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Order of the Electronically Induced Crystallographic Semiconductor-to-Metal Transition

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The electronically induced crystallographic semiconductor-to-metal (Adler-Brooks) transition is reconsidered in the tight-binding approximation. In contrast to other work, it is found that both first- and second-order phase transitions can occur, depending on the relative magnitude of lattice compressibility and transfer integral. An analytical expression for the second-order phase-transition temperatures as a function of these quantities is obtained.

The electronically induced crystallographic semiconductor-to-metal transition is calculated in the tight-binding approximation. Inclusion of the exponential character of the wave functions leads in a straightforward way to first- as well as second-order phase transitions. The transition temperatures, as well as the order of the transition, can be determined numerically. In a set of recent papers, Adler and Brooks,[1] as well as Hallers and Vertogen,[2–4] investigated theoretically the electronically induced crystallographic semiconductor-to-metal transition. A distinctive feature of all theoretical treatments so far is that an unmodified symmetry-split band system yields only second-order semiconductor-to-metal transitions. In connection with phase transitions tetracyanoquinodimethan (TCNQ) salts,[5] we recently had occasion to reinvestigate the problem in the tight-binding approximation. It is the purpose of this paper to show that if one takes the exponential character of the orbitals into account, both first- and second-order phase transitions are possible, depending on the ratio of the electronic-binding to the lattice-repulsion energy.

In our model we consider a simple one-dimensional lattice consisting of N sites with, on the average, one electron per site. In the semiconductor phase, the distances alternate (r_1, r_2) and in the metallic phase they are equal ($r_1 = r_2 = \frac{1}{2}a$). The alternation parameter is defined by $r_{1,2} \equiv \frac{1}{2}a(1 \mp \xi)$, with $0 \leqslant \xi < 1$, where a is the lattice parameter.

In the tight-binding approximation the electronic states of this system are given by[6]

$$E^{\pm}(k) = \pm E_c[g^2 + \cos^2 \tfrac{1}{2}ak]^{1/2} . \tag{1}$$

The parameters E_c and g are related to the transfer integrals h_1 and h_2 between the two unequivalent neighbors:

$$E_c = 2(h_1 h_2)^{1/2} \tag{2}$$

$$g = \sinh[\tfrac{1}{2}\ln(h_1/h_2)] .$$

The bandwidth E_b and the gap $2E_g$ are given by

$$E_b = E_c[(g^2+1)^{1/2} - g] = 2\,|\,h_2\,|$$

and

$$E_g = E_c g = |\,h_1\,| - |\,h_2\,| \quad \text{with } |\,h_1\,| < |\,h_2\,| .$$

The transfer integrals $h_{1,2} = \int \psi^*_{1,2} v' \psi_0 \, d\tau$ depend on the intersite distance and therefore on the alternation parameter ξ. In the tight-binding approximation we can approximate $h_{1,2}$ by

$$h_{1,2} \approx (\text{const}) e^{-c r_{1,2}}$$

or

$$h_{1,2} \approx h_0 e^{\pm b \xi} , \tag{3}$$

where h_0 is the transfer integral in the nondistorted case. The constant b will, of course, depend on the type of wave functions used and on the intersite distances. (Table I gives a list of values for b to be used in the various cases, using molecular two-center integrals, as evaluated by Lofthus.[7])

The lattice energy will be approximated by

$$E_1(\xi) = \tfrac{1}{2}N(Br_1^{-n} + Br_2^{-n}) = \tfrac{1}{2}N\Omega[(1-\xi)^{-n} + (1+\xi)^{-n}] , \tag{4}$$

where $\Omega = B(\frac{1}{2}a)^{-n}$ and B is a measure of the lattice repulsion. The role of lattice vibrations will be neglected, since they do not contribute to the problem considered here. Their contribution was evaluated, and it could be shown that their effect is limited to a small change in the transition temperature.

The partition function of the electronic system can now be evaluated:

$$Z_{\text{el}} = \prod_k [(1 + e^{[-E^-(k)/kT]^2})(1 + e^{[-E^+(k)/kT]^2})] ,$$

from which we obtain the free energy of the crystal:

$$\begin{aligned} F(\xi, T) = (-2/\pi)NE_c \int_0^{\pi/2} &((g^2 + \cos^2 \tfrac{1}{2}ak)^{1/2} \\ &+ 2(kT/E_c)\ln\{1 + \exp[-(E_c/kT) \\ &\times (g^2 + \cos^2 \tfrac{1}{2}ak)^{1/2}]\})\, d(\tfrac{1}{2}ak) \\ &+ \tfrac{1}{2}N\Omega[(1-\xi)^n + (1+\xi)^n] . \end{aligned} \tag{5}$$

TABLE I. b values, entering in the approximate transfer integral expression (2.3), for different types of wave function φ; $c = (Z'/n)a_0^{-1}$ = orbital exponent/Bohr radius.

φ_0 $(=\varphi_{1,2})$	b
1s	$\frac{1}{2}ac - 1$
2p	$\frac{1}{2}ac - 3$
3p	$\frac{1}{2}ac - 5$
3d	$\frac{1}{2}ac - 5$

In principle we can now calculate this function numerically for certain types of systems, but since we are primarily interested in the order of the phase transition, we will, according to Landau,[8] consider the free energy in the neighborhood of a transition point and expand $F(\xi, T)$ as a power series of ξ:

$$F(\xi, T) = F_0 + A\xi^2 + C\xi^4 + G\xi^6 + \cdots \; , \qquad (6)$$

A, C, G, ... are all functions of T and the parameters of the system. Odd terms in ξ are zero for this symmetrical case. Since in the semiconductor-to-metal transition a symmetry element is added to the system, we know at least that a second-order transition is allowed.[9] With the power series for F we can investigate the various possibilities for the order of the phase transition.

In Eq. (6), $A > 0$ corresponds to the symmetrical phase and $A < 0$ to the nonsymmetrical phase. The curve of second-order transition points is determined by

$$A = 0, \quad C > 0 \; , \qquad (7)$$

whereas the transitions will occur as first-order phase transitions if

$$A > 0, \quad C < 0, \quad G > 0 \; . \qquad (8)$$

The first-order-transition curve joins on to the second-order curve at the critical point, which is defined by

$$A_{\mathrm{cr}} = 0 \; , \quad C_{\mathrm{cr}} = 0 \; , \quad \text{and } G_{\mathrm{cr}} > 0 \; . \qquad (9)$$

Now, we will examine the sign of the fourth derivative of $F(\xi, T)$ with respect to ξ in $\xi = 0$, because the sign of C clearly is decisive in determining the order of the phase transition.

Because the analytical treatment can be continued further with the approximated relation between g and ξ

$$g = b \mid \xi \mid \; , \qquad (10)$$

which is the linear term in the expansion of (2), we will first consider this case and show that it always leads to $C > 0$ and, therefore, to second-order phase transitions only, in agreement with previous authors.[1,2]

From (5) and (10) we derive

$$24C = \left(\frac{\partial^4 F(\xi, T)}{\partial \xi^4}\right)_{\xi=0} = n(n+1)(n+2)(n+3)N\Omega - b^4 I_4(E_c/kT)NE_c \; , \qquad (11)$$

in which the integral $I_4(E_c/kT)$ is a function of E_c/kT only, given by the following expression, with $y \equiv (E_c/kT)\cos\frac{1}{2}ak$:

$$I_4(E_c/kT) = (6/\pi)(E_c/kT)^3 \times \int_0^{\pi/2} [y^{-2}(1+\cosh y)^{-1} - y^{-3}\tanh\tfrac{1}{2}y]\, d(\tfrac{1}{2}ak)$$

$I_4(E_c/kT)$ was evaluated numerically as a function of E_c/kT, and its sign turned out to be negative for each E_c/kT value, indicating that the sign of C is positive definite. According to (7), only second-order phase transitions are possible. The transition points can be found by the requirement $A = 0$. From (5) and (10),

$$2A = \left(\frac{\partial^2 F(\xi, T)}{\partial \xi^2}\right)_{\xi=0} = n(n+1)N\Omega - b^2 I_2(E_c/kT)NE_c \; , \qquad (12)$$

in which

$$I_2(E_c/kT) = (2/\pi)(E_c/kT) \int_0^{\pi/2} y^{-1} \tanh\tfrac{1}{2}y \, d(\tfrac{1}{2}ak)$$

and the second-order transition point is uniquely determined by

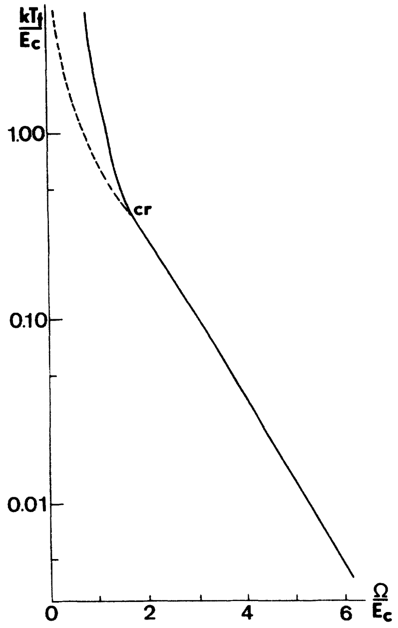

FIG. 1. First- and second-order transitions lines, joined by the critical point (cr). The broken line is the continuation of the second-order transition line. The curves were constructed with $n = 6$, $b = 8$.

$$I_2(E_c/kT_t) = n(n+1)b^{-2}\,\Omega/E_c\ . \qquad (13)$$

For $E_c/kT > 1$, the integral I_2 can be approximated by $I_2 \approx 1.5 + \ln E_c/kT$. We then find for the transition temperatures

$$T_t \approx 4.5\,E_c/k\exp[-n(n+1)b^{-2}\Omega/E_c]\ . \qquad (13a)$$

In Fig. 1, for selected values of n and b, the reduced transition temperatures kT_t/E_c are given graphically as a function of Ω/E_c, which measures the ratio between the repulsive energy of the lattice and the electronic binding energy of the valence electrons.

An example of the temperature dependence of the total free energy in such a case, leading to a second-order transition, is given in Fig. 2(a), whereas the equilibrium distortion as a function of temperature is plotted in Fig. 3(a). The temperature dependence of the energy-band gap is identical in this approximation.

If, however, we use the more realistic expression (2),

$$g = \sinh b\,|\,\xi\,|\ ,$$

we are confronted with second- *and* first-order phase transitions. The expression (12) for A remains unaltered, but from (5) and (10) we now find for C

$$24C = n(n+1)(n+2)(n+3)N\Omega - b^4[I_4(E_c/kT) + 4I_2(E_c/kT)]NE_c\ , \qquad (14)$$

which is no longer positive definite.

First of all we derive from (14), by calculating the integrals $I_4(E_c/kT)$ and $I_2(E_c/kT)$ numerically, that C is always positive for $E_c/kT > 3.4$. Therefore, from our model, first-order transitions can only be expected in the region

$$E_c/kT_t < 3.4\ . \qquad (15)$$

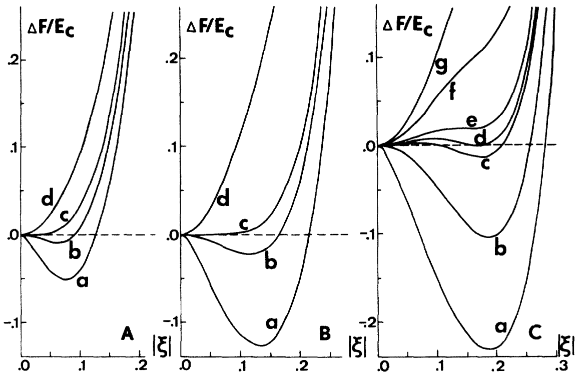

FIG. 2. $F(\xi)$ curves, calculated with $n=6$ and $b=8$, at different temperatures, showing the order of the semiconductor-to-metal transitions. A $\Omega/E_c = 2.00$; $kT/E_c = 0.010$ (a), 0.215 (b), 0.270 (c): second-order transition 0.400 (d). B $\Omega/E_c = 1.67$; $kT/E_c = 0.010$ (a), 0.313 (b), 0.362 (c): critical transition, 0.667 (d). C $\Omega/E_c = 1.50$; $kT/E_c = 0.010$ (a), 0.333 (b), 0.445 (c), 0.460 (d): first-order transition, 0.483 (e), 0.588 (f), 0.770 (g).

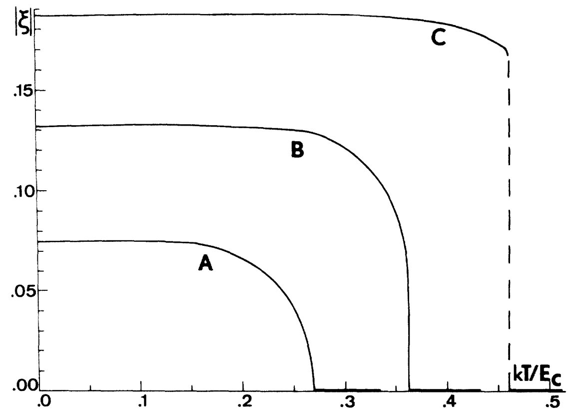

FIG. 3. Behavior of the equilibrium distortion with temperature for the three distinct cases of Fig. 2, leading to a (A) second-order, (B) critical, and (C) first-order phase transition.

These transitions occur if the following two conditions (derived from $A > 0$, $C < 0$) are fulfilled:

$$n(n+1)b^{-2}\Omega/E_c > I_2(E_c/kT_t)\ , \qquad (16)$$

$$n(n+1)b^{-2}[4-(n+2)(n+3)b^{-2}]\Omega/E_c > -I_4(E_c/kT_t)\ . \qquad (17)$$

The first-order-transition points are not easily found. Near a critical transition, they can be determined by $C^2 = 4AG$.[8] However, an exact determination of the transition points is only possible by computing $F(\xi, E_c/kT)$ for a set of Ω/E_c values for n and b.

Because the right-hand side of (17) is positive definite, we derive a necessary condition for the possible occurrence of a first-order transition,

$$(n+2)(n+3) < 4b^2\ . \qquad (18)$$

A critical transition will be obtained if Eqs. (16) and (17) are satisfied simultaneously, after having replaced the inequality signs by signs of equality. The critical transition point is evidently determined by

$$-I_4(E_c/kT_{\rm cr})/I_2(E_c/kT_{\rm cr}) = 4-(n+2)(n+3)b^{-2}\ . \qquad (19)$$

Second-order-phase-transition points ($C > 0$) are again given by (14).

In Fig. 1 the first- and second-order transitions lines are depicted. The ratio Ω/E_c was taken as a variable. As an example, we have selected values for n and b that are appropriate for the M^+TCNQ$^-$ salts.[5] In Fig. 2 we have drawn a number of $F(\xi)$ curves at various temperatures with $\Omega/E_c = 2.00$, 1.67, and 1.50, leading to second-order, critical, and first-order transitions, respectively. The temperature dependence of the equilibrium distortion in these three cases is given in Fig. 3. The behavior of the energy-band gap with temperature is now given by $2E_g = 2E_c \times \sinh b|\xi|$. For small ξ values these $E_g(T)$ curves will be similar to the $|\xi|(T)$ curves.

In conclusion, it is clear that inclusion of the exponentional character of the wave functions adds sufficient "cooperativeness" to the model to lead to first-order phase transitions, which in the tight-binding approximation can be quite accurately calculated.

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