PAPER REFERENCE: A2772

Hard-materials surface prediction of one-dimensional electron gas

B. Razaznejad[1], C. Ruberto, P. Hyldgaard, and B. I. Lundqvist

Department of Applied Physics, Chalmers University of Technology and Göteborg University, SE-412 96 Göteborg, Sweden

Abstract

A new and robust one-dimensional electron gas (1DEG) is predicted on the $(00\bar{1})$ surface of κ-Al_2O_3 by means of a density-functional-theory (DFT) study. Our first-principles calculations show that this surface is Al terminated, with the Al atoms lying in [100] zigzag lines, and has an excess of electrons due to the charge asymmetry in the bulk κ-Al_2O_3. The κ-Al_2O_3 phase itself is metastable up to 1000K. To test the robustness of our materials-theory prediction of the 1DEG along the zigzag Al lines, the critical temperature due to Peierls metal-insulator instability has been estimated to be in the temperature range [0,1] K, using a tight-binding model, where the model parameters are determined with additional DFT calculations. The virtues of both the materials-theory design and the possible 1DEG realization is also discussed.

Keywords: phase transitions, state and surface phonons, density functional calculations

1. Introduction

In the last few years, due to the rapid development of DFT calculations, new and interesting materials are not only found in the experimental laboratory, but could as well be designed

[1]Corresponding author: Tel. +46 31 772 8423; Fax: +46 31 772 8426; E-mail: behrooz@fy.chalmers.se

in computer simulations and then synthesized experimentally. Furthermore, such theoretical predictions of new materials and their properties are made much faster than in experiments. A strength of the materials-theory studies is that their consistency and robustness can be directly tested by using these first-principles calculations as input for phenomenological models with a few number of parameters. Such combination with model systems offers not only a wider range of experimental probing but direct test of the robustness of the materials-theory predictions.

In this paper, a new 1D hard-material on the $(00\bar{1})$ surface of the metastable κ-Al_2O_3 is predicted by means of first-principles DFT calculations [1]. A wide range of 1D materials has been predicted and studied intensively during the last twenty years. Most noticibly is the Carbon nanotubes (CN) [2] but also inorganics (MX chains [3], the platinocyanate chain compound $K_2Pt(CN)_4Br_{0.3}3H_2O$ [4] and the charge-density-wave compounds $NbSe_3$ and $K_{0.3}MoO_3$ [5]) and organics (*trans*-polyacetylene $(CH)_x$ [6], the charge-transfer (CT) salt TTF-TCNQ [7], and the so-called Bechgaard salts [8, 9]). It is well-known that the metallic behavior characteristic of 1D metals breaks down below some critical temperature, associated with a structural transition, called Peierls transition, of the conducting chains of atoms. An energy bandgap appears at the Fermi energy with semiconducting behavior as a result. The critical temperature varies dramatically in the above-mentioned "traditional" 1D materials. For the inorganic systems the transition temperature is around 200 K. For CT salts it is around 60 K, and for the *trans*-polyacetylene it is far above room temperature (here the gap is specified in eVs). This effect is responsible for making Polyacetylene and most other polymers insulating except upon special difficult doping. Our hard-materials surface predictions offer a new 1DEG-realization, which like the CN present a wide temperature range to explore the 1D nature of the electron gas.

In testing the robustness of our materials-theory prediction, the critical temperature of the metal-insulator (MI) transition for our system has been calculated with a tight-binding model, where the model parameters are determined with additional DFT calculations. Along the 1DEG it is then shown that the critical temperature is below the 1 K regime. Since κ-Al_2O_3 has a high thermal stability, with transition temperature above 800 K, the 1D-system is metallic over a much wider temperature range, compared to the existing systems mentioned above. Hence, the experimental verification of this 1DEG is both important and challenging. Waiting for the experimental study of the κ-Al_2O_3-system, it is interesting to mention that the low value of the critical temperature for the metal-insulator (MI) transition makes it a good candidate as a robust low-temperature laboratory for studying electron-electron correlations, *e.g.* Luttinger liquid theory, transport through grain boundary [10], and out of equilibrium transport (Kondo impurity) [11].

2. Materials: κ-Al_2O_3

Both materials and fundamental science aspects of κ-Al_2O_3 have received impressive attention. The metastable κ phase of alumina has many interesting and important industrial applications, *e.g.* in wear-resistant coatings on cemented-carbide cutting tools. Upon cleavage of the bulk κ-Al_2O_3, perpendicular to its main axis, two different surfaces are created, namely the (001) and the $(00\bar{1})$ surfaces. Our first-principles DFT calculations show [1] that the most stable termination of the $\kappa(001)/(00\bar{1})$ occurs in the middle of an Al layer. The (001) surface exhibits a huge inward relaxation (-117%) of the Al atoms making this surface O terminated. This is due to the open structure of the crystal. On the other hand, the inward relaxation of the Al atoms for the $(00\bar{1})$ surface is much less compared to the relaxation for the other surface, which makes the $(00\bar{1})$ surface Al terminated. By studying the geometric structure of the latter surface, it is seen that the Al atoms are lying in zigzag lines (2.4 Å apart) along the [100] direction. The distance between two adjacent Al lines is 8.4 Å . Due to the charge asymmetry in bulk κ-Al_2O_3 there exists an excess of electrons at the $(00\bar{1})$ surface. The bandstructure $E(\mathbf{k})$ is calculated for a slab with both surfaces relaxed, which clearly shows that $E(\mathbf{k})$ has a parabolic form along the [100] direction and is almost flat along the [010] direction. In fact, a calculation of the effective mass of this band yields a value of $1.4 \cdot m_e$ at Fermi energy, where m_e

is the electron mass. From this calculation the Fermi wavevector k_F is estimated to $k_F = \frac{\pi}{8a}$, where a is the distance between two Al atoms. To understand the localization of the surface electrons, the 3D charge density profile has been calculated and plotted in real space as shown in Fig. 1. The surface state is clearly localized around the surface Al atoms, which gives it the character of a pseudo-1D electron gas along the [100] zigzag surface Al line.

To understand the MI transition in this system and estimate the critical temperature from first-principles, a supercell that is four times larger than the one used here is required. This is due to the fact that the calculated wavevector is $k_F = \frac{\pi}{8a}$. A direct calculation is beyond the power of existing computer resources. However, the problem can be addressed by bridging the atomscale DFT calculations with model studies.

3. The Theoretical Model

In order to study the MI transition in our system, we have used the Su-Schrieffer-Heeger (SSH) Hamiltonian [6], which was originally introduced to explain the bond alternation and the energy bandgap in the quasi-1D organic molecule *trans*-Polyacytelene (TPA). This Hamiltonian, which is a one-electron Hamiltonian with electron-phonon interaction explicitly included, assigns both fact in Polyacetylene, mentioned above, to Peierls instability in the system and can be written as:

$$H = H_{e-e/ph} + H_{ph}, \tag{1}$$

where

$$\begin{aligned} H_{e-e/ph} &= \sum_{n,s} t_{n+1,n}(c^\dagger_{n+1,s}c_{n,s} + c^\dagger_{n,s}c_{n+1,s}), &(2)\\ H_{ph} &= \sum_{n} \left[\frac{p_n^2}{2M} + \frac{K}{2}(u_{n+1}-u_n)^2\right], &(3)\end{aligned}$$

with u_n being the displacement of the n:th Al-atom, p_n its conjugate momentum, M the mass of the Al atom, K the effective spring constant, and $c^\dagger_{n,s}/c_{n,s}$ the fermionic creation/annihilation operators. The electron-phonon interaction is included in the hopping integral $t_{n+1,n}$ which, to first order, can be expanded around δ = u_{n+1}-u_n = 0, giving:

$$t_{n+1,n} = t_0 - \alpha(u_{n+1} - u_n). \tag{4}$$

In the limit of infinite mass the first term in H_{ph} can be dropped and for simplicity the spin index is going to be suppressed in the following.

A natural way of solving the Hamiltonian is to transfer it to the k-space. Since Peierls instability occurs for a reciprocal-lattice vector $G = 2k_F$, the displacement coordinates u_n is considered to be $u_n = u\cos(2k_F na)$. This makes H_{e-ph} invariant under spatial translations $\frac{\pi}{k_F}$, which implies that the Hamiltonian can be diagonalized in the reduced zone [-k_F,k_F]. Since the Fermi wavevector in our system is estimated to $k_F = \frac{\pi}{8a}$, an eight-band analysis is required to fully account for the MI transition within the model. Presenting such a detailed study elsewhere [12], here the simple two-band model is considered to estimate the critical temperature (T_c). The Hamiltonian can, after Fourier transformation and diagonalization, be written as: [6]

$$H = \sum_{k,\gamma} E_{k\gamma}\tilde{n}_{k,0} + 2NKu^2, \quad \gamma = 0, 1. \tag{5}$$

Here $\tilde{n}_{k\gamma} = \tilde{c}^{\dagger}_{k\gamma}\tilde{c}_{k\gamma}$ is the number operator for the band γ and $E_{k,\gamma}$ are the eigenvalues of the full Hamiltonian, which are given by: [6]

$$E_{k,0} = -E_{k,1} = 2t_0\sqrt{1 + (4z^2 - 1)sin^2(ka)}, \tag{6}$$

where z = $\alpha u/t_0$. The Hamiltonian looks like that for an ideal Fermi gas. The fermionic opreators $\tilde{c}^{\dagger}_{k\gamma}/\tilde{c}_{k\gamma}$ are the collective modes of the system.

The critical temperature (T_c) is estimated by studying the expression for the total energy, *i.e.* the free energy together with the phonon energy. In the two-band model it is

$$E_T(u) = 2NKu^2 - \frac{2k_BTNa}{\pi}\int_0^{k_F} dk \ln\left[1 + \cosh\left(\beta E_{k,0}(u)\right)\right], \tag{7}$$

where k_B is the Boltzmann constant and $\beta = 1/k_BT$. In obtaining the above expression an assumed particle-hole symmetry is used to set the change in chemical potential equal to zero [13].

4. Results and Discussions

Since the proposal of Su-Schrieffer-Heeger (SSH) model in 1979 for the quasi-one-dimensional conductor TPA with bond alternation, Peierls instability for a one-dimensional electron system coupled with phonons has been studied extensively. The huge interest in one-dimensional systems has led to the discovery of a wide range of such quasi-one-dimensional systems, which exhibit a variety of physical properties depending on temperature, pressure e.t.c. Here a new 1DEG is predicted by means of extensive DFT calculations and its MI transition studied with the SSH model, where the model parameters are estimated using additional DFT calculations. In the presented model, there are three model parameters, namely the electronic bandwidth t_0, the electron-lattice constant α, and the effective spring constant K.

To determine the effective spring constant K, total energies have been calculated for five different changes in the relative coordinate between two Al atoms, denoted by $n\Delta r$, where $n = 0, \pm 1$, and ± 2 and $\Delta r = 0.03$ Å. These total energies have been fitted to a quadratic function (see Fig. 2) and K has been calculated to a value of K = 18 eV/Å^2 (see Tab. 1). Comparing this value of K to the one for polyacetylene [6] (K = 21 eV/Å^2 given in Tab. 1) indicates that the one-dimensional Al line also constitutes a hard material. Although a much better estimation [12] for the effective force constant K could be obtained by considering the full dynamical matrix of the system, yielding the surface-phonon spectra, the above estimated value is good enough to account for the MI-transition in the simple two-band model.

The parameters α and t_0 are determined by calculating bandstructures for expanded and contracted supercells, the expansion/contraction (δ) being 0, ± 0.125, $+0.25$, and 0.5 Å, and fitting the result to a quadratic as well as a trigonometric function. The insert in Fig. 3 shows the bandstructure calculations for the equilibrium (δ = 0 Å) and the contracted (δ = -0.125 Å) supercells. In this way the hopping integral $t_{n+1,n}$ is obtained as a function of δ and plotted in Fig. 3. Linearizing $t_{n+1,n}$, according to Eq. 4, gives $t_0 = 0.48/0.52$ eV and $\alpha = 0.2/0.8$ eV/Å for the quadratic/trigonometric approximations, respectively.

An analytical expression for T_c is obtained in the two-band model by expanding the dispersion $E_{k,0}$ around the Fermi wavevector and minimizing the expression for the total energy $E_u(T)$, given in Eq. 7, w.r.t the displacement coordinate u. Noticing that $z \ll 1$, $E_{k,0}$ can be approximated by $E_{k,0} \sim 2t_0\sqrt{4z^2 + a^2(k-k_F)^2}$. Putting this into Eq. 7, and calculating the minima of the total energy $E_u(T)$ in the limit u$\rightarrow$0, gives:

$$k_B T_c = \xi 2t_0 \pi \exp(-\frac{\pi K t_0}{4\alpha^2}), \tag{8}$$

where $\xi = 2.67$. It is clear that the critical temperature is very sensitive to the model parameters, in particular α. As mentioned earlier, two fitting functions are used to estimate t_0 and α. These are the extreme values for the model parameters, which will give us a temperature range for T_c where the MI transition could occur. The expression above gives $T_c \approx 0$ for t_0 = 0.48 eV and α = 0.2 eV/Å, and $T_c \approx 1$ K for t_0 = 0.52 eV and α = 0.8 eV/Å. Hence, the critical temperature for the MI transition in our system should be in the range [0,1] K. The low value of the T_c makes this system a model system for Luttinger Liquid theory. The big change in the critical temperature for the Al chain system of κ-Al_2O_3 compared to TPA is mainly due to the difference in the electron-phonon constant α, which is much smaller for the κ-Al_2O_3-system reducing T_c. The underlying physics is that the electron-phonon coupling term in the Hamiltonian spontaneously breaks the symmetry of the system. A small value of α will make this term negligible and the critical temperature to almost vanish.

The shortcomings of the model are that explicit electron-electron interaction is not taken into account and that phonons are treated classically. Since the model parameters are determined using DFT calculations for the exchange correlation effects, some of the electron-electron interaction are already included in t_0 and α. In other words, the values for t_0 and α can be considered as the screened values and not the bare ones. More accurate considerations of the electron-electron correlation effects should be taken into account when calculating physical properties of the system, such as the electrical and thermal conductivities. The second assumption in the model, namely the classical treatment of the Al atoms, is justified by the fact that the mass of the Al atoms is large compared to the mass of the electrons.

5. Conclusions

In summary, a new one-dimensional electron-gas consisting of the Al zigzag chains is predicted on the $(00\bar{1})$ surface of the metastable κ-Al_2O_3 along the [100] direction. Furthermore, the Peierls MI instability in this system is studied, showing that the critical temperature is below the 1 K regime. The low value for the critical temperature makes it an interesting low-temperature system. The prediction is based on extensive first-principles DFT calculations and the phase transition has been studied by means of the combination of a phenomenological tight-binding model and additional DFT calculations to determine the model parameters.

6. Acknowledgements

The work is supported by the Swedish Natural Research Council and the Swedish Foundation for Strategic Research (SSF) via Materials Consortia No. 9 and ATOMICS, which is gratefully acknowledged.

References:

[1] C. Ruberto, Y. Yourdshahyan, and B. I. Lundqvist, Phys. Rev. Lett. **88** (2002) 226101.

[2] S. Iijima, Nature **354** (1991) 56-58.

[3] J. T. Gammel *et al*, Phys. Rev. B. **45** (1992) 6408 and references therein.

[4] C. F. Eagan, S. A. Werner, and R. B. Saillant, Phys. Rev. B. **12** (1975) 2036.

[5] M. Sato *et al*, J. Phys. C **18** (1985) 2603.

[6] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42** (1979) 25.

[7] Y. Bouveret and S. Megtert, J. Phys. (Paris) **50** (1989) 1649.

[8] A. Schwartz, S. Donovan, M. Dressel, L. Degiorgi and G. Grüner, Synth. Met. **86** (1994) 2129.

[9] V. Vescoli, L. Degiorgi, W. Henderson, G. Grüner, K. P. Sarkey and L. K. Montgomery cience **281** (1998) 1181.

[10] C. L. Kane and Mathew P. A. Fisher, Phys. Rev. Lett. **68** (1992) 8.

[11] A. Schiller and S. Hersfield, Phys. Rev. B, **51** (1995) 18.

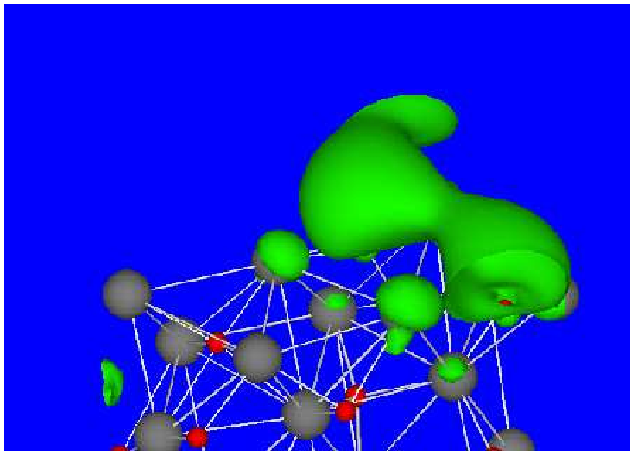
[12] B. Razaznejad, C. Ruberto, P. Hyldgaard, and B. I. Lundqvist, *submitted to* PRL (2002).

[13] J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68** (1992) 631.

Figure 1: Modulus squared of the KS wavefunction corresponding to the surface state of the relaxed κ-$Al_2O_3(00\bar{1})$ surface at $E = E_F$. Large balls are O atoms and small ones are Al atoms. The surface Al atoms lie inside the electron cloud.

Figure 2: Total energy as a function of the relative change of the coordinate ($n\Delta r$) between two Al atoms. The calculations are performed for five cases (n = 0, ± 1, and ± 2) and been interpolated by means of a quadratic function.

Figure 3: The hopping integral $t_{n+1,n}$, obtained by a quadratic (dashed line) and a trigonometric fitting (solid line), as a function of the $\delta = u_{n+1}$-u_n. The inserted figure shows the calculated bandstructre for the equilibrium (δ = 0 Å) and contracted (δ = -0.125 Å) supercells.

Fig.1 

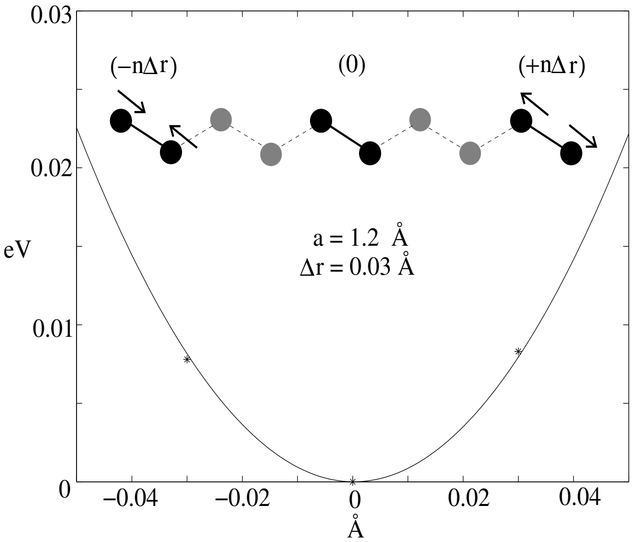
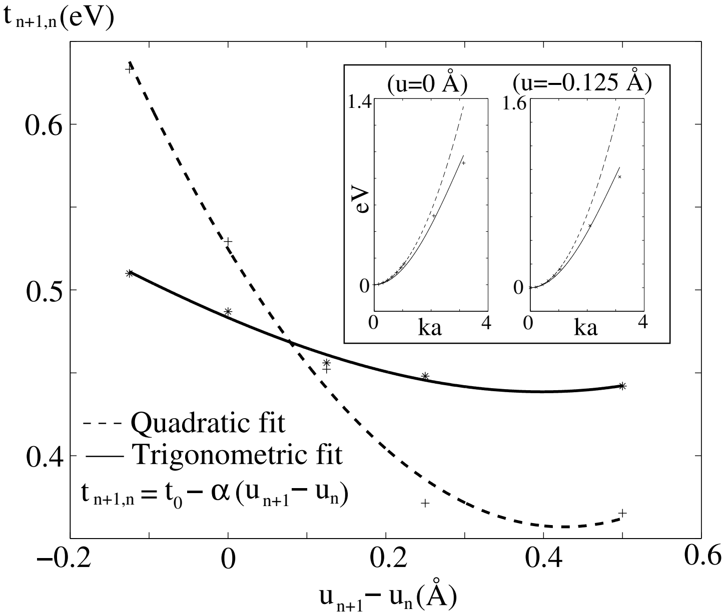


Fig.2



$t_{n+1,n}$(eV)
0.6
0.5
0.4
−0.2
0
0.2
0.4
0.6
$u_{n+1}-u_n$(Å)
(u=0 Å)
(u=−0.125 Å)
1.4
1.6
eV
0
0
4
ka
ka
Quadratic fit
Trigonometric fit
$t_{n+1,n}=t_0-\alpha(u_{n+1}-u_n)$

Fig.3

Table 1: The model parameters, energy bandgap E_g and critical temperature T_c for the κ-Al_2O_3 system, TPA, inorganics, and CT-salts. † and ⋆ are the parameters obtained by means of trigonometric and quadratic fits, respectively.

	κ-Al_2O_3	TPA [6]	inorganics[3, 4, 5]	CT-salts [7]
K(eV/Å^2)	18	36	-	-
t_0(eV)	$0.48^{\dagger}/0.52^{\star}$	2.5	-	-
α(eV/Å)	$0.2^{\dagger}/0.8^{\star}$	4.1	-	-
E_g(eV)	-	1.35	-	-
T_c(K)	[0,1]	-	$\sim$200	$\sim$60