determined while the dashed line is obtained from the original BCS theory. Note that the curve for a weak coupling superconductor like Al agrees excellently with the BCS weak coupling theory, but the strong coupling superconductors Pb and Hg deviate considerably. The circle denotes values for Pb obtained from a strong coupling modification of the BCS theory by Swihart et al. [224].

Peter et al. [214] does suggest coexistence in $Gd_xCe_{1-x}Ru_2$. Mössbauer measurements [215] show that $Eu_{.01}La_{.99}$ enters a magnetically ordered state at 0.66 K although it became superconducting already at 2.15 K.

4.3.9. *Other attractive mechanisms than the electron-phonon coupling.* Are there any interactions other than the electron–phonon interaction which can give rise to an attraction needed for pairing? Kohn and Luttinger [216] have proposed a general mechanism for an electron gas which leads towards an instability in favour of pair formation. It is connected with the sharpness of the Fermi surface. The singularity of the dielectric function $\varepsilon(q)$ at a momentum transfer $q = 2k_F$ leads to a screening, long-range oscillatory, potential of the form $\cos(2k_F r + \varphi)/r^3$, when a charge is placed in a metal (so-called Friedel [217] oscillations). Similarly the electrons themselves will experience a long-range oscillatory force that will be attractive within a certain spatial range. By taking advantage of the attractive regions, Cooper pairs can form and superconductivity results. However, the resulting interaction is quite weak and the superconducting transition temperature will be very low, too low to be observable at the present time.

Matthias [218] has argued that a mechanism other than the electron-phonon interaction is responsible for superconductivity in some transition and rare earth metals. His idea is basically that a conduction electron polarizes an atom it passes by polarizing the core. A second electron then uses this polarization to get an attraction.

Little [219], Ginzburg [220], and Allender et al. [221] have invoked excitonic mechanisms where electrons move either in one-dimensional organic chains polarizing side-links or in two-dimensional layers exchanging excitons through dielectric or semiconducting overlayers. These mechanisms have been opposed on the ground that fluctuations will prevent the existence of true long-range order in one- and two-dimensional systems [222]. On the other hand, in a realistic composite of filaments or layers, the fluctuations will be strongly suppressed due to coupling between the filaments.

Other non-phonon mechanisms have also been considered, for example exchange of spin waves (magnons), interaction between electrons in different bands (e.g. the *s–d* interaction) or the mechanism derived from nuclear forces which gives rise to superfluidity of protons in a neutron star [223]. However, no superconductor has, as yet, been found where one can say definitely that a different mechanism is the cause of the superconductivity. One has, up till now, always been able to twist around and explain deviations from the BCS-model within the framework of the electron–phonon mechanism. The origin of superconductivity in transition metals, for example, has been disputable. However, tunneling into several transition elements and compounds do give realistic phonon spectra as mentioned in section 4.3.2.

4.4. *Strong coupling superconductivity*

While many superconductors, like Al, are well described by the BCS theory, there are some exceptions, notably Pb and Hg but also to a smaller extent La, In, Tl, Sn, and Nb, that show deviations from the predictions of the theory. The cause of the deviations has to be sought in the details of the interaction responsible for superconductivity, the electron–phonon coupling. Where the coupling is strong, i.e. when $N(0)V = \{\ln(\theta_D/T_c)\}^{-1}$ is large ($\gtrsim 0.25$), the deviations are most notable. These metals are usually also characterized by a low Debye temperature. The contribution to the phonon frequencies from the bare ion–ion interaction is cancelled to a large degree (in Pb about 80%) by coupling to the electrons. The stronger the coupling, the lower the resulting vibrational frequencies.

As mentioned, ratios $2\Delta(0)/k_B T_c > 3.53$ are measured (cf. Table I). The observed average values are about 4.3 for Pb and 4.6 for Hg. The superconducting condensation energy of Pb is about 25% lower than the BCS value, while the jump in the specific heat at T_c is larger than the BCS value of 1.43 × (the

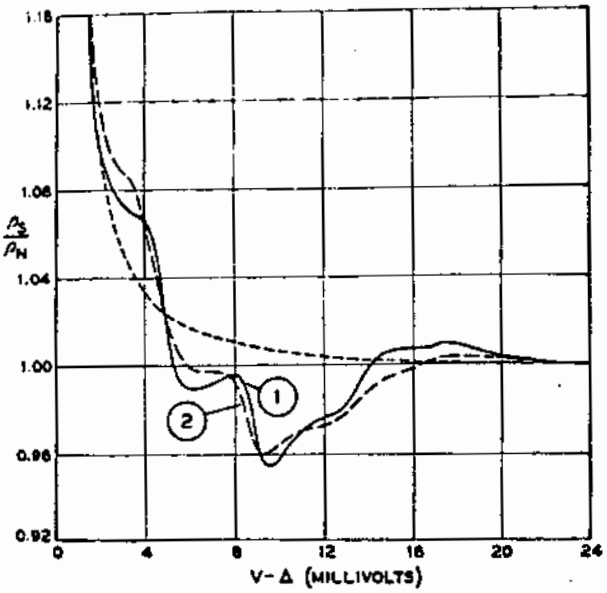


Fig. 31. The effective tunneling density of states vs. energy (counted from the gap energy) for Pb. The full line (1) is calculated from the strong coupling theory as developed by Schrieffer et al. [228] where the phonon spectrum of Pb has been approximated by two Lorentzian peaks centred at the estimated frequencies of transversal and longitudinal phonons. The experimentally obtained curve (by Rowell et al. [225]) is the long dashed line (2), while the short dashed line is calculated from the simple BCS theory. (From Rowell and Kopf [147].)

specific heat in the normal state at T_c). The temperature dependence of the critical magnetic fields for a few superconductors is shown in Fig. 30. The BCS theory (in weak-coupling limit) predicts a negative deviation from the two-fluid model parabola. The weak-coupling superconductor Al follows this prediction very well, but Pb and Hg, again our "bad actors", do not obey at all. They even have a positive deviation from the quadratic dependence.

Already the first tunneling curves of Giaever [55] performed on Pb showed structure at voltages corresponding to typical phonon frequencies (see Fig. 16). Later experiments resolved the structure in great detail [225]. It was, in fact, this tunneling structure that provided the strongest motivation for developing a theory which could account for the behaviour of strong-coupling superconductors.

The role of the electron–phonon interaction in metals had become clear from works by Migdal [226] on normal metals and Eliashberg [93] and others [227] on superconductors. Perturbation series for the electron–phonon coupling could be summed to obtain self-energies for the electrons which are accurate to lowest order in (electron mass/ion mass)$^{\frac{1}{2}}$. Morel and Anderson [126] used the Eliashberg equations for an Einstein frequency spectrum and a screened Coulomb interaction to obtain values for T_c. Schrieffer and co-workers [228] developed a model using two Lorentzian peaks for the phonon distribution that reproduced the experimental tunneling curve of Rowell et al. [225] fairly well as seen in Fig. 31. We shall try to give a brief sketch of the strong-coupling theory in the next few paragraphs [229].

In the original BCS theory, it was assumed that the electrons could be described as long-lived well-defined quasi-particles as done in Landau's theory of a Fermi liquid [230]. Furthermore, the electron–electron interaction was approximated by an attractive, instantaneous and isotropic interaction, $-V$, only acting upon electrons within an energy shell, $2\hbar\omega_c$, around the Fermi energy. This would also imply a gap parameter of constant value within the same energy shell.

In a strong-coupling superconductor, however, the electron–phonon coupling is of such a strength, that the electron-like excitations from the ground state are no longer simple and well-defined. The lifetime of an excitation with an energy of the order of a Debye energy is so short that the width of the state (defined by the half-width $\Delta E = \hbar$/the lifetime) is of the order of the excitation energy itself. Then one can no longer describe the state by "quasi-free electrons" with effective parameters (like an effective mass). The Coulomb interaction between two electrons can of course always be regarded as an instant repulsion but the attraction mediated through the vibrations of the much heavier ions is retarded. A time elapses between the emission and reabsorption of a virtual phonon. The attractive, square box potential of the BCS model is evidently an approximation. When the coupling between electrons and phonons is no longer weak one has to go back to the full dynamic equations of the system including both the electrons and the phonons and their mutual interaction.

Self energy. Regard a free, non-interacting electron of energy ε_k^0 relatively the Fermi level. As the interaction with other electrons and with ions are switched on, the "bare" particle is dressed. The most direct effects are that its energy is shifted and its lifetime shortens. The behaviour can be described by introducing an energy-dependent complex self-energy, Σ. The real part of Σ shifts the energy whereas the imaginary part has to do with the finite lifetime, and because of the energy dependence of Σ one has in general a complicated non-Lorentzian spectral distribution. The spectral distributions, i.e. the relative probability per unit energy of finding the particle, are sketched in Fig. 32 for non-interacting and interacting particles.

The problem of calculating energies, spectral distributions, and density of states is reduced to a calculation of the self-energy. We shall briefly sketch how Σ is obtained for a normal metal and for a superconductor.

The self-energy, or the mass operator, can be obtained by applying perturbation theory. We are interested in finding the Coulomb and the lowest order electron–phonon contributions to Σ. They are of the form:

$$\Sigma = \Sigma_c + \Sigma_{ph}$$

Σ_c is an integral function of Σ and U_c^*

Σ_{ph} is an integral function of Σ and $\alpha^2(\omega)F(\omega)$

where U_c^* is the screened Coulomb repulsion $4\pi e^2/q^2\epsilon(q, \omega)$,

$F(\omega)$ is the phonon density of states and $\alpha^2(\omega)$ measures the energy-dependent strength of the electron–phonon interaction.

It is possible to solve the self-energy expressed in the two para-

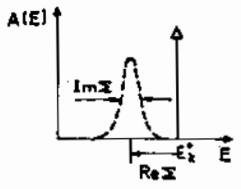


Fig. 32. The spectral function, i.e. the probability of finding a particle with a certain energy is shown for noninteracting (the delta function at ε_k^*) and interacting (the dashed curve) particles.

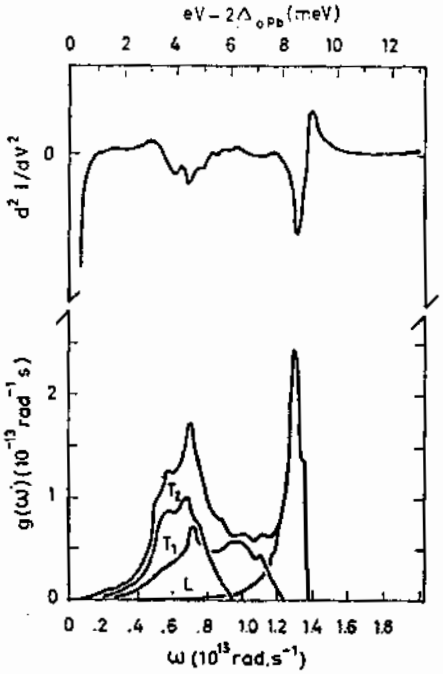


Fig. 33. The second derivative of the $I-V$ characteristics vs. applied voltage for an Al–AlO_x–Pb junction compared with the phonon spectrum of Pb determined by neutron diffraction (Stedman et al. Ref. 262). There is a remarkable coincidence between structure in the tunneling characteristic and singularities in the phonon distribution. (The L, T_1, and T_2 curves in the phonon density of states denote longitudinal and transversal branches.)

meters $\alpha^2(\omega)F(\omega)$ and μ^* the latter of which is a product of the density of electron states at the Fermi level, $N(0)$, and the averaged value of U_c^*.

In a superconductor, the same formalism is used. However, it is convenient not to use the usual creation and annihilation operators, but rather to introduce two-component field operators:

$$\psi_k \cdot \begin{pmatrix} c_{k\uparrow} \\ c^+_{-k\downarrow} \end{pmatrix}$$

($c_{k\uparrow}$ and $c^+_{-k\downarrow}$ give the same excited state in the superconductor. The number of particles in the ground state is changed, but that does not matter as we have already argued in section 3.3.)

In our two-component formalism the self-energy is expressed by a two by two matrix:

$$\hat{\Sigma} = \begin{pmatrix} \Sigma_{11} & \Phi_{12} \\ \Phi_{21} & \Sigma_{22} \end{pmatrix}$$

where the non-diagonal terms are those of greatest interest, since they describe the occurence of long-range order in the electron system.

After a lengthy analysis one arrives at an energy-dependent Eliashberg gap equation:

$$\Delta(\omega) \sim \Phi(\omega) = \text{function}\,(\alpha^2(\omega)F(\omega), \mu^*)$$

Now we are in business! Once $\Delta(\omega)$ is known, we can calculate properties like the condensation energy and the density of states for excitations. Specifically we have for the latter entity the expression [54]:

$$N_s(E) = N(0)\,\mathrm{Re}\left\{\frac{|E|}{\sqrt{E^2 - \Delta^2(E)}}\right\}$$

At $T=0$, the tunneling dI/dV is proportional to $N_s(E)$. (At $T \neq 0$, exponential tails of the Fermi function complicate the expression for dI/dV somewhat).

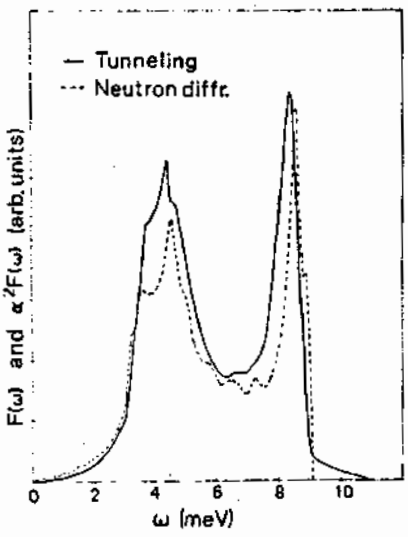


Fig. 34. The energy dependence of the phonon density of states for Pb calculated from results obtained experimentally by neutron diffraction (Stedman et al. [262]) and by electron tunneling (McMillan and Rowell [144]).

Comparison with experiments. By approximating the phonon distribution with two Lorentzian peaks centered around the frequencies of transversal and longitudinal phonon modes found from neutron diffraction on Pb, Schrieffer et al. were able to qualitatively reproduce the tunneling curves of Rowell et al. as shown in Fig. 31. However the fit is not ideal. The phonon density of states for a metal is not as simple as two bell-shaped peaks. Scalapino and Anderson [231] showed that structure in the second derivative of the tunnel current, d^2I/dV^2, is in a one-to-one correspondence with critical points, van Hove singularities, in the phonon distribution. An example of such a correlation is given in Fig. 33.

McMillan and Rowell [73, 144] have devised a sophisticated computer program that calculates the parameters μ^* and $\alpha^2(\omega)F(\omega)$ from careful measurements of dI/dV vs. V and of the energy gap $\Delta_0 = \Delta(\Delta_s)$. An example of the surprisingly good agreement between $\alpha^2(\omega)F(\omega)$, determined by tunneling into a film of Pb, and $F(\omega)$ determined from neutron diffraction with a single Pb crystal is given in Fig. 34. Another example of the method's reliability is given in Fig. 35.

The circle is closed. One can measure normal state parameters like μ^* and $\alpha^2(\omega)F(\omega)$ via superconductivity measurements. As the theory of superconductivity seems to be correct within an accuracy of 1 %, it would be logical to use the theory to compute superconductivity properties with this accuracy from normal state properties. However, the normal state parameters needed are not known to such an accuracy. The theory and the knowledge of the "normal state" is usually ten times less accurate than of the superconducting state. Instead one can use the strong-coupling theory to calculate properties of the normal state, notably the phonon density of states, the Coulomb interaction and the electron-phonon coupling strength.

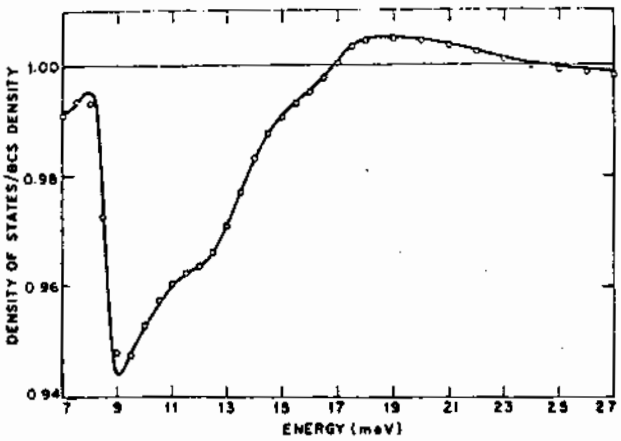


Fig. 35. Calculated (full line) and measured (circles) tunneling density of states for Pb vs. $E-\Delta_0$. The calculated curve is obtained utilizing the phonon spectrum calculated from the data for $E-\Delta_0<11$ meV. As the data for $E-\Delta_0>11$ meV have not been used in the fitting procedure to get the phonon distribution, the comparison of calculated and measured values in the energy interval shown is a good test of the theory. (Reprinted from Ref. [144], p. 609, by courtesy of Marcel Dekker, Inc.)

5. Superfluidity in ^{3}He

The usual helium isotope, ^{4}He, undergoes a Bose type condensation into a superfluid state (no, or rather very low, viscosity) at a temperature, T_λ, of 2.17 K. ^{3}He, on the other hand, possesses an odd number of nucleons. It is a Fermi particle and would not participate in any Bose-Einstein condensation. But pairs of ^{3}He might, as in a superconductor, form a condensed state. In this case, the pairs are kept together by a van der Waal interaction and possibly form triplets (parallel spins) instead of singlets.

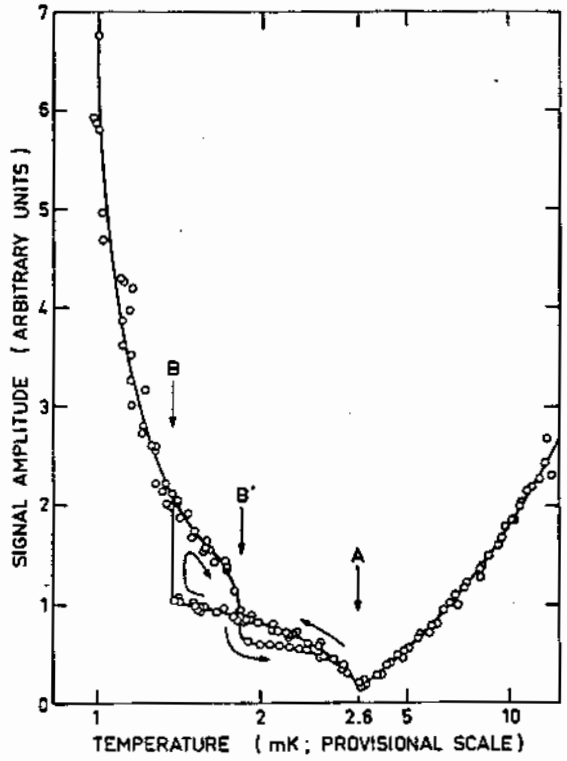


Fig. 36. The signal amplitude of a vibrating-string viscosimeter is plotted against temperature in a liquid ^{3}He medium. The temperature is lowered by increasing the pressure in a Pomeranchuk type cell (note the change of scales at 2.6 mK). The signal amplitude is assumed to be proportional to $\eta\rho^{-1/2}$, where η is the viscosity. Two types of transitions are noted, the "A" and "B" (or "B'"). At temperatures higher than 2.6 mK, the curve is fairly close to one expected from a η, proportional to T^{-3} dependence. The largest measured signal (at the lowest temperature) corresponds to a viscosity 1 000 times smaller than at "A". Further details are given in Ref. [237]. (Figure supplied by T. A. Alvesalo.)

Two transitions, one designated "A" at about 2.6 mK and another called "B" below 2 mK, have recently been found in several different experiments, and are probably due to a type of superfluidity or "superconductivity". Osheroff, Richardson and Lee [232] detected anomalies in the cooling vs. pressure curve for Pomeranchuk cells and later in nuclear magnetic resonance [233]. The "A" peak splits in magnetic fields as evidenced by ultrasonic attenuation [234]. A discontinuity in the specific heat at the "A" transition, a behaviour characteristic of a second order phase transition has also been found [235, 236]. The viscosity decreases at "A" and "B" as reported by Alvesalo et al. [237] and shown in Fig. 36. But it is still finite. It is estimated to be of the order of 6 000 times smaller in the "superfluid" phase at 1 mK than the extrapolated normal Fermi liquid value at the same temperature.

The theoretical description of the condensed state is not complete [238, 239], although experiments [237] seem to support a suggestion that the liquid ^{3}He is a superfluid in which the energy gap disappears in certain directions for temperatures between "A" and "B", while the transition at "B" may be to an isotropic superfluid [239].

Although the BCS model can be applied to the superfluid ^{3}He in principle, strong correlations might greatly affect its properties. If the pair is a spin triplet, the coherence effects could be greatly altered.

6. The vexed question of high temperature superconductors

The microscopic theory of superconductivity has been attacked by some scientists as not leading to any really usable predictions. It describes the superconducting state well, one says, but it does not tell us how to mix and treat elements in order to produce an alloy with a high transition temperature, a high critical field, and a large current density. The original BCS expression for T_c contains one parameter V, which is not easily measureable by other experiments. The modification of the theory in the strong coupling limit expresses T_c in properties such as the phonon distribution, the electron–phonon coupling strength and the screened Coulomb repulsion. It is possible to measure these properties, but it is not an easy task. In principle they could be calculated with sufficiently accurate crystal potentials, but such do not generally exist at present. Furthermore, one does not know how the properties are affected by alloy concentration, degree of structural order and other physical or metallurgical parameters. Our understanding of the properties of normal metals is indeed far from sufficient for detailed predictions. It is much easier to directly measure T_c and let experience and intuition be a guide towards more or less successful results [240]. One can compare the situation with the one regarding mechanical strength of metals or the one in drug manufacture where empirical knowledge and rules of thumb still are the dominant factors despite the large investment of man-hours and money in these fields.

Does the theory supply an upper limit of T_c? In practice one has managed to reach slightly above 20 K, the highest values at present being 22–23 K for sputtered Nb_3Ge films [241] and 21 K for ternary $Nb_3(Al, Ge)$ alloys [242]. (The high T_c values for

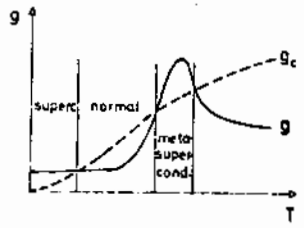


Fig. 37. The figure shows a fictive situation where the interaction strength $g(T_c \approx \theta_D e^{-1/g})$ may be stronger than a critical value g_c within a limited temperature interval that does not include $T=0$. A kind of metasuperconductivity would then exist within that temperature interval and neither above nor below. Such a situation might be caused by e.g. soft phonons in a second order phase transformation.

sputtered films are promising as one is utilizing a new fabrication method, which allows a change of several parameters in the process!) The maximal value of T_c has developed almost linearly with time since Kamerlingh-Onnes' first discovery, but on the other hand, the number of known superconductors has increased much more rapidly. Doubts whether T_c's much larger than 25 K can be found have been raised [240]. The BCS theory in its first approximation only indicates a T_c considerably lower than θ_D. McMillan [142] has combined the theory of strong coupling superconductivity with semi-empirical rules and has obtained an expression for T_c, which does not exceed a maximal value, different for different classes of materials.

The strong coupling theory gives

$$kT_c \sim \hbar\omega_c \exp\left\{\frac{-(1+\lambda)}{\lambda-\mu^*-(\langle\omega\rangle/\omega_c)\lambda\mu^*}\right\}$$

where ω_c is the cut-off phonon frequency, μ^* the screened Coulomb interaction multiplied by $N(0)$, and the electron–phonon coupling $\lambda = 2\int d\omega\alpha^2(\omega)F(\omega)/\omega = N(0)\langle J^2\rangle/M\langle\omega^2\rangle$.

McMillan found that the product of the density of electron states at the Fermi level $N(0)$ and the average of the squared matrix element J^2 was approximately constant for a given class of materials. This implies that the parameter λ, which is the most important parameter determining T_c, is an inverse function of the atomic mass, M, and the mean squared phonon frequency $\langle\omega^2\rangle$ (or θ_D^2). It is then possible to seek a maximum of T_c as a function of λ (or of the mean phonon frequency). McMillan found that T_c had a broad maximum for $\lambda = 2$. In most superconductors λ is considerably smaller than 2, and hence T_c will increase if λ increases, i.e. if the phonon frequencies can be lowered. A good example of this effect is a disordered film. If a very disordered film can be fabricated, the phonon frequencies will be lowered, compared with a well-ordered film, and T_c usually increases. In Pb however, where one is close to a maximum, T_c decreases in a disordered film.

Table III. *Theoretical maximal values of* T_c *(by McMillan* [142]*) for three classes of materials together with observed values*

Class of metal	T_c	T_c max (K)	Observed maximum T_c(K)	Material
Pb	7.2	9.2	8.8	Pb–Bi
Nb	9.2	22	10.8	Nb–Zr
Nb_3Sn	18.2	28	21	Nb_3(Al, Ge)
			23	Nb_3Ge

The predicted maximal T_c values for three different classes of materials are given in Table III together with observed maximal values. In some cases, the upper limit exceeds the experimental values considerably, but later calculations [243–245] have, alas from the point of applications, depressed the theoretical, maximal T_c values. From tunneling determinations of the phonon spectrum of Nb_3Sn, Shen [165] has concluded that the maximal T_c of this group of materials is of the order of 22 K, alarmingly close to the highest T_c ever found but, on the other hand, lower than the actual value for Nb_3Ge.

To get a high T_c, one needs a strong electron-phonon coupling, i.e. a low average phonon frequency. But too low phonon frequencies indicate that the system is close to an instability at which the crystal would make a transition to another structure [245, 246]. In this fact lies another limitation—a material that would have a high T_c in a certain structure might not form, it will be unstable. As a matter of fact, several of the high T_c alloys display a tendency towards a martensitic deformation of the lattice at temperatures above T_c. It is not clear whether the high T_c in sputtered Nb_3Ge films (or other A-15 compounds) is due to a narrow peak in the density of electron states at the Fermi energy, or to the instability close to a lattice transformation.

Soft modes close to a second-order crystallographic transformation might be a solution (cf. Fig. 37). A number of compounds is known where martensitic and other transformations occur as they are cooled to low temperatures. In a temperature range around the transformation temperature, $\langle\omega^2\rangle$ can be reduced considerably, and within this temperature interval a kind of metasuperconductivity might exist.

Results that might be along these lines have recently been reported by Coleman et al. [47]. They measured the conductivity of organic, layered salts and found that it increased considerably within a critical temperature range (around 60 K), just before the metallic state transforms into an insulating one. In a few of the many samples investigated, the conductivity of (TTF) (TCNQ) was larger than 10^4 (ohm-cm)$^{-1}$ at 58 K; a value about 500 times higher than the room temperature value and actually twice the value of copper at room temperature. Such a high conductance cannot be easily understood on the assumption of conventional metallic conduction in such materials. The group believes that due to the soft modes at the metal-insulator transformation, the electron–phonon interaction is enhanced almost to the point of superconductivity. The $(T-T_c)^{-3/2}$ dependence of the conductivity above 58 K suggested fluctuations in the order parameter in a one-dimensional system (the exponent 3/2 is characteristic of one dimension; compare section 4.1.5). One is now investigating the possibilities to stabilize the metallic state until a true superconducting state is reached, a difficult task. The experimental results are controversial, as they are difficult to reproduce by other measurements. Doubts regarding the measuring technique have been raised [246a]. Theoretically, there have been suggestions that the giant conductivity may be due to a Fröhlich type of superconductivity occuring at a Peirls instability in a linear chain. Recent works are quoted in Ref. [246b].

An obstacle against high T_c superconductors might be pair breaking by low frequency phonons. Allen [247] claims that the electron–phonon interaction is repulsive for phonon energies less than kT_c and the attraction is diminished below about $4\,kT_c$. At a very high T_c (comparable with θ_D), the phonons would give a strong repulsion and make such values of T_c unlikely. On

the other hand, Bergmann and Rainer [247a] have recently come to the conclusion that all frequency regions yield a positive contribution to T_c; the most effective range being phonon energies slightly above $2\pi k_B T_c$.

Metallic hydrogen (hydrogen supposedly becomes metallic at an enormously high pressure of the order of 2 Mbar) has been suggested to be a high temperature superconductor [248, 249]. In contrast to the other metals mentioned, hydrogen might have a high θ_D, so the limitations mentioned would not be so severe. In order to make a useful high temperature superconductor, though, several conditions have to be fullfilled: (i) hydrogen must be made metallic, (ii) it should not only be a superconductor with a high T_c, but (iii) it should remain stable (or at least safely metastable) even after the pressure has been released.

It is possible to dissolve large amounts of hydrogen in some metals and thereby get so small distances between hydrogen atoms that the density approaches the one needed for the metallic state. By shooting hydrogen (or deuterium) ions into pre-hydrated palladium at helium temperature [250], it was possible to obtain a superconducting sample ($T_c \approx 9$ K). This is far below the predicted T_c of metallic hydrogen, and furthermore the interpretation is not clearcut—maybe the T_c is characteristic of a compound or of Pd without spin fluctuations. The *d*-band in Pd is known to fill up, and the abnormally high susceptibility goes down, as monovalent elements are added. By adding silver to palladium and then dissolving deuterium in that matrix, it was possible to increase T_c to about 16 K [251]. T_c shows a maximum at about 25 at. % Ag in Pd.

As mentioned in 4.3.9, other attractive mechanisms than the phonon coupling have been proposed to give superconductivity, some of them with a very high T_c in the liquid nitrogen range or even at room temperature. Experimental results have been rare and not undisputable. A French group [252] has recently reported that Pb filaments embedded in a PbTe matrix seem to be superconducting up to 20 K. No superconductivity could be detected resistively, only via susceptibility measurements.

However, even an increase in T_c of a few K would be of great technical and economic importance. We are today on the verge of large-scale applications of superconductivity. Applications such as large and strong electromagnets [253], transportation [254], electrical motors and generators [255], power transmission [256], and sensitive electrical measurements [257] have been made or are in the project or prototype stage.

Superconductors of 25-30 K, and the more economic refrigeration schemes that are sufficient to reach such a temperature, would greatly enhance the economic feasibility of superconducting applications.

7. Concluding remarks

In this review we have briefly mentioned a number of the most striking experimental results which support the BCS microscopic theory of superconductivity. There are many more experiments that could have been mentioned, but the body of experimental results is much too large to be summarized in a review of this format. As far as we are aware, there is no conclusive experimental evidence against the theory. Questions raised by deviations from the theoretical predictions have mostly been resolved by natural extensions of the theory and in some cases by more careful and accurate experiments.

Did the successful theory, which solved an almost 50-year-old famous problem and gave its orginators the 1972 Nobel Prize in Physics, mean the end of superconductivity? Indeed not, it marked the starting point of a new development and implied a renaissance of research, experimental as well as theoretical, in the field of superconductivity. Due to the high accuracy of the theory of superconductivity it has even become possible to study some important properties of the normal state, in particular the electron-phonon coupling and the phonon spectra, by using the superconducting data.

It has already been remarked that the theory of superconductivity has not been of direct importance for the development of high temperature superconductors. Indeed the direct application of a microscopic theory to practical problems is very rare. However, indirectly the theory has been of importance. It also gives a framework for the search for other mechanisms that might lead to superconductivity and which may become important in the future. Some consequences of the theory such as the macroscopic quantum phenomenon in superconductors seem to be finding important technical applications. A report on the theory of superconductivity would be incomplete unless one mentioned the great importance the BCS theory has had within theoretical physics. It was the first real solution of a genuine many-body problem for a system with properties essentially different from such systems where an independent particle theory could be used. The success of the BCS-theory inspired a great development of many-body theory with applications in many areas. The BCS-model and parts of the theory such as the pairing concept have been used as models in nuclear physics [258], particle physics [259, 260] and astrophysics [261] and the important notion of symmetry-breaking seems to have been introduced for the first time in connection with the BCS-theory.

Acknowledgements

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References

1. Bardeen, J., Cooper, L. N. and Schrieffer, J. R., Phys. Rev. 108, 1175 (1957).
2. Kamerlingh Onnes, H., Leiden Comm. 1206, 1226 (1911), Suppl. 34 (1913).
3. Roberts, B. W., *in* Progress in Cryogenics, Vol. IV (ed. K. Mendelssohn), p. 160 Heywood, London, 1964: NBS Techn. Notes 482 and 724, U.S. Gov. Print. Off., Washington, D.C., 1969 and 1972.
4. Meissner, W. and Ochsenfeld, R., Naturwiss. 21, 787 (1933).
5. Becker, R., Heller, G. and Sauter, F., Z. Physik 85, 772 (1933).
6. London, F., Superfluids, Vol. 1. Wiley, New York, 1950.
7. Pippard, A. B., Roy. Soc. (London) A216, 547 (1953).
8. Gorter, C. J. and Casimir, H. B. G., Physik. Z. 35, 963 (1934); Z. Tech. Phys. 15, 539 (1934).
9. Ginzburg, V. L. and Landau, L. D., Zh. Eksperim. i. Teor. Fiz. 20, 1064 (1950).
10. Landau, L. D., Phys. Z. Sowjet. 11, 545 (1937).
11. Fröhlich, J., Phys. Rev. 79, 845 (1950).
12. Maxwell, E., Phys. Rev. 78, 477 (1950).
13. Reynolds, C. A., Serin, B., Wright, W. H. and Nesbitt, L. B., Phys. Rev. 78, 487 (1950).
14. Bardeen, J., Phys. Rev. 79, 167 (1950); 80, 567 (1950); 81, 829 (1950).
15. Bardeen, J. and Pines, D., Phys. Rev. 99, 1140 (1955).
16. Cooper, L. N., Phys. Rev. 104, 1189 (1956).
17. Giaever, I. and Megerle, K., Phys. Rev. 122, 1101 (1961).
18. Anderson, P. W., J. Phys. Chem. Solids 11, 26 (1959).

19. Linde, J. O., Phys. Letters 24A, 111 (1967).
20. Ginsberg, D. M. and Hebel, L. C., *in* Superconductivity, Vol. 1 (ed. R. D. Parks), p. 193. Marcel Decker, New York 1969.
21. Ref. 6, p. 152.
22. Deaver, B. S., Jr, and Fairbank, W. M., Phys. Rev. Letters 7, 43 (1961).
23. Doll, R. and Näbauer, M., Phys. Rev. Letters 7, 51 (1961); Z. Physik 169, 526 (1962).
24. Goodman, W. M., Willis, W. D., Vincent, D. A. & Deaver, B. S., Jr, Phys. Rev. B4, 1530 (1971).
25. Byers, N. and Yang, C. N., Phys. Rev. Letters 7, 46 (1961); Onsager, L., Phys. Rev. Letters 7, 50 (1961); Blatt, J. M., Phys. Rev. Letters 7, 82 (1961); Bardeen, J., Phys. Rev. Letters 7, 162 (1961); Keller, J. B. and Zumino, B., Phys. Rev. Letters 7, 164 (1961); Brenig, W., Phys. Rev. Letters 7, 337 (1961); Maki, K. and Tsuneto, T., Progr. Theoret. Phys. (Kyoto) 27, 228 (1962); Bohr, A. and Mottelson, B. R., Phys. Rev. 125, 495 (1962); Lüders, G., Z. Naturforsch. 17*a*, 181 (1962); Weller, W., Z. Naturforsch. 17*a*, 182 (1962); Phys. Letters 1, 222 (1962); Lipkin, H. J., Peshkin, M. and Tassie, L. J., Phys. Rev. 126, 116 (1962); Schwabl, F. and Thirring, W., Nuovo Cimento 25, 175 (1962); Ginsburg, V. L., Zh. Eksperim. i Teor. Fiz. 42, 299 (1962) (Sov. Phys. JETP 15, 207 (1962)); Peshkin, M. and Tobocman, W., Phys. Rev. 127, 1865 (1962); Bloch, F. and Rorschach, H. E., Phys. Rev. 128, 1697 (1962); Tinkham, M., Phys. Rev. 129, 2413 (1963); Peshkin, M., Phys. Rev. 132, 14 (1963); Douglass, D. H., Phys. Rev. 132, 513 (1963); Rapoport, L. P., Zh. Eksperim. i Teor. Fiz. 45, 1453 (1963) (Sov. Phys. JETP 18, 1003 (1964)).
26. Little, W. A. and Parks, R. D., Phys. Rev. Letters 9, 9 (1962); Groff, R. P. and Parks, R. D., in Proc. of the Tenth Int. Conf. on Low Temp. Physics, Vol. IIA (ed. M. P. Malkov), p. 253. Viniti, Moskva, 1967.
27. Josephson, B. D., Phys. Letters 1, 251 (1962); Advances in Physics 14, 419 (1965).
28. Anderson, P. W. and Rowell, J. M., Phys. Rev. Letters 10, 230 (1963).
29. Jaklevic, R. C., Lambe, J., Silver, A. H. and Mercereau, J. E., Phys. Rev. Letters 12, 159 (1964); Phys. Rev. 140, A1628 (1965); Zimmerman, J. E. and Silver, A. H., Phys. Letters 10, 47 (1964); 10, 208 (1964); Sol. State Comm. 4, 133 (1966); de Bruyn Ouboter, R. and de Waele, A. Th. A. M., *in* Progr. in Low Temp. Phys., Vol. IV (ed. C. J. Gorter), North-Holland, Amsterdam, 1970; Mercereau, J. E., *in* Tunneling Phenomena in Solids (ed. E. Burstein and S. Lundqvist), p. 461, Plenum Press, New York, 1969.
30. Shapiro, S., Phys. Rev. Letters 11, 80 (1963); Yanson, I. K., Svistunov, V. M. and Dmitrenko, I. M., Sov. Phys. JETP 21, 650 (1965); Giaever, I., Phys. Rev. Letters 14, 904 (1965); Langenberg, D. N., Scalapino, D. J., Taylor, B. N. and Eck, R. E., Phys. Rev. Letters 15, 294 (1965).
31. Parker, W. H., Taylor, B. N. and Langenberg, D. N., Phys. Rev. Letters 18, 287 (1967); Finnegan, T. F., Denenstein, A. and Langenberg, D. N., Phys. Rev. B4, 1487 (1971); Taylor, B. N., Parker, W. H. and Langenberg, D. N., Rev. Mod. Phys. 41, (1969).
32. Clarke, J., Phys. Rev. Letters 21, 1566 (1968).
33. Parker, W. M. and Simmonds, M. B., *in* Precision Measurements and Fundamental Constants (ed. D. N. Langenberg and B. N. Taylor), p. 243. NBS Spec. publ. 343, Washington, 1971.
34. Scalapino, D. J., ibid., p. 195.
35. See e.g. Solymar, L., Superconductive Tunneling and Applications, Chapman and Hall, London, 1972 (containing also a review of reviews, p. 344); Mercereau, J. E., *in* Superconductivity, Vol. 1 (ed. R. D. Parks), p. 393, Marcel Decker, New York, 1969; Josephson, B. D., ibid., p. 423.
36. Abrikosov, A. A., Zh. Eksperim. i Teor. Fiz. 32, 1442 (1957); Sov. Phys. JETP 5, 1174 (1957).
37. For a pedagogical account of superconductivity in the spirit of Ginzburg and Landau, we refer the reader to de Gennes, P. G., Superconductivity of Metals and Alloys, Benjamin, New York, 1966.
38. Foner, S., McNiff, E. J., Jr, Matthias, B. T., Geballe, T. M., Willens, R. H. and Corenzwit, E., Phys. Letters 31A, 349 (1970).
39. Cribier, D., Jacrot, B., Madhav Rao, L. and Farnoux, B., Phys. Letters 9, 106 (1964).
40. Seeger, A., Met. Trans. 1, 2987 (1970); Träuble, H. and Essmann, U., Phys. Stat. Sol. 18, 813 (1966); J. Appl. Phys. 39, 4052 (1968) Essmann, U. and Träuble, H., Phys. Stat. Sol. 32, 337 (1969); Phys. Letters 24A, 526 (1967).
41. Gorkov, L. P., Zh. Eksperim. i Teor. Fiz. 34, 735 (1958); 36, 1918 (1959); 37, 1407 (1959); Soviet Phys. JETP 7, 505 (1958); 9, 1364 (1959); 10, 998 (1960).
42. Deutscher, G. and de Gennes, P. G., *in* Superconductivity, Vol. 2 (ed. R. D. Parks), p. 1005. Marcel Decker, New York, 1969.
43. Hilsch, P., Z. Physik 167, 511 (1962).
44. Glover III, R. E., *in* Superconductivity, Proc. Int. Conf. on the Science of Superconductivity (ed. F. Chilton), p. 3. North-Holland, Amsterdam, 1971.
45. Aslamazov, L. G. and Larkin, A. I., Phys. Letters 26A, 238 (1968).
46. Geballe, T. H., Scientific American, November 1971.
47. Coleman, L. B., Cohen, M. J., Sandman, D. J., Yamagishi, F. G., Garito, A. F. and Heeger, A. J., Sol. State Comm. 12, 1125 (1973).
48. Douglas, D. H., Jr and Falicov, L. M., *in* Progress in Low Temp. Phys., Vol. IV (ed. C. J. Gorter), p. 97, North-Holland, Amsterdam, 1964, Meservey, R. and Schwartz, B. B., *in* Superconductivity, Vol. 1 (ed. R. D. Parks), p. 141. Marcel Decker, New York, 1969.
49. Giaever, I., Phys. Rev. Letters 5, 147; 464 (1960).
50. Fischer, J. C. and Giaever, I., J. Appl. Phys. 32, 172 (1961).
51. Harrison, W. A., Phys. Rev. 123, 85 (1961).
52. Bardeen, J., Phys. Rev. Letters 6, 57 (1961); 9, 147 (1962).
53. Duke, C. B., *in* Tunneling Phenomena in Solids (ed. E. Burstein and S. Lundqvist), p. 31. Plenum Press, New York, 1969.
54. Schrieffer, J. R., *in* Tunneling Phenomena in Solids (ed. E. Burstein and S. Lundqvist), p. 287. Plenum Press, New York, 1969.
55. Giaever, I., Hart, H. R., Jr and Megerle, K., Phys. Rev. 126, 941 (1962).
56. Douglas, D. H., Jr and Meservey, R., Phys. Rev. 135, A19 (1964).
57. Zavaritskii, N. V., Zh. Eksperim. i Teor. Fiz. 41, 657 (1961); Soviet Phys. JETP 14, 470 (1961).
58. David, R. and Poulis, N. H., *in* Proc. of the Eighth Int. Conf. on Low Temp. Physics, London, 1962 (ed. R. O. Davies). Butterworths, London, 1963.
59*a*. Biondi, M. A. and Garfunkel, M. P., Phys. Rev. 116, 853, 862 (1959); Phys. Rev. Letters 2, 143 (1959); Miller, P. B., Phys. Rev. 118, 928 (1960).
59*b*. Kumbhare, P., Tedrow, P. M. and Lee, D. M., Phys. Rev. 180, 519 (1969).
60*a*. Yoshihiro, K. and Sasaki, W., J. Phys. Soc. Japan 24, 426 (1968).
60*b*. Yoshihiro, K. and Sasaki, W., J. Phys. Soc. Japan 28, 262 (1970).
61. Keister, J. C., Straus, L. S. and Gregory, W. D., J. Appl. Phys. 42, 642 (1971).
62. Hart, H. R. and Roberts, B. W., Bull. Am. Phys. Soc. 7, 175 (1962).
63. Bermon, S. and Ginsberg, D. M., Phys. Rev. 135, A306 (1964).
64. Richards, P. L. and Tinkham, M., Phys. Rev. 119, 575 (1960).
65. Ginsberg, D. M. and Tinkham, M., Phys. Rev. 118, 990 (1960).
66. Hauser, J. J., Phys. Rev. Letters 17, 921 (1966).
67. Shen, L. Y. L., *in* Superconductivity in d- and f-Band Metals, (ed. D. H. Douglas), AIP Conf. Proc. No. 4, Am. Inst. Physics, New York, 1972, p. 31.
68. Leslie, J. D., Cappelletti, R. L., Ginsberg, D. M., Finnemore, D. K., Spedding, F. H. and Beandry, B. J., Phys. Rev. 134, A309 (1964).
69. Townsend, P. and Sutton, J., Phys. Rev. 128, 591 (1962); in Proc. of the Eighth Int. Conf. on Low Temp. Physics (ed. P. O. Davies), p. 182, Butterworth, London, 1963.
70. MacVicar, M. L. A. and Rose, R. M., J. Appl. Phys. 39, 172 (1968); Phys. Letters 26A, 510 (1968).
71*a*. Dobbs, E. L. and Perz, J. M., Rev. Mod. Phys. 36, 257 (1964).
71*b*. Almond, D. P., Lea, M. J. and Dobbs, E. R., Phys. Rev. Letters 29, 764 (1972).
72. Cappelletti, R. L., Ginsberg, D. M. and Hulm, J. K., Phys. Rev. 158, 340 (1967).
73. McMillan, W. L. and Rowell, J. M., Phys. Rev. Letters 14, 108 (1965).
74. Blackford, B. L. and March, R. H., Phys. Rev. 186, 397 (1969); Blackford, B. L., Physica 55, 475 (1971).
75. Lykken, G. I., Geiger, A. L., Dy, K. S. and Mitchell, E. N., Phys. Rev. B4, 1523 (1971).
76. Love, R. E., Shaw, R. W. and Fate, W. A., Phys. Rev. 138, A1453 (1965).
77. Leslie, J. D. and Ginsberg, D. M., Phys. Rev. 133, A362 (1964).
78. Ochiai, S., MacVicar, M. L. A. and Rose, R. M., Phys. Rev. B4, 2988 (1971).
79. Jones, C. K. and Rayne, J. A., Phys. Letters 21, 510 (1966).
80. Zavaritskii, N. V., Zh. Eksperim. i Teor. Fiz. 48, 837 (1965); Soviet Phys. JETP 21, 557 (1965).
81. Bezuglyi, P. A., Galin, A. A. and Korolyuk, A. P., Zh. Eksperim. i Teor. Fiz. 39, 7 (1960) (Sov. Phys. JETP 12, 4 (1961)).
82. Morse, R. W., Olsen, T. and Gavenda, J. D., Phys. Rev. Letters 3, 15 (1959).

83. Brenig, M. A., Garfunkel, M. P. and McCoubrey, A. O., Phys. Rev. 108, 495 (1957).
84. Levy, M., Kagiwada, R. and Rudnik, I., *in* Proc. of the Eighth Int. Conf. on Low Temp. Physics, London, 1962 (ed. R. O. Davies). Butterworths, London, 1963.
85. Haskell, B. A., Keeler, W. J. and Finnemore, D. K., Phys. Rev. B5, 4364 (1972).
86. Taylor, B. N. and Burstein, E., Phys. Rev. Letters 10, 14 (1963).
87. Sanders, G. A. and Lawson, A. W., Phys. Rev. 135, A1161 (1964).
88. Weil, R. and Lawson, A. W., Phys. Rev. 141, 452 (1966).
89. Giaever, I., in Proc. of the Eighth Int. Conf. on Low Temp. Physics (ed. P. O. Davies), p. 171. Butterworth, London, 1963.
90. Bohm, H. V. and Horowitz, N. H., *in* Proc. of the Eighth Int. Conf. on Low Temp. Physics, London, 1962 (ed. R. O. Davies). Butterworths, London, 1963.
91. Donaldson, G. B., in Proc. of the Tenth Int. Conf. on Low Temp. Physics, Moscow, 1966, Vol. IIB (M. P. Malkov, ed. in chief), p. 291. Viniti, Moscow, 1967.
92. Landau, L. D., Zh. Eksperim. i Teor. Fiz. 30, 1058 (1956); Sov. Phys. JETP 7, 996 (1958).
93. Eliashberg, G. M., Zh. Eksperim. i Teor. Fiz. 38, 996 (1960); Sov. Phys. JETP 11, 696 (1960).
94. Scalapino, D. J., *in* Superconductivity, Vol. 1 (ed. R. D. Parks), p. 449. Marcel Decker, New York, 1969.
95. Schrieffer, J. R., Theory of Superconductivity. W. A. Benjamin, New York, 1964.
96. Schrieffer, J. R. and Wada, Y., Bull. Am. Phys. Soc. 8, 307 (1963).
97. Wada, Y., Rev. Mod. Phys. 36, 253 (1964).
98. Swihart, J. C., Scalapino, D. J. and Wada, Y., Phys. Rev. Letters 14, 106 (1965).
99. Swihart, J. C., in Proc. of the Tenth Int. Conf. on Low Temp. Physics, Moscow, 1966, Vol. IIB (ed. M. P. Malkov), p. 275. Viniti, Moscow, 1967.
100. Leslie, J. D., Chen, J. T. and Chen, T. T., J. Phys. 48, 2783 (1970).
101. Knorr, K. and Barth, N., Sol. State Comm. 8, 1085 (1970).
102. Bergmann, G., Phys. Rev. B3, 3797 (1971).
103. Granqvist, C. G. and Claeson, T., Phys. Letters 39A, 271 (1972).
104. Granqvist, C. G. and Claeson, T., J. Low Temp. Phys. 13, 1 (1973).
105. Campbell, C. K. and Walmsley, D. G., Can. J. Phys. 45, 159 (1967).
106. Claeson, T. and Grimvall, G., J. Phys. Chem. Solids 29, 387 (1968).
107. Campbell, C. K., Dynes, R. C. and Walmsley, D. G., Can. J. Phys 44, 2601 (1966).
108. Geilikman, B. T. and Kresin, V. Z., Zh. Eksperim. i Teor. Fiz. 40, 970 (1961); Soviet Phys. JETP 13, 677 (1961).
109. Bennett, A. J., Phys. Rev. 140, A1902 (1965).
110. Clem, J. R., Phys. Rev. 148, 391 (1966).
111. Tomasch, W. J., Phys. Rev. Letters 15, 672 (1965); 16, 16 (1966); 16, 352 (1966).
112. Tomasch, W. J., *in* Tunneling Phenomena in Solids (ed. E. Burstein and S. Lundqvist), p. 315. Plenum Press, New York, 1969.
113. McMillan, W. L. and Anderson, P. W., Phys. Rev. Letters 16, 85 (1966).
114. Burstein, E., Langenberg, D. N. and Taylor, B. N., Phys. Rev. Letters 6, 92 (1961).
115. Eisenmenger, W., *in* Tunneling Phenomena in Solids (ed. E. Burstein and S. Lundqvist), p. 385. Plenum Press, New York, 1969.
116. Tien, P. K. and Gordon, J., Phys. Rev. 129, 647 (1963).
117. Granqvist, C. G. and Claeson, T., Phys. Rev. Letters 31, 456 (1973).
118. Dayem, A. H., Miller, B. I. and Wiegand, J. J., Phys. Rev. B3, 2949 (1971); Dayem, A. H. and Wiegand, J. J., Phys Rev. B5, 4390 (1972); Dynes, R. C. and Narayanamurti, V., Phys. Rev. B6, 143 (1972); Sol. State Comm. 12, 341 (1973); Long, A. R. and Adkins, C. J., Phil. Mag. 27, 865 (1973); Kinder, H., Z. Physik 262, 295 (1973); Forkel, W., Welte, M. and Eisenmenger, W., Phys. Rev. Letters 31, 215 (1973); these articles give references to previous works.
119. Schrieffer, J. R. and Wilkins, J. W., Phys. Rev. Letters 10, 17 (1963).
120. Wilkins, J. W., *in* Tunneling Phenomena in Solids (ed. E. Burstein and S. Lundqvist), p. 333. Plenum Press, New York, 1969.
121. Taylor, B. N. and Burstein, E., Phys. Rev. Letters 10, 14 (1963).
122. Toxen, A. M., Basavaiah, S. and Levine, J. L., in Proc. 13th Low Temp. Conf., to be published.
123. Rowell, J. M., Rev. Mod. Phys. 36, 215 (1964).
124. Rowell, J. M. and Feldmann, W. L., Phys. Rev. 172, 393 (1968).
125. Giaever, I. and Zeller, H. R., Phys. Rev. B1, 4278 (1970); Physica 55, 455 (1971).
126. Morel, P. and Anderson, P. W., Phys. Rev. 125, 1263 (1962).
127. Garland, J. W., Phys. Rev. Letters 11, 114 (1963); Phys. Rev. 153, 460 (1967).
128. Olsen, J. L., Cryogenics 2, 356 (1963).
129. Palmy, C., Phys. Letters 29A, 373 (1969).
130. Matthias, B. T., Geballe, T. M., Corenzwit, E. and Hull, G. W. Jr, Phys. Rev. 129, 1025 (1963).
131. Bucher, E. and Palmy, C., Phys. Letters 24A, 340 (1967).
132. Geballe, T. M., Matthias, B. T., Hull, G. W., Jr and Corenzwit, E., Phys. Rev. Letters 6, 275 (1961).
133. Shaw, R. W., Mapother, D. E. and Hopkins, D. C., Phys. Rev. 121, 86 (1961); Hake, R. R., Mapother, D. E. and Decker, D. L., Phys. Rev. 118, 1522 (1958).
134. Maxwell, E., Rev. Mod. Phys. 36, 144 (1964).
134*a*. Serin, B., Reynolds, C. A. and Lohman, C., Phys. Rev. 86, 162 (1952).
134*b*. Lock, J. M., Pippard, A. B. and Schoenberg, D., Proc. Camb. Phil. Soc. 47, 811 (1951).
135. Maxwell, E., Phys. Today, 5 No. 12, p. 14.
136. Fowler, R. D., Lindsay, J. D. G., White, R. W., Hill, H. H. and Matthias, B. T., Phys. Rev. Letters 19, 892 (1967); Hill, H. H., Physica 55, 195 (1971).
137. Lindsay, J. D., White, R. W., Tinkle, M. C., Hayter, S. W. and Fowler, R. D., Phys. Rev. B7, 4290 (1973).
138. Geballe, T. H. and Matthias, B. T., in Proc. of the Eighth Int. Conf. on Low Temp. Phys. (ed. R. Davies), p. 159. Butterworth, London, 1964.
139. Fassnacht, R. E. and Dillinger, J. R., Phys. Rev. Letters 17, 255 (1966).
140. Bucher, E., Muller, J., Olsen, J. L. and Palmy, C., Phys. Letters 15, 303 (1965).
141. Bogoliubov, N. N., Tolmachev, V. V. and Shirkov, D. V., A New Method in the Theory of Superconductivity. Academy of Sciences, Moscow. 1958, transl. Consultants Bureau, New York, 1959.
142. McMillan, W. L., Phys. Rev. 167, 331 (1968).
143. Schrieffer, J. R., *in* Proc. 3rd Symp. 1969 Spring Superconducting Symposia (ed. R. A. Hein). Naval Research Laboratory Rep. 6986, Washington, D. C., 1969, p. 44; Capellmann, H. and Schrieffer, J. R., Phys. Rev. Letters 21, 1060 (1968).
144. McMillan, W. L. and Rowell, J. M., *in* Superconductivity, Vol. I (ed. R. D. Parks), p. 561. Marcel Decker, New York, 1969.
145. Hubin, W. N. and Ginsberg, D. M., Phys. Rev. 188, 716 (1969).
146. Dynes, R. C., Phys. Rev. B2, 644 (1970).
147. Rowell, J. M. and Kopf, L., Phys. Rev. 137, A907 (1965).
148. Rowell, J. M., McMillan, W. L. and Feldmann, W. L., Phys. Rev. B3, 4065 (1971).
149. Wyatt, A. F. G., Phys. Rev. Letters 13, 160 (1964).
150. Hansma, P. K. and Rochlin, G. I., Bull. Am. Phys. Soc. 17, 46 (1973).
151. Chen, T. T., Chen, J. T., Leslie, J. D. and Smith, H. J. T., Phys. Rev. Letters 22, 526 (1969).
152. Hauser, J. J., Phys. Rev. B3, 1611 (1971); Claeson, T., Granqvist, C. G. and Ivarsson, J., private comm.
153. Adler, J. G. and Ng, S. C., Can. J. Phys. 43, 594 (1965).
154. Adler, J. G., Jackson, J. E. and Will, T. A., Phys. Letters 24A, 407 (1967).
155. Rowell, J. M., McMillan, W. L. and Feldmann, W. L., Phys. Rev. 178, 897 (1969).
156. Dynes, R. C., Carbotte, J. P., Taylor, D. W. and Campbell, C. K., Phys. Rev. 178, 713 (1969).
157. Dynes, R. C. and Rowell, J. M., Phys. Rev. 187, 821 (1969).
158. Rowell, J. M., McMillan, W. L. and Anderson, P. W., Phys. Rev. Letters 14, 633 (1965).
159. Adler, J. G., Jackson, J. E. and Chandrasekhar, B. S., Phys. Rev. Letters 16, 53 (1966).
160. Sood, B. R. and Chandrasekhar, B. S., Phys. Letters 36A, 385 (1971).
161. Sood, B. R., Phys. Rev. B6, 136 (1972).
162. Granqvist, C. G. and Claeson, T., Phys. kondens. Materie 16, 113 (1973).
163. Dynes, R. C., Phys. Rev. B2, 644 (1970).
164. Dynes, R. C., to be published.
165. Shen, L. Y. L., Phys. Rev. Letters 29, 1082 (1972).
166. Granqvist, C. G. and Claeson, T., Thin Solid Films 16, 65 (1973); J. Low Temp. Phys. 13, 1 (1973).
167. Merriam, M. F., Rev. Mod. Phys. 36, 152 (1964); Phys. Rev. 144, 300 (1966).
168. Havinga, E. E., Damsma, H. and van Maaren, M. H., J. Phys. Chem. Solids 31, 2653 (1970).

169. Claeson, T., Phys. Rev. **147**, 340 (1966); Claeson, T. and Östlund, O., Sol. State Comm. **8**, 851 (1970).
170. Tsuei, C. C. and Newkirk, L. R., Phys. Rev. **183**, 619 (1969).
171. Matthias, B. T., Geballe, T. H. and Compton, V. B., Rev. Mod. Phys. **35**, 1 (1963).
172. Claeson, T., Luo, H. L. and Merriam, M. F., Phys. Rev. **141**, 412 (1966).
173. Mota, A. C., Brewster, P. and Wang, R., Phys. Letters **41A**, 99 (1972).
174. Gladstone, G., Jensen, M. A. and Schrieffer, J. R., *in* Superconductivity, Vol. 2 (ed. R. D. Parks), p. 665. Marcel Decker, New York, 1969.
175. Mattheiss, L. F., Phys. Rev. **134**, A970 (1964); **139**, A1893 (1965); **151**, 450 (1966).
175*a*. Jensen, M. A., thesis, Univ. of Calif., San Diego, 1965 (unpublished); see also Ref. [174].
176. Matthias, B. T., Phys. Rev. **97**, 74 (1955); in Progress in Low Temp. Physics, Vol. II (ed. C. J. Gorter), p. 138. North-Holland, Amsterdam, 1957.
177. Bucher, E., Heiniger, F., Müller, J. and Olsen, J. E., Low Temp. Physics, LT9, Part A (ed. J. G. Danut et al.), p. 616. Plenum Press, New York, 1965.
178. Geballe, T. H., Rev. Mod. Phys. **36**, 134 (1964).
179. Andres, K. and Jensen, M. A., Phys. Rev. **165**, 533 (1968).
180. Jensen, M. A. and Andres, K., J. Appl. Phys. **38**, 1255 (1967).
181. Suhl, H., Matthias, B. T. and Walker, L. R., Phys. Rev. Letters **3**, 552 (1959); Kondo, J., Progr. Theor. Phys. (Kyoto) **29**, 1 (1963); Kuper, C. G., Jensen, M. A. and Hamilton, D. C., Phys. Rev. **134**, A15 (1964); ref. 136; Matthias, B. T., *in* Superconductivity, Vol. 1 (ed. P. R. Wallace), p. 227. Gordon and Breach, New York, 1969.
182. Berk, N. F. and Schrieffer, J. R., Phys. Rev. Letters **17**, 433 (1966).
183. For a review, see Maple, M. B., *in* Magnetism, Vol. V (ed. Rado and Suhl, H.), in press.
184. Matthias, B. T., Suhl, H. and Corenzwit, E., Phys. Rev. Letters **1**, 92 (1958); J. Phys. Chem. Solids **13**, 156 (1960); Geballe, T. H. and Matthias, B. T., IBM J. Res. Dev. **6**, 256 (1962).
185. Boato, G., Gallinaro, G. and Rizzuto, C., Phys. Rev. **148**, 353 (1966).
186. Matthias, B. T., Compton, V. B., Suhl, H. and Corenzwit, E., Phys. Rev. **115**, 1597 (1959); Raub, Ch. J. and Anderson, C. A., Z. Physik **175**, 105 (1963); Raub, Ch. J. and Hull, G. W., Jr, Phys. Rev. **133**, A932 (1964).
187. Abrikosov, A. A. and Gorkov, L. P., Zh. Eksperim. i Teor. Fiz. **39**, 1781 (1960); Soviet Phys. JETP **12**, 1243 (1961).
188. Skalski, S., Betbeder-Matibet, O. and Weiss, P. R., Phys. Rev. **136**, A1500 (1964).
189. Maple, M. B., Phys. Letters **A26**, 513 (1968).
190. Guertin, R. P., Ph.D. Thesis, Univ. of Rochester, New York, 1968.
191. Hein, R. A., Falge, R. L., Jr, Matthias, B. T. and Corenzwit, E., Phys. Rev. Letters **2**, 500 (1959); Crow, J. E. and Parks, R. D., Phys. Letters **21**, 376 (1966).
192. Kondo, J., Progr. Theor. Phys. (Kyoto) **32**, 37 (1964).
193. Müller-Hartmann, E. and Zittartz, J., Phys. Rev. Letters **26**, 428 (1971).
194. Riblet, G. and Winzer, K., Sol. State Comm. **9**, 1663 (1971).
195. Maple, M. B., Fertig, W. A., Mota, A. C., DeLong, L. E., Wohlleben, D. and Fitzgerald, R., Sol. State Comm. **11**, 829 (1972).
196. Reif, F. and Woolf, M. A., Phys. Rev. Letters **9**, 315 (1962); Woolf, M. A. and Reif, F., Phys. Rev. **137**, A557 (1965).
197. Edelstein, A. S., Phys. Rev. Letters **19**, 1184 (1967); Phys. Rev. **180**, 505 (1969); Tsuda, N., J. Phys. Soc. Japan **27**, 1025 (1969).
198. Dick, G. J. and Reif, F., Phys. Rev. **181**, 774 (1969).
199. Finnemore, D. K., Johnson, G. L., Ostenson, J. E., Spedding, F. H. and Beaudry, B. J., Phys. Rev. **137**, A550 (1965).
200. Decker, W. R., Peterson, D. T. and Finnemore, D. K., Phys. Rev. Letters **18**, [illegible] (1967); Phys. Rev. **172**, 430 (1968).
201. Cappelletti, R. L. and Finnemore, D. K., Phys. Rev. **188**, 723 (1969).
202. Maki, K., *in* Superconductivity, Vol. 2 (ed. R. D. Parks), p. 1035. Marcel Decker, New York, 1969.
203. Fulde, P., *in* Tunneling Phenomena in Solids (ed. E. Burstein and S. Lundqvist), p. 427. Plenum Press, New York, 1969.
204. Guyon, E., Martinet, A., Martinet, J. and Pincus, P., Phys. Rev. **138**, A746 (1965).
205. Levine, J. L., Phys. Rev. **155**, [illegible] (1967).
206. Millstein, J. and Tinkham, M., Phys. Rev. **158**, 325 (1967).
207. Adkins, C. J. and Kington, R. W., Phil. Mag. **18**, 871 (1968).
208. Hauser, J. J., Phys. Rev. **2**, 2439 (1970).
209. Guyon, E., Martinet, A., Martinet, J. and Pincus, P., Phys. Kondens. Materie **5**, 123 (1966).
210. Claeson, T. and Gygax, S., Sol. State Comm. **4**, 385 (1966); Claeson, T., Gygax, S. and Maki, K., Phys. kondens. Materie **6**, 23 (1967); Claeson, T., *in* Tunneling Phenomena in Solids (ed. E. Burstein and S. Lundqvist), p. 443. Plenum Press, New York, 1969.
211. Fischer, G. and Klein, R., Phys. Rev. **165**, 578 (1968); Phys. kondens Materie **7**, 12 (1968).
212. Matthias, B. T., IBM J. Res. Dev. **6**, 250 (1962).
213. Gorkov, L. P. and Rusinov, A. J., Sov. Phys. JETP **19**, 922 (1964).
214. Peter, M., Donzé, P., Fischer, O., Junod, A., Ortelli, J., Treyrand, A., Walker, E., Wilhelm, M. and Hillenbrand, B., Helv. Phys. Acta **44**, 345 (1971).
215. Steiner, P., Gumprecht, D. and Hüfner, S., Phys. Rev. Letters **30**, 1132 (1973).
216. Kohn, W. and Luttinger, J. M., Phys. Rev. Letters **15**, 524 (1965); Luttinger, J. M., Phys. Rev. **150**, 202 (1966).
217. Friedel, J., Adv. Phys. **3**, 446 (1954); Nuovo Cimento, Suppl. **2**, 287 (1958).
218. Matthias, B. T., Peter, M., Williams, H. J., Clogston, A. M., Corenzwit, E. and Sherwood, R. C., Phys. Rev. Letters **5**, 542 (1960); Engelhardt, J. J., Webb, G. W. and Matthias, B. T., Science **155**, 191 (1967); see also ref. 181.
219. Little, W. A., Phys. Rev. **A134**, 1416 (1964); *in* Superconductivity, Proc. Int. Conf. Science of Superconductivity, (ed. F. Chilton), p. 50. North-Holland, Amsterdam, 1971.
220. Ginzburg, V. L., Contemporary Physics **9**, 355 (1968).
221. Allender, D., Bray, J. and Bardeen, J., Phys. Rev. **B7**, 1020 (1973).
222. Ferrell, R. A., Phys. Rev. Letters **13**, 330 (1969); Hohenberg, P. C., Phys. Rev. **158**, 383 (1967).
223. Ginzburg, V. L., *in* Superconductivity, Proc. Int. Conf. Science of Superconductivity. (ed. F. Chilton), p. 207, North-Holland, Amsterdam, 1971; Pines, D., Proc. 12th Int. Conf. Low Temp. Physics (ed. E. Kanda), p. 7. Academic Press of Japan, Tokyo, 1971.
224. Swihart, J. C., Scalapino, D. J. and Wada, Y., Phys. Rev. Letters **14**, 106 (1965).
225. Rowell, J. M., Anderson, P. W. and Thomas, D. E., Phys. Rev. Letters **10**, 334 (1963).
226. Migdal, A. B., Zh. Eksperim. i Teor. Fiz. **34**, 1438 (1958); Sov. Phys. JETP **7**, 996 (1958).
227. Nambu, Y., Phys. Rev. **117**, 648 (1960).
228. Schrieffer, J. R., Scalapino, D. J. and Wilkins, J. W., Phys. Rev. Letters **10**, 336 (1963); Scalapino, D. J., Schrieffer, J. R. and Wilkins, J. W., Phys. Rev. **148**, 263 (1966).
229. Several excellent reviews are available, see Refs. 94, 95, and 144.
230. Landau, L. D., Zh. Eksperim. i Teor. Fiz. **30**, 1058 (1950); Sov. Phys. JETP **7**, 996 (1958).
231. Scalapino, D. J. and Anderson, P. W., Phys. Rev. **133**, A291 (1964).
232. Osheroff, D. D., Richardson, R. C. and Lee, D. M., Phys. Rev. Letters **28**, 885 (1972).
233. Osheroff, D. D., Gully, W. J., Richardson, R. C. and Lee, D. M., Phys. Rev. Letters **29**, 920 (1972).
234. Lawson, D. T., Gully, W. J., Goldstein, S., Richardson, R. C. and Lee, D. M., Phys. Rev. Letters **30**, 541 (1973).
235. Webb, R. A., Greytak, T. J., Johnson, R. J. and Wheatley, J. C., Phys. Rev. Letters **30**, 210 (1973).
236. Anufriev, Yu. D., Alvesalo, T. A., Collan, H. K., Oppheim, N. T. and Wennerström, P., Phys. Letter **43A**, 175 (1973).
237. Alvesalo, T. A., Anufriyev, Yu. D., Collan, H. K., Lounasmaa, O. V. and Wennerström, P., Phys. Rev. Letters **30**, 962 (1973).
238. Leggett, A. J., Phys. Rev. Letters **29**, 1227 (1972).
239. Anderson, P. W., Phys. Rev. Letters **30**, 368 (1973).
240. Matthias, B. T., *in* Superconductivity, Proc. Int. Conf. Science of Superconductivity (ed. F. Chilton), p. 69. North-Holland, Amsterdam, 1971.
241. Gavaler, J. R., Appl. Phys. Letters **23**, 480 (1973); Testardi, L. R., Wernick, J. H. and Royer, W. A., Sol. State Comm., in press; Robinson, A. L., Science **183**, 293 (1974).
242. Foner, S., McNiff, Jr., E. J., Matthias, B. T. and Corenzwit, E., Proc. LT 11, Vol. 2 (ed. J. F. Allen, D. M. Finlayson, and D. M. McCall), p. 1025. St. Andrews, 1969.
243. Garland, J. W. and Allen, P. B., *in* Superconductivity, Proc. Int. Conf. Science of Superconductivity (ed. F. Chilton), p. 669. North-Holland, Amsterdam, 1971.
244. Hertel, P., Z. Physik **248**, 272 (1971).
245. Cohen, M. L. and Anderson, P. W., *in* Superconductivity in d- and f-Band Metals, AIP Conf. Proc. No. 4 (ed. D. H. Douglass), p. 17. Am. Inst. Phys., New York, 1972.
246. [illegible], J. C., Phys. Rev. Letters **26**, 543 (1971); **29**, 1551 (1972).

246*a*. See e.g. Robinson, A. L., Science **182**, 1334 (1973).

246*b*. "Attempts to explain and observe TCNQ behavior at 60 K", Physics Today, Sept. 1973, p. 17; Delhaes, P. and Aly, F., Sol. State Comm. **12**, 1099 (1973); Chaikin, P. M., Kwak, J. F., Jones, T. E., Garito, A. F. and Heeger, A. J., Phys. Rev. Letters **31**, 601 (1973); Bardeen, J., Sol. State Comm. **13**, 357 (1973); Anderson, P. W., Lee, P. A. and Saitoh, M., Sol. State Comm. **13**, 595 (1973); Lee, P. A., Rice, T. M. and Anderson, P. W., Phys. Rev. Letters **31**, 462 (1973); Patton, B. R. and Sham, L. J., Phys. Rev. Letters **31**, 631 (1973); Bloch, A. N., Ferraris, J. P., Cowan, D. O. and Poehler, T. O., Sol. State Comm. **13**, 753 (1973); Bright, A. A., Garito, A. F. and Heeger, A. J., Sol. State Comm. **13**, 943 (1973); Rice, M. J. and Strässler, S., Sol. State Comm. **13**, 697 (1973); Chu, C. W., Harper, J. M. E., Geballe, T. H. and Greene, R. L., Phys. Rev. Letters **31**, 1491 (1973); Schafer, D. E., Wudl, F., Thomas, G. A., Ferraris, J. P. and Cowan, D. O., Sol. State Comm. **14**, 347 (1974); Cohen, M. J., Coleman, L. B., Garito, A. F. and Heeger, A. J., to be published.

247. Allen, P. B., Sol. State Comm. **12**, 379 (1973).

247*a*. Bergmann, G. and Rainer, D., Z. Physik **263**, 59 (1973).

248. Ashcroft, N. W., Phys. Letters **23**, 48 (1966).

249. Schneider, T. and Stoll, E., Physica **55**, 702 (1971).

250. Stritzker, B. and Buchel, W., Z. Physik **257**, 1 (1972).

251. Buchel, W. and Stritzker, B., Phys. Letters **43A**, 403 (1973).

252. Lasbley, A., Rolland, S. and Granger, R., to be published.

253. Wood, M. F., *in* Advanced Cryogenics (ed. C. A. Bailey), p. 293, Plenum Press, London, 1971; Bibliography of References, Superconducting Magnets, Cryogenic Data Center, NBS, Boulder, 1972; Hulm, J. K., Kasun, D. J. and Mullan, E., Phys. Today, August 1971, p. 48.

254. Guderjahn, C. and Wipf, S. L., Cryogenics **11**, 171 (1971); Ed. note, Interavia **5**, 520 (1972).

255. Appleton, A. D., Cryogenics **9**, 147 (1969); Bibliography of References, Superconducting Motors and Generators, Cryogenic Data Center, NBS, Boulder, 1972.

256. Merriam, M. F., Underground Engineering, April/May 1971, p. 41; Meyerhoff, R. W., Cryogenics **11**, 91 (1971); Bibliography of References, Superconducting Transmission Lines, Cryogenic Data Center, NBS, Boulder, 1972.

257. Doyle, O., Electronics, March 1, 1971, p. 38; Bibliography of References, Superconducting Detectors, Cryogenic Data Center, NBS, Boulder, 1972.

258. Bohr, A., Mottelson, B. R. and Pines, D., Phys. Rev. **110**, 936 (1958); Migdal, A. B., Nuclear Physic **13**, 658 (1959).

259. Nambu, Y. and Jona-Lasinio, G., Phys. Rev. **122**, 345 (1961).

260. Goldstone, J., Nuovo Cimento **19**, 154 (1961); Weinberg, S., Phys. Rev. Letters **19**, 1264 (1967).

261. Ginzburg, V. L. and Kirzhnits, D. A., Zh. Eksperim. i Teor. Fiz. **47**, 2006 (1964); translated in Sov. Phys. JETP **20**, 1346 (1965); Pines, D., Baym, G. and Pethnik, C., Nature **224**, 673 (1969).

262. Stedman, K., Almquist, L., Nilsson, G. and Raunio, G., Phys. Rev. **162**, 545 (1967); **162**, 549 (1967).