

XI. JAKT PÅ HÖGTEMPERATURSUPRALEDARE

En supraledare vid rumstemperatur skulle innebära en teknologisk revolution. Men även supraledare i betydligt lägre temperaturintervall, t ex vid flytande luftens temperatur, skulle vara av allra största, rentav revolutionerande, betydelse. Gränsen för industriellt genombrott brukar sättas till 25-30 K. Då kan man använda sig av flytande väte (20 K, 1 atm) som kylmedium och ändå vara väl under T_C så att H_{C2} och I_C är fullt utbildade. I verkligheten tycks det dock vara svårt att nå de höga temperaturerna. T_C har ökat med 2K per decennium i genomsnitt, men till allt större arbetsinsats. Idag (1983) är 23 K rekordet (för Nb_3Ge) och det är ca tio år sedan senaste ökningen av T_C .

Vi har sett att även teoretiskt har man indikationer av en övre gräns hos T_C . Denna är av samma storleksordning som de högsta experimentella värdena. Men finns det andra, gynnsamma strukturer för högtemperatursupraledning och finns det andra typer av attraktiva växelverkningar än elektron-fonon-kopplingen, som skulle kunna ge högre T_C ?

Little föreslog tidigt (se Scientific American, Febr. 1965, s 21) en sorts en-dimensionell supraledning, där man har långa molekylära, organiska kedjor till vilka är kopplade polariserbara molekyler. Elektroner går längs "ryggraden" i riktade orbitaler och polariserar då "revbenen", dvs sidokedjorna. Eftersom polarisationen här ombesörjes av lätta elektroner istället för tunga joner, som i en metall, så skulle isotopeffekten kunna ge en hög T_C . Mot förslaget talar att fluktuationer motverkar en-dimensionell supraledning. Experiment har ej givit några högtemperatursupraledare (åtminstone hittills), men en intressant utveckling av ledande polymerer har skett de senaste åren.

Ginzburg föreslog (se Contemp. Phys. 9, 355, 1968) en slags tvådimensionell supraledning, där man har excitationer, dvs polarisering, i ett dielektrikum i kontakt med en metall. Även detta förslag är öppet mot kritik i form av fluktuationer. Geballe (se Scientific American, November 1971) redogör för hur man kan placera långa organiska kedjor mellan atomplan och hur detta påverkar supraledning. Mätningar av susceptibiliteten tydde på att supraledning skulle börja bildas (fluktuationer) vid så hög temperatur som 35 K även om full supraledning var utbildad först vid en tiopotens lägre temperatur.

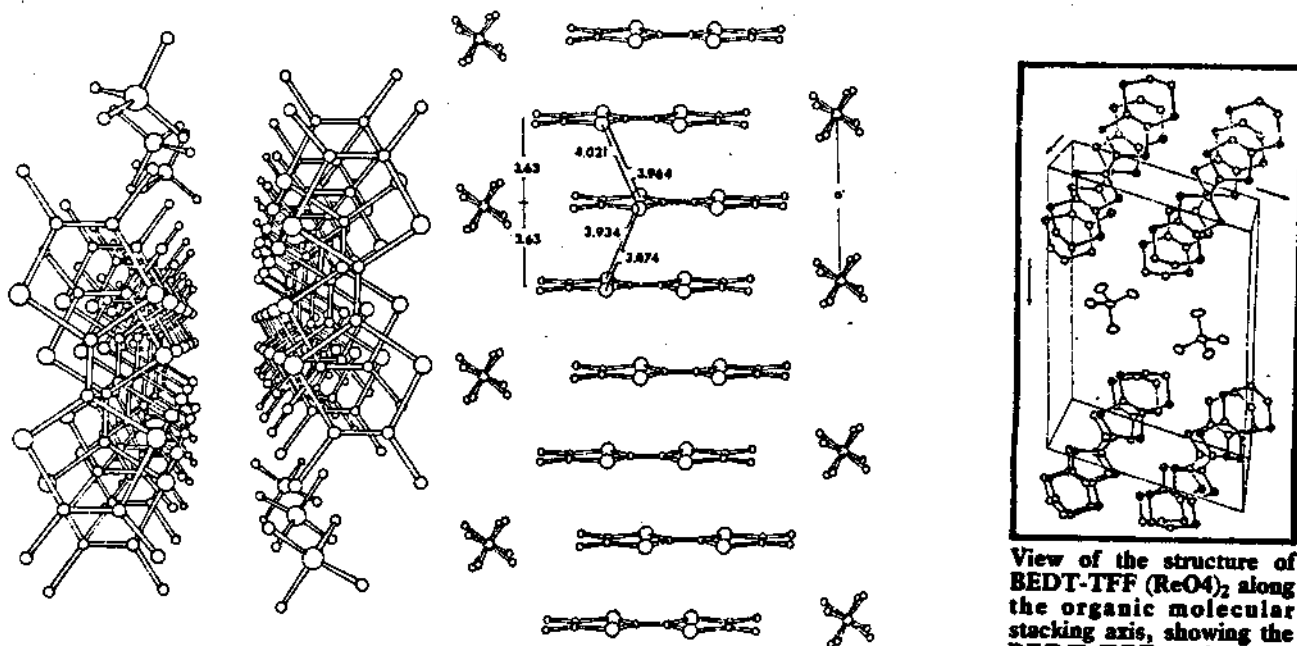
Organiska supraledare har nyligen framställts på elektrokemisk väg (Bechgaard är en pionjär). T_C är av storleksordningen högst någon K hos dessa kvasi-en-dimensionella organiska ledare av typ $(TMTSF)_2X$ (där X är t ex ClO_4 , ReO_4 , PF_6 , AsF_6 , TaF_6) vars struktur skisseras i figur XI.1.

I de flesta fall måste man ansätta ett tryck för att få supraledning. (En andra klass av organiska supraledare, av typ BEDT-TTF (ReO_4)₂, har rapporterats 1983; fler typer kommer säkert att framställas. variationsmöjligheterna är mycket rika.) Jerome har rapporterat att supraledande fluktuationer av en-dimensionell supraledning skulle uppträda redan vid 40 K där den tre-dimensionella övergången är ca 1 K i vissa organiska supraledare. Dock bör det nämnas att det finns andra, mera konventionella, tydningar av experimenten, varför aktsamhet anbefalls. Liknande fluktuationer i TTF-TCNQ för några år sedan kunde slutligen förklaras med de ytterst anisotropa ledningsegenskaper dessa närmast en- eller två-dimensionella ledare har parat med svårigheter med experimentella mätningar på ytterst små kristaller.

Arbetet med organiska supraledare är under stark frammarsch och utvecklingen inom detta intressanta fält (som också inbegriper ledande och halvledande polymerer) bör hållas under uppsikt.

Resultat som tyfts som supraledning vid relativt hög temperatur (rentav rumstemperatur) har även rapporterats för oorganiska föreningar av kopparklorid, kadmiumsulfid, titanborid och särskilt preparerade kolfilmer. Igen anbefalles skepsis. Reproducerbarhet erfordras. Signaler kan orsakas av andra typer av fenomen, etc.

Ett antal möjligheter till ökning av T_C diskuteras i den artikel av J.R. Schrieffer "Theories of Enhancement Effects", som följer. Den ger goda fysikaliska resonemang. Diskussion finns också i C-L avsnitt 6. Bl a berörs metalliskt väte samt betydelsen av lågfrekventa ("soft") fononer. Även om vi betonat elektronstrukturens betydelse bör man ej försumma fononstrukturen. Hög T_C hör ofta ihop med låga fononfrekvenser (liksom instabiliteter). Å andra sidan finns samband mellan elektroner och fononer, så vi är tillbaka till hönan och ägget.



View of $(\text{TMTSF})_2\text{ReO}_4$ along the stacking direction, a-axis (left). The ReO_4 ions show alternating order along the a-axis ($T < 180 \text{ K}$) leading to a 2a potential. Side-view of $(\text{TMTSF})_2\text{ClO}_4$ (right). The dimerization is clearly visible in the Se-Se intermolecular contacts.

View of the structure of $\text{BEDT-TFF}(\text{ReO}_4)_2$ along the organic molecular stacking axis, showing the BEDT-TFF molecules (shaded and open circles correspond to S and C atoms respectively; H atoms are not shown) and ReO_4 anions.

Fig. XI.1

XI.1. A15 supraledare

En klass av supraledare bör särskilt framhävas, då vi diskuterar högttemperatursupraledare. Intermediära föreningar med struktur A15, också kallad $\beta\text{-W}$, och med sammansättning A_3B har ofta höga T_c . A är en övergångsmetall, speciellt ger Nb och V hög T_c , medan B är en icke-övergångsmetall (t ex Ge, Si, Sn, Pb, Al, Ga, Sb). Strukturen är kubisk med A-atomerna uppordade i tre ortogonala kedjor längs kubens sidor enligt figur XI.2. Avståndet mellan exempelvis Nb-atomerna i kedjorna är mindre än atomavståndet i ren Nb. Elektrontätheten och ledningen är störst längs, de närmast en-dimensionella, kedjorna. Dock är det betydelsefullt att man har en koppling mellan kedjorna, ty annars skulle fluktuationer trycka ned supraledningen. Tillståndstätheten vid Fermienergin är mycket hög i de A15-supraledare som har hög T_c (det har man tillskrivit den närmast en-dimensionella strukturen).

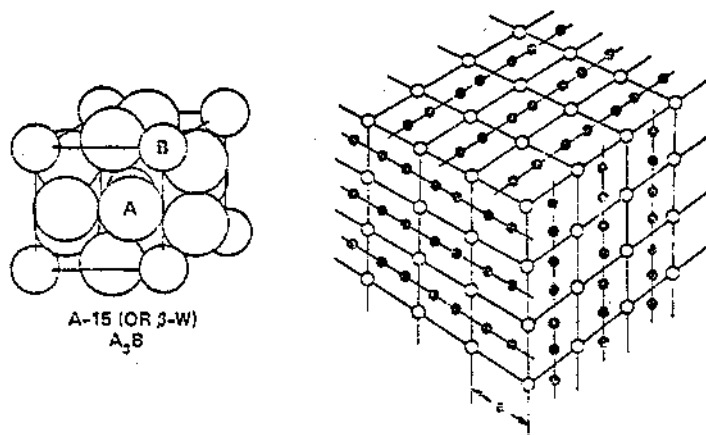


Fig. XI.2 I en A15-struktur finns B-atomer i kubbörn $(0,0,0)$ medan A-atomer besätter plattor på kantens sidor $(1/4, 1/2, 0)$. Atomernas utsträckning är mycket större än vad som skisserats här.

* samt kubmitt $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

Elektron-fonon-kopplingen är hög för relativt låga fononfrekvenser. $\alpha^2(\omega)F(\omega)$, som fås från tunnelexperiment, har ovanligt hög styrka för små ω . Instabiliteter uppträder för en del av föreningarna; man får s k martensitiska fasomvandlingar, med en liten tetragonal distorsion, inom väl definierade temperaturområden. Sådana omvandlingar uppträder i Nb₃Sn och V₃Si vid ca 40 resp 20 K och leder till högre fononfrekvenser. Omvandlingarna föregås av dynamiska distorsioner av A-kedjorna, vilket visats av röntgenmätningar.

T_c är mycket beroende av ordningen i A15-supralederen. Bestrålar man den med t ex neutroner kommer T_c att minska drastiskt. Speciellt viktigt är att A-kedjorna behålls intakta. Detta innebär också att stökiometrin är viktig. Avvikelser i sammansättning från 75:25 ger i allmänhet lägre T_c.

I många fall omfattar A15-fasen ej den stökiometriska sammansättningen. Den är t ex stabil endast vid 18-23% B. I vissa fall når faser den rätta sammansättningen endast vid hög temperatur. I andra fall är själva faser stabil endast vid hög temperatur och måste snabbkylas till rumstemperatur. Och i ytterligare andra fall är faser ej stabil alls. Den går att få i metastabil form t ex genom kondensation på ett varmt substrat, t ex vid 700-1200°C. Eller man kan få epitaxiell tillväxt av en svår A15-supraleder på ett underlag av en annan A15-supraleder eller rentav på en film av samma A15-supraleder, som har en sådan sammansättning att det går att bilda den under normala omständigheter. En låg nivå av restgas (t ex O₂, Cl₂) har visat sig vara gynnsam för nukleering av Nb₃Ge - när strukturen väl är nukleerad kan den växa vidare. Man arbetar med att söka framställa väl ordnade A15-supraleder i nya materialkombinationer. Således har det förutspåtts Nb₃Si en rekordhög T_c - om den nu kan bildas i rätt proportion och ordning.

Andra metallurgiska komplikationer uppträder. T ex påverkas den topografiska strukturen av filmtjocklek och av tillsatta ämnen. A15-faser har en tendens att växa i kolonner då det första skiktet väl har bildats. Det metallurgiska tillståndet har stor betydelse för bl a i_c.

Det finns en tendens till anrikning av B-material vid ytan. Detta innebär bl a en nedtryckning (och utsmetning) av gapfunktionen i ytskiktet (koherenslängden är nämligen liten i en A15 supraleder, så även ett relativt tunt ytskikt är betydelsefullt). Detta kan ha negativ betydelse för t ex tunnelövergångar eller resonatorer.

Den teknologiska betydelsen och den vetenskapliga komplexibiliteten har lett till mycket omfattande arbeten med A15 supraleder och en rik litteratur. En sammanfattning av T_c för många undersökta supraleder ges i figur XI.3.

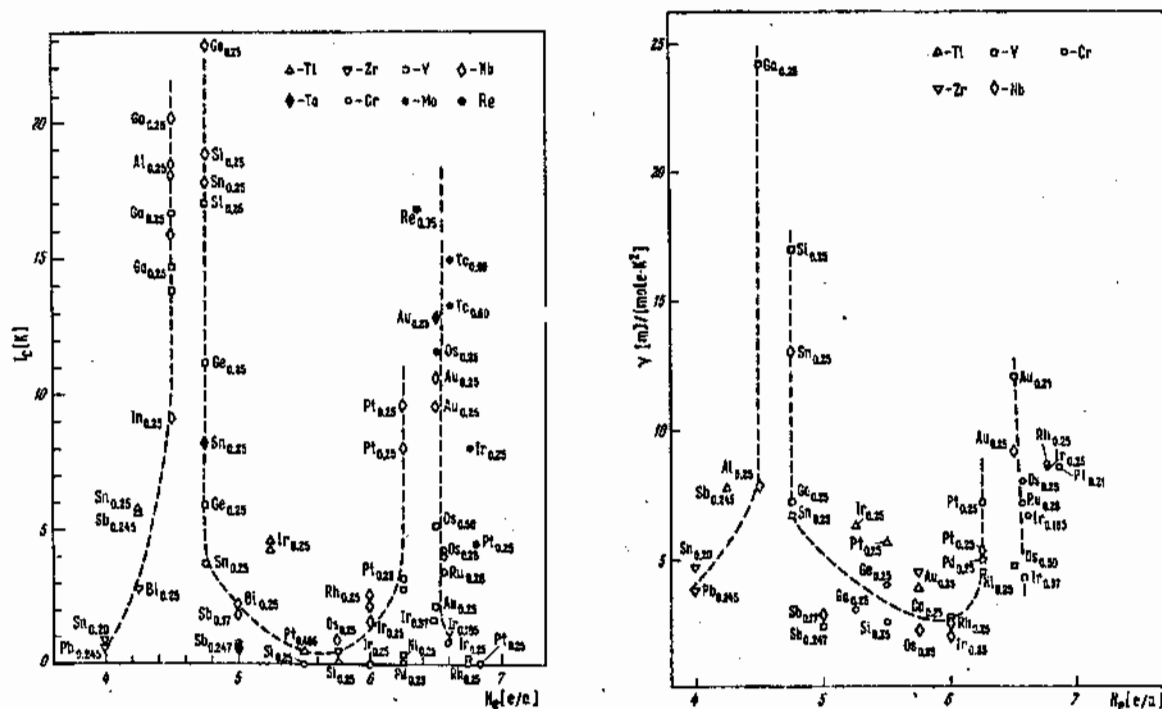


Fig. XI.3

THEORIES OF ENHANCEMENT EFFECTS

J. R. Schrieffer
University of Pennsylvania
Philadelphia, Pennsylvania

I must say that I am not one of the theorists who has been involved in enhancement effects and, therefore, I hope I can give a somewhat more dispassionate speech than most other theorists, if that is ever possible for a theorist. My own feeling is that this venture into "Alice in Wonderland" has not been totally useless and, much like the Moon program, there has been a lot of scientific fallout from chasing a distant star or moon, independent of whether you get there or not. The analogy, I'm afraid, at least in my view, stops there because I think we are going to get to the moon, while I wouldn't hazard much of a guess about 2000K, or even room-temperature, superconductors.

I thought I'd just briefly go over some of the ideas which have been discussed here this morning, and perhaps some other ideas in this quest for pay-dirt of high T_c . Roughly speaking, I've divided the mechanisms into three parts: (a) enhancing what we already know, i.e., the phonon mechanism, (b) nonphonon mechanisms and what one can do there, and (c) geometrical effects which don't work directly on the mechanism but try to increase T_c by influencing the density of states.

As for the first part, that is, the phonon-like mechanisms, we've heard that there has been a certain amount of progress in the prediction of how T_c should vary with metal parameters over and beyond the original simple idea that Bardeen, Cooper, and I had some twelve years ago. Our original ideas predicted that T_c was of the order

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

where θ_D is the Debye temperature, $N(0)$ is the density of states at the Fermi surface of the metal, and V is some "pairing interaction." For simplicity, and because we didn't know what better to do, we said that V was the sum of a phonon interaction V_{ph} plus a repulsive Coulomb interaction V_c . We had in mind for V_{ph} something like the Bardeen-Pines-Fröhlich interaction. This Bardeen-Pines-Fröhlich interaction was later pointed out to be incorrect in detail, although correct in its general form that the interaction is attractive at low frequency and repulsive at high frequency. We saw this morning the equations of strong-coupling superconductivity due to the Soviet physicist Eliashberg. We know that in the limit of weak coupling the Eliashberg equations go over exactly to the Bardeen-Pines-Fröhlich interaction and the BCS expression for T_c .

The Coulomb potential was originally included in the theory in a cutoff form and the so-called Coulomb pseudopotential effects were not taken into account. A couple of years after our original work, Bogoliubov, Shirkov, and Tolmachev suggested that the effective Coulomb interaction v_c^* is weaker than v_c for a simple physical reason, although they didn't mention this reason in their paper. All three of them are distinguished field theorists and they prefer to talk in terms of Fredholm solutions to integral equations rather than the physics of electrons pushing on one another; but the v_c^* vs v_c story is basically the fact that things that repel stay apart, and if they stay apart their interaction energy is less than it would be if they were to move in an uncorrelated fashion. That is, suppose

THEORIES OF ENHANCEMENT EFFECTS

you take two particles moving along in space and ask how strongly they interact with each other. If they move in an uncorrelated fashion their interaction energy is large when they are on top of one another. If they interact via a repulsive potential, then they detour around one another and the strength with which they interact, including the correlation or detour effects, is certainly less than in the case where you don't include those effects. The detour correlation effects reduce the Coulomb interaction energy by a factor of roughly two or three for typical metals. So it is all very simple when viewed in this way.

For strong-(phonon)-coupling superconductors, V_c^t is not of importance, while for weak-coupling materials the correlation effects, depending implicitly on the Debye frequency, lead to a reduction of the isotope effect from $\alpha = -1/2$ toward $\alpha = 0$. Turning to the phonon interaction for strong-coupling superconductors, Eliashberg wrote down the correct equations some years ago. Solutions of these have been carried out for various types of models, and the one that has received the most fame is that of McMillan. As we saw earlier for the case of a transition metal vibration spectrum, namely for niobium, McMillan found that, except for small numerical corrections, T_c is of the order

$$T_c = \theta_D e^{-\frac{1+\lambda}{\lambda-\mu^*}}$$

where μ^* is given by the density of states at the Fermi surface times V_c^* , and λ , by definition, is the density of states at the Fermi surface times V_{phonon} , namely $\mu^* = N(0)V_c^*$ and $\lambda = N(0)V_{\text{ph}}$. So except for the factor $1 + \lambda$ in the numerator, the new theory and the old theory are, in fact, identical.

Now this $1 + \lambda$ factor has a very simple origin. It has to do with what is called renormalization effects. We know that the electron-phonon interaction in a crystal changes the electron's band mass m to a quasi-particle effective mass m^* , the ratio being $m^*/m = 1 + \lambda$. You can derive this relation from perturbation theory very simply. Thus, the mass enhancement of an electron moving through a normal metal measures exactly the electron-phonon coupling constant. The quasi-particle density of states, being proportional to m^* , increases with λ , and therefore you would have a factor of $1 + \lambda$ in the denominator from this mass enhancement effect, i.e., $N(0) \rightarrow (1+\lambda)N(0)$. In addition to the mass enhancement, there is another factor entering T_c . Not only is the mass of the electron renormalized, but so is its interaction with phonons renormalized. The electron-phonon matrix elements are decreased by the factor $1 + \lambda$. Since the λ in the denominator of the expression for T_c involves this matrix element squared, this matrix element renormalization gives you a reduction of the effective interaction $V_{\text{ph}} \rightarrow V_{\text{ph}}/(1+\lambda)^2$ by the square of the mass enhancement. Therefore, the phonon interaction is changed according to

$$N(0) V_{\text{ph}} \rightarrow [N(0) (1 + \lambda)] [V_{\text{ph}}/(1 + \lambda)^2] \rightarrow N(0) V_{\text{ph}}/(1 + \lambda)$$

in accord with the strong-coupling result.

Why have I gone into this detail? It is to try to take a little of the mystery out of formulas that are being used and accepted as being correct. There is no mystery, and, in fact, I don't think they are really correct in detail either. As McMillan writes it,

$$\lambda = \left\langle \frac{N(0) g^2}{m \omega^2} \right\rangle$$

J. R. SCHRIEFFER

Here \mathcal{J} is the electron-phonon matrix element in suitable units, M is the ionic mass, ω is the phonon frequency, and the expression is to be averaged over all phonon modes.

Now in simple metals, that is, nontransition metals, there is a scheme called the pseudopotential scheme which says that an electron scatters off an ion via an effective potential which is not the Coulomb potential, but a potential much weaker than the Coulomb potential. This is due to the simple fact that if you take an atomic potential $V(r)$ which goes something like $e^{-\alpha r}$, then an electron coming along and scattering from this atom will see not only the attractive Coulomb potential, but it will also see an effective repulsive potential which comes about from the Pauli principle. As the electron comes near the atom the Pauli principle forbids the electron that's coming in from having wiggles in its wave function which match the wiggles in the wave function of the occupied core states. Since the incoming electron has, of necessity, wiggles which are similar to those of the core electrons the incoming electron must deform its wave function in such a way that the core pushes the conduction electron away from the core region. The incoming electron is thereby not allowed to feel the strong Coulomb attraction, and hence the effective potential, i.e., the Coulomb potential plus this effective repulsive Pauli potential, leads to a weak residual potential. The weakness of this total effective potential (pseudopotential) accounts for the fact that conduction electrons in most simple metals are almost free electron in character. The electron-phonon interaction \mathcal{J} is just the Fourier transform of this pseudopotential.

Now it turns out that in simple metals one can roughly, very roughly, calculate the phonon frequencies of the wave vector q (denoted as ω_q) in the following way. If you calculate the frequencies of phonons for the ionic lattice with the electrons in the conduction band held fixed, that is, you allow the ions to vibrate without the conduction electrons moving, then the result is, in effect, the ionic plasma frequency Ω_q , which is of a very high frequency. From this quantity, to get the physical or observable phonons you must subtract the electronic part ω_q^{el} in the form $\omega_q^2 = \Omega_q^2 - (\omega_q^{el})^2$. This subtraction is the screening effect that corresponds to the fact that when two ions vibrate, the electrons move in between them to screen out the fields generated by the moving ions. Now, ω_q^{el} is the response of the electrons to moving ions. From this picture we see that ω_q^{el} is proportional to the electron-phonon coupling — just as Dr. Paskin said this morning. So, $(\omega_q^{el})^2$ is proportional to \mathcal{J}^2 . You can now see why λ is supposed to vary mainly with ω_q^2 , rather than through $N(0)\mathcal{J}^2$. The reason is rather simple, namely that the observed frequencies are very small compared to the bare frequencies, and therefore $(\omega_q^{el})^2 \propto \mathcal{J}^2$ has cancelled almost all of the ionic plasma term Ω_q^2 for the observed coupling strengths. $(\omega_q^{el})^2$ is about 75 to 95% of Ω_q^2 even for zone boundary phonons. Therefore, for a given percentage change of \mathcal{J} , you see, the change in ω_q^2 is amplified greatly by having the dominant effect already cancelled out by ω_q^{el} . In the expression for λ , the percentage variation of the explicit $N(0)\mathcal{J}^2$ is small compared to the variation of the ω_q^2 . Again, this is just because the leading effect for the phonons is cancelled out and the small percentage change of \mathcal{J} makes a much larger percentage change of ω_q .

I think that these arguments, while not precise for nontransition metals in infinite crystals which are perfectly ordered, are more questionable when you go to simple metals which are amorphous, or to thin films. I don't know of any theoretical justification which is as good as the one I outlined above for a constant $N(0)\mathcal{J}^2$ in λ and which applies to the cases of amorphous or thin-film superconductors, or both, and yet these are the situations to which people apply the formula. So I put up a red flag here: there might be troubles.

A case where there is definitely trouble is when one takes this formula for λ and applies it blindly to transition metals. For transition elements there is no theoretical

THEORIES OF ENHANCEMENT EFFECTS

reason that I know, as to why the above expression for λ , with $N(0)\beta^2$ roughly constant, has anything to do with nature. The phonons in transition metals have their frequencies determined in a way which is very different from that discussed above because the pseudopotential concept mentioned above doesn't work for transition metals. The d-electrons have to be described more by a tight-binding scheme. The d-shell d-shell interactions are very important and this simple pseudopotential idea just doesn't work. A consequence of this is that while you can parameterize T_c phenomenologically by saying, roughly speaking, that the ω_q^2 should be the observed one and $N(0)$ is the density of states at the Fermi surface, I don't think this is more than a rough parameterization for the transition elements, since β^2 is not expected to be a constant in these materials.

An interesting point is that if you look at the pressure effect for nontransition metals, if you squeeze the crystals, then the atoms getting closer together have stronger repulsive interactions. Vibrational frequencies go up so that, as the pressure goes up on nontransition elements, the frequencies go up, and hence λ , being proportional to $1/\omega_q^2$ goes down. If the interaction goes down, T_c should go down and this argument works for nontransition metals. Yet, for transition elements, the same condition of increasing pressure makes ω_q^2 go up as the lattice gets more rigid or stiff, but that doesn't bother superconductivity. T_c goes up, in general! Therefore, either you don't talk about the predicted pressure dependence for transition elements, or else you get worried about it — and people do both things. One has to take the argument about $\lambda \propto 1/(\omega^2)$ with a great grain of salt when you look at transition elements.

Now, you might say, why does T_c go up for the transition elements? We know when you squeeze on them, the bands broaden. Broader bands make weaker screening. Weaker screening makes stronger interactions, so β^2 should probably go up. But $N(0)$ is going down and ω_q^2 is going up, and so you see it's a rat's nest trying to figure out the chicken or the egg of why T_c goes up. The reason is probably very complicated.

Let me mention another possible way of increasing T_c within the phonon mechanism. This one I am interested in because I think it has some possibilities. Suppose you look at the density of states $N(E)$ for transition metals as a function of E , as shown in Fig. 1(a). You know there are all sorts of peaks, depending on which row and which particular element you are looking at. For example, niobium, which has a fairly high T_c , is sitting near a peak in the density of states. Molybdenum, which has a very low T_c , is sitting down in the minimum. Thus, for the purer elements you would say naively that if $N(0)$ is high, so is T_c , while if $N(0)$ is low, T_c is low. If you make disordered films, make short mean free paths, you would expect that the sharp peaks in the density of states, which after all come from coherent scattering off of many atoms, will be diminished so that you smear out $N(E)$. The minima get filled up and the maxima decrease, probably giving something more like the dotted line in the figure. If you are able to make samples with a very short mean path, the whole curve would just be smeared out and you wouldn't see anything particularly interesting. So, one effect of the short mean free path of amorphous materials is to make low- T_c superconductors into medium- T_c materials by making them more like everybody else. The other effect is to make high T_c into medium T_c . If you are in the business of making high T_c you can advertise that you have raised T_c from a millidegree to 5K for a low- T_c element, but what you are actually doing is bringing it into a democratic situation where everybody is roughly the same T_c . I would characterize bismuth as a good example of this, plus a lot of other examples. There may be other residual effects, but I would say this change of T_c is a zero-order effect, and unfortunately, as such, it is something that is often not discussed (for obvious reasons). I hope you don't mind the side comments here. I get a kick out of them after being chided for so many years about not being able to produce a 2000K superconductor.

J. R. SCHRIEFFER

So where does that leave us? Well you might say, "How about making a bunch of alloys which are perfectly periodic and hence not mean-free-path spoiled. Then maybe we can find a density of states which is fantastically high." Well, when you talk with experimentalists, they will tell you that high density of states doesn't necessarily mean high T_c . There are many examples of this situation. You raise the density of states, as measured by γ , and T_c goes down. Then the theorist says, "Well, things are complicated because V can have the reverse dependence and more than compensate for the change in $N(0)$." I think it is still an interesting and profitable game to try to find very high density-of-states materials. Nb_3Sn has a very high density of states. Moreover, I think there is a particular type of high density of states which should be sought for, namely a density of states which has a *high, sharp peak*, as shown in Fig. 1(b). This is probably the most desirable case, for a rather simple reason. If you have a high, sharp peak of the density of states at the Fermi surface, then while $N(0)$ is large, the screening tends to be small, since, as we know, the screening effects depend on an average of the density of states over a relatively large region in energy about the Fermi surface. Therefore, while the average density of states (which determines the screening) may be relatively low, and hence the interactions strong, the density of states at the Fermi surface can be high for this case, and you can have your cake and eat it too. One must take care, however, that the reduced screening does not increase $\langle \omega^2 \rangle$ unduly, thereby reducing $\langle \omega^2 / \omega^2 \rangle$.

You might say, how do you find things that have very high peaks? One way is to make *ordered* binary alloys. People have been doing this for many years and little dramatic has occurred. Maybe what you are doing is hopping through parameter space in steps that are much too big, because the distance between different binary alloys is fairly

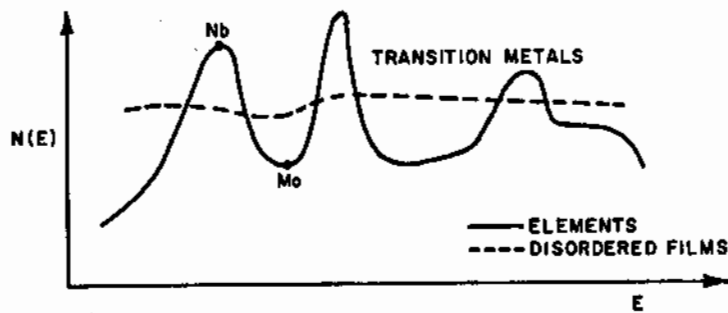


Figure 1(a)

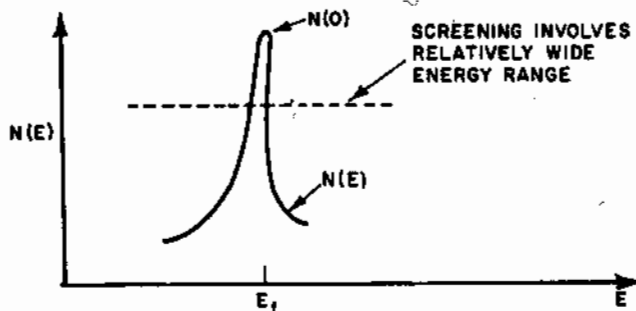


Figure 1(b)

THEORIES OF ENHANCEMENT EFFECTS

large on the interesting scale of $N(E)$ vs E . There are ternary alloys, quaternary, etc., and you get a much finer mesh in parameter space by going to more complicated *ordered* systems. However, you don't want to drop the order in these alloys because, presumably, that would lead to mean-free-path averages of the peaks. I don't know whether the case of sharply peaked $N(E)$ is a fairy story or not, but it is an interesting possibility, being pursued by several groups at present.

Let me proceed to a final idea about the phonons, and that is the question of phase transitions and soft modes. We have heard about the soft modes in the thin films. They seem to work in increasing T_c and this looks reasonable. How about the soft modes that come about when one is near a second-order crystallographic phase transition? It is known that a number of these intermetallic compounds are systems in which there are martensitic transformations and other low-temperature crystallographic transformations. For a second-order crystallographic transformation, $\langle \omega^2 \rangle$ should be reduced at the transformation temperature T_x , relative to its value on either side. If you plot λ as a function of temperature (see Fig. 2) perhaps λ has a fiducial value something like that shown in the figure, but goes up near T_x because of the soft-mode effect. Then if the critical value of λ_c required to get T_c at any temperature is given by something like the dotted line, you could have a range of T near T_x in which there is superconductivity. Thus, you might see a "metasuperconductivity" near some T_x , just as one sees metamagnetism between one temperature and another. I don't say that this will occur, but it was one of the ideas brought up at Brookhaven as a possibility for using the soft modes of phase transitions to make locally a large value of λ , and hence a large T_c .

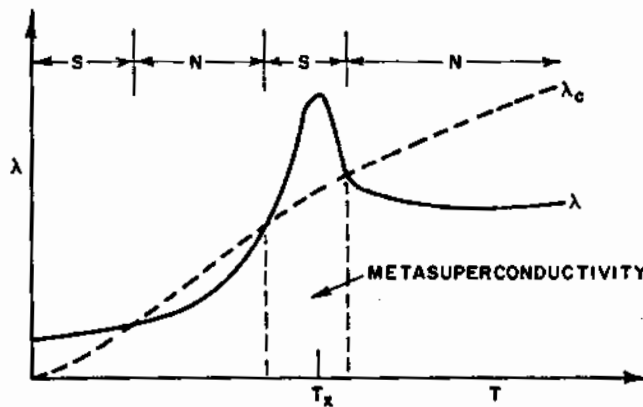


Figure 2

We have heard a fair amount today about the nonphononic mechanisms. I'll just make a few brief comments. There are the exciton and the plasmon types of mechanisms. You can call these whatever you like, but basically all of these different mechanisms correspond to a dielectric anomaly, and you can summarize them all in the following sort of rough way. Suppose that you have two electrons that are trying to be paired as they move through the crystal, one with up-spin and the other with down-spin. They interact with each other through some sort of an effective interaction that you would like to be strongly attractive. Except for details that have to do with band structure and things like this, which are important in detail but not for the purpose of this rough argument, you can write an effective interaction between the electrons which is the bare Coulomb interaction

J. R. SCHRIEFFER

$4\pi e^2/q^2$ divided by the dielectric constant $\epsilon(q, \omega)$, where q and ω are Fourier transform variables. This is what enters for an electron which goes from k to $k + q$, its mate going from $-k$ to $-k - q$. Thus the effective interaction is

$$\theta(q, \omega) = \frac{4\pi e^2/q^2}{\epsilon(q, \omega)}$$

The dielectric constant gives the dynamic "screening" effects. Now, in a crystal we know the dielectric constant has the form

$$\epsilon(q, \omega) = 1 + 4\pi \alpha_{ion}(q, \omega) + 4\pi \alpha_{el}(q, \omega)$$

where the α 's are the ionic polarizability and the electronic polarizability. From this interaction all of superconductivity should flow. This is the effective interaction including all the effects of phonons, Coulomb repulsion, excitons, etc.

For example, the phonon frequencies are given in the following way. A set of zeros of the dielectric constant for a given q as a function of ω are at the phonon frequencies ω_q . You can see, then, that when the electrons exchange a phonon the interaction $\theta(q, \omega)$ has a singularity if the phonon that is involved is exchanged with its natural frequency.

Now, how about the electronic polarizability α^{el} ? The way people usually treat this, for simple metals, is to say that the typical frequency variation α^{el} is on the scale of electron volts. It is the electronic plasma frequency which determines the frequency scale of $\alpha_{el}(q, \omega)$, while the frequency variation of $\alpha_{ion}(q, \omega)$ is on the scale of hundredths of an electron volt, i.e., the ionic plasma frequency. Therefore, the standard scheme, which doesn't say anything about excitons or plasmons being involved in superconductivity, replaces $\alpha_{el}(q, \omega)$ by its static value $\alpha_{el}(q, 0)$. Matthias, Little, and others suggest that we should look more carefully at this quantity $\theta(q, \omega)$. As shown schematically in Fig. 3 they suggest that the effective interaction has structure not only at the phonon frequencies, where $\epsilon(q, \omega)$ is going to zero due to the phonons, but also out at higher frequencies where there are dielectric anomalies associated with electronic transitions. Unfortunately, a standard pitfall that some people have gotten into over the

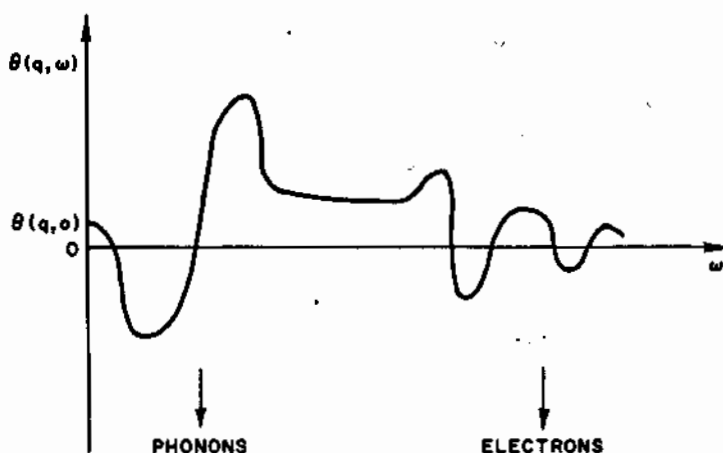


Figure 3

THEORIES OF ENHANCEMENT EFFECTS

years (with the aid of some wishful thinking) amounts to saying that, neglecting the ions, $1/\epsilon$ is given approximately by

$$\frac{1}{\epsilon(q, \omega)} = \frac{1}{1 + 4\pi \alpha_{el}(q, \omega)} = 1 - 4\pi \alpha_{el}(q, \omega), \text{ if } 4\pi \alpha_{el}(q, \omega) \ll 1.$$

It is clear that the electronic polarizability *reduces* the Coulomb repulsion. However, they use this $1 - 4\pi\alpha$ approximation, which is good only for $4\pi \alpha_{el}(q, \omega) \ll 1$, in the regime where $4\pi \alpha_{el}(q, \omega) > 1$. So you start with an interaction $V(q)$ that is positive definite. By forgetting what you did the day before, you then crank $4\pi \alpha_{el}$ up to make it bigger than 1, so that $1 - 4\pi \alpha_{el} < 0$ and hence you *predict* an attraction. There were a number of papers which did this some time ago until the difficulty was pointed out. It may sound naive, but this has been a source of confusion for some time, because people did not calculate consistently.

You can show from very general arguments that, for $\omega = 0$, $\epsilon(q, 0)$ is necessarily nonnegative, and hence that the effective interaction $\theta(q, \omega)$ must be *positive* at zero frequency. If $\theta(q, \omega)$ were negative (attractive) for zero frequency, the system would be unstable, and it would simply polarize chargewise, making a transition to a normal state of different symmetry, e.g., doubling of the unit cell, or some such transformation, such that the system would become stable at least within the Hartree approximation. Thus, the Hartree effects correspond to the zero-frequency terms, and Hartree instabilities, involving large energies, must be stabilized first. Then you have to again ask how $\theta(q, \omega)$ varies with frequency in the new Hartree stabilized state.

Since the potential is nailed down by the Hartree stability condition to be repulsive at zero frequency, you then have to play on a beating of the attractive and repulsive regions of θ as a function of ω to get superconductivity. Thus, to make a calculation of what T_c is, you see, is a pretty subtle matter. It is for this reason one can get any answer one likes depending on how you emphasize the attractive versus repulsive regions in various approximate treatments.

The Matthias argument is basically that as an electron comes by an atom, it polarizes the atom by polarizing the core, and then another electron uses that polarization to get an attraction. I think, in principle, this is a perfectly good mechanism if you could ever predict or measure how strong an effect it is. Proposals have been made to measure the optical properties of crystals, and hence determine the size of the dielectric anomaly associated with atomic (electronic) polarization. A difficulty with the proposal is that light waves have wavelengths which are very long compared to atomic sizes for the frequencies of interest, and hence by this means you can only see electric dipole transitions in atoms. For example, you cannot see transitions between states of the same parity. If you had a p to f transition in an atom, the levels have the same parity, and hence there is no dipole field generated. It is a quadrupole field that is generated. Hence you will not couple to that transition by long-wavelength light waves. This doesn't bother the electrons because the electrons, having wavelengths of the order of an angstrom, can work as well on a quadrupole field as they can on a dipole field. So it may be that by doing optical experiments you miss something which is in fact present to produce an actual attraction between electrons. On the other hand, you may see an anomaly at the small q accessible to light waves which is *not present* for large q , which are those of overwhelming importance in determining T_c , thereby overestimating the effect.

There has been a proposal by Matthias for alpha uranium suggesting that the material is superconducting because of the core polarization mechanism and gave the "proof" that this was the case because of the isotope effect in uranium being M^{+2} . I am sorry

J. R. SCHRIEFFER

that I don't have time to go through the theoretical discussion here, but you might ask how a nonphonon mechanism can give an isotope effect if the ion vibrations aren't involved. You should see $T_c \propto M^\alpha$ if phonons are not involved. Matthias suggested that a Mössbauer-like effect is involved here. A careful treatment of this particular mechanism gives only $\alpha \approx 0.01$! There is an argument however, which gives a *large* positive isotope effect for this nonphononic mechanism. The argument given by Capellmann and Schrieffer involves modulation of the energy levels by zero-point vibrations of the atoms. This mechanism gives an effect which is $\alpha \approx 1/2$, although I am sorry I don't have time to talk about this topic in detail. So, at least we can't rule out for uranium this other mechanism, although I think the importance of the mechanism is highly unlikely for any metal, including U. In addition, experimentalist friends tell me to eye the experimental results with considerable skepticism, since the experiments are very difficult to perform and the scatter of the data is uncomfortably large.

One can essentially rule out nonphononic mechanisms for transition metals from the tunneling experiments of Rowell, et al., of which niobium and tantalum tunneling studies similar to those Dr. Leslie talked about today, show nice, well-developed phonon anomalies. The experiments show, at least for these transition metals, that they are phononic in nature and, by implication, since there is no difference in superconductivity between these and the other transition elements, that all transition elements are phononic.

That brings me to the end, except for a few words about geometrical effects. The problem of a thin film has been looked at as far as how the thinness of the film changes

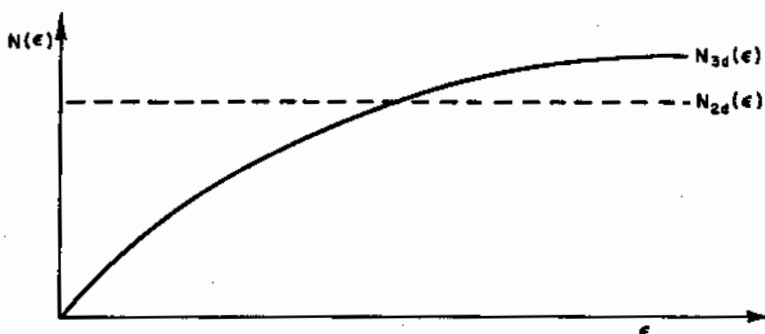


Figure 4(a)

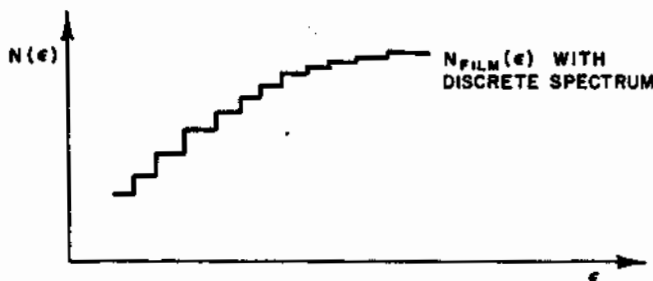


Figure 4(b)

THEORIES OF ENHANCEMENT EFFECTS

the density of electron states. We know that the density of states for a simple three-dimensional electron gas varies as $N_{3d}(\epsilon) \propto V\epsilon$, Fig. 4(a). A two-dimensional film in principle has a square density of states, $N_{2d}(\epsilon)$ being just a constant out to infinity. If you worry about how the motion goes not only in the film direction but in the transverse direction, and if you put in the discreteness of a spectrum in the third dimension, you find that $N_{film}(\epsilon)$ has kinks or steps instead of just being flat, as shown in Fig. 4(b).

Parmenter has looked at these quantization effects on the density of states to see what happens to T_c , i.e., whether T_c increases, decreases, or stays the same. He assumes that the matrix elements are constant, that is, that the quantization effects on the bands and density of states don't affect the matrix element, and he concludes that T_c goes up when you go from a smooth to a rough density of states. I am personally doubtful of this scheme and feel that more careful work, including matrix element effects and sample inhomogeneities, must be included before one can assess the validity of the scheme.

Well, where does all this leave us? I am reasonably pessimistic, except for fallout. Maybe one fallout would be the brilliant student who accidentally hits on the right idea or experiment, and that would be great. I think some of the ideas having to do with looking at the dielectric function as a function of frequency, or the phonon modes near phase transitions, might be interesting in themselves, and perhaps there is something there. By and large, I guess, I am still of the view that intelligent experimentalists will win out by doing the same thing that drug manufacturers do: get 4000 bottles off of the shelf and mix them together, along with a liberal dose of inspired intuition gained from previous experiments, and hope for the best.