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Electronically Induced Crystallographic Transition

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In this paper a model is presented which exhibits a so-called electronically induced crystallographic transition. The model consists of two interpenetrating one-dimensional identical lattices of attractive δ potentials. Shifting one sublattice with respect to the other defines a distortion, where the nondistorted system is assumed to have a periodicity which is half the periodicity of such a sublattice. The model is closely related to one discussed by Adler and Brooks. It is shown by a computer calculation that the competition between the lattice and electronic energies results in a second-order phase transition. The narrow band limit is discussed in terms of a two- and four-level scheme. It appears that only a second-order phase transition can occur, unless the repulsive term in the lattice energy is too weak. In that case the two sublattices will coincide at zero temperature, which is an unphysical situation.

I. INTRODUCTION

During the last 10 years a great deal of work has been performed in the field of the metal-nonmetal transition, a phenomenon which appears in the oxides and sulfides of the transition metals. These materials are semiconducting at low temperatures but suddenly become metallic at a certain temperature or over a small temperature range. The conductivity can change by a factor 10^7, e.g., V_2O_3, at these critical temperatures.

The metal-nonmetal transition can be explained in several ways (see review articles by Adler[1,2]). One of these explanations is in terms of the electronically induced crystallographic transition. The mechanism of this type of transition is based on the competition between the lattice energy and the energy of the electrons. The total energy of the electrons in a half-filled band is lowered if that band is split up by some crystalline distortion, while the lattice energy increases by this distortion.

Adler and Brooks[3] demonstrated this effect by calculating the free energy as a function of the distortion parameter for the case of a linear chain of δ potentials in the limit of extremely narrow bands. As a result, they obtained a first-order phase transition. They also considered a model with bands which are spherical around the conduction- and valence-band edges. It appeared that a spontaneous distortion at $T=0$ could only occur if the bandwidth was less than half the energy gap between the bands. Labbé and Friedel[4,5] calculated the change in free energy for a linear-chain model of V_3Si under the assumption of a tetragonal distortion, which increased the lattice parameter in one direction but decreased this parameter in the other two directions. In this way a first-order phase transition was obtained. Labbé and Friedel[6,7] also considered the stability of the system against a periodic distortion in a tight-binding approximation; they considered the influence of the filling of the bands and, qualitatively, the influence of the temperature.

In this paper a linear chain of δ potentials is considered. The free energy of the system is calculated as a function of both the distortion parameter and the temperature. It will be shown that a second-order phase transition occurs.

This paper is organized in the following way: In Sec. II the free energy of the system is given. Both the lattice and electronic contribution to the free energy are discussed. In Sec. III the results of a computer calculation are presented. In Sec. IV the narrow band limit is treated in terms of a two- and four-level scheme. Finally, the results are discussed in Sec. V.

II. FREE ENERGY OF MODEL

Consider a one-dimensional crystal with period $\frac{1}{2}d$. The system can be regarded as composed of two interpenetrating lattices of period d. Shifting one sublattice with respect to the other doubles the periodicity of the one-dimensional crystal. In this way a distortion of the original lattice is obtained. Calling the nearest-neighbor distances b_1 and b_2, a distortion parameter q can be defined as

$$q=(b_2-b_1)/d \quad ,$$

where $b_1+b_2=d$. The interaction between the electron and the ions, whose equilibrium positions are situated at the lattice sites, is assumed to be an attractive δ potential of strength A. The resulting periodic potential for the electrons is drawn in Fig. 1. The total Hamiltonian of the system reads

$$H=\sum_i \frac{p_i^2}{2m}-\sum_{i,j} A\delta(r_i-R_j)+\sum_i \frac{P_i^2}{2M}$$

$$+\frac{1}{2}\sum_{i\neq j} V(R_i-R_j)+\frac{1}{2}\sum_{i\neq j} W(r_i-r_j)\ , \tag{2.1}$$

where r_i and p_i denote the position and momentum operators of the electrons and R_i and P_i those of the ions.

A. Electronic Contribution

Neglecting the electron-electron and electron-phonon interaction, the energy spectrum of the electrons can be calculated from the following part of the Hamiltonian:

$$H_{el}^0=\sum_i \frac{p_i^2}{2m}-\sum_{i,j} A\delta(r_i-R_j^q), \tag{2.2}$$

where R_j^q denotes the equilibrium position of the jth ion. Defining

$$x_0=(m/\hbar^2)Ad \tag{2.3}$$

and

$$E=-(\hbar^2/2md^2)x^2\ , \tag{2.4}$$

the secular equation reads

$$\cos kd=\left(1+\frac{x_0^2}{x^2}\right)\cosh x-\frac{x_0^2}{x^2}\cosh qx$$

$$-2\frac{x_0}{x}\sinh x\ . \tag{2.5}$$

The energy of the electron $E(k,q)$ as a function of the wave vector k and the distortion parameter q is obtained by solving this transcendental equation, which has to be done numerically in most cases. In Fig. 2 it is shown by a computer calculation in which way the original band changes with increasing q in case $x_0=6$ and $E_0=+4$ eV, where E_0 is the absolute value of E for $x=x_0$. The calculations have been performed up to distortions of about 50%. In case $q\neq 0$, a gap appears between the two branches of the dispersion curve due to the fact that the periodicity is doubled. The gapwidth increases with increasing q, the upper band shifts upwards, and the lower one downwards.

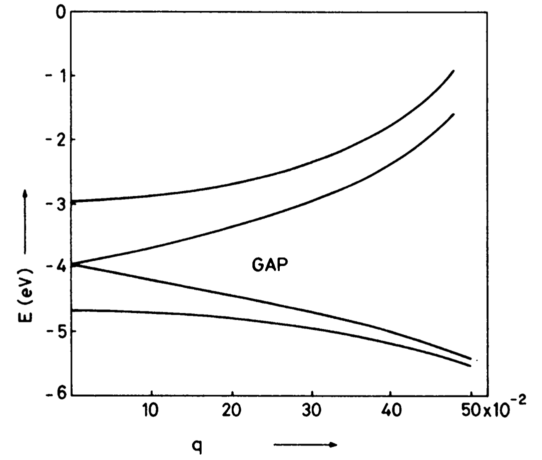

FIG. 2. Band energies as a function of q in case $x_0=6$ and $E_0=4$ eV.

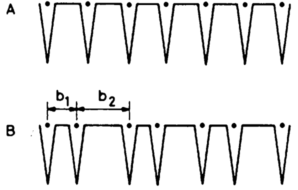

FIG. 1. Periodic potential. (A) for the case $q=0$, (B) for $q\neq 0$.

In the following, the case of one electron per ion is considered. Clearly the electrons favor a situation with a distortion which is as large as possible. Neglecting the effect of the higher-situated bands, the expression for the free energy per electron reads (see Huang[8])

$$F_{el}(q,T)=\mu-\frac{2}{N_0\beta}\sum_{\sigma=+,-}\ \sum_{k=-\pi/d}^{\pi/d}\ln\left(1+e^{\beta[\mu-E^\sigma(k,q)]}\right)\ , \tag{2.6}$$

where $E^+(k,q)$ denotes the energy spectrum in the upper band and $E^-(k,q)$ the energy spectrum in the lower band. N_0 is the total number of electrons or ions present, and $\beta=1/kT$. The Fermi energy μ is determined by

$$\sum_{\sigma=+,-}\ \sum_{k=-\pi/d}^{\pi/d}\frac{2}{1+\exp\{\beta[E^\sigma(k,q)-\mu]\}}=N_0. \tag{2.7}$$

In the limit $N_0\to\infty$ expressions (2.6) and (2.7) are equivalent to

$$F_{el}(q,T)=\mu-\frac{1}{\pi\beta}$$

$$\times\sum_{\sigma=+,-}\int_0^\pi \ln\left(1+e^{\beta[\mu-E^\sigma(kd,q)]}\right)d(kd) \tag{2.8}$$

and

$$\sum_{\sigma=+,-}\int_0^\pi \frac{1}{1+\exp\{\beta[E^\sigma(kd,q)-\mu]\}}\,d(kd)=\pi\ . \tag{2.9}$$

B. Lattice Contribution

Neglecting the electron-phonon interaction, the lattice energy results from

$$H_{\mathrm{lat}}=\sum_i \frac{P_i^2}{2M}+\frac{1}{2}\sum_{i\neq j} V(R_i-R_j)\,. \tag{2.10}$$

Expanding this Hamiltonian around the new equilibrium positions R_n^q of the ions (assuming that the distortion is already a fact) and neglecting phonon-phonon interactions, the following Hamiltonian is obtained:

$$H_{\mathrm{lat}}=\sum_i \frac{P_i^2}{2M}+\frac{1}{2}\sum_{i\neq j} V(R_i^q-R_j^q)+\sum_i A_i\delta R_i+\frac{1}{2}\sum_{i,j} B_{ij}\delta R_i\delta R_j\,, \tag{2.11}$$

where $\delta R_i = R_i - R_i^q$ and

$$A_i=\sum_{j,j\neq i}\frac{\partial V(R_i^q-R_j^q)}{\partial R_i}\,,$$

$$B_{ij}=\frac{\partial^2 V(R_i^q-R_j^q)}{\partial R_i\partial R_j} \quad \text{for } i\neq j\,, \tag{2.12}$$

$$B_{ii}=\sum_{j,j\neq i}\frac{\partial^2 V(R_i^q-R_j^q)}{\partial R_i^2}\,,$$

(see Pines[9]).

For small values of the distortion parameter q the static term results in the following energy per ion:

$$\frac{1}{2N_0}\sum_{i\neq j} V(R_i^q-R_j^q)=\frac{1}{2N_0}\sum_{i\neq j} V(R_i^0-R_j^0)+B_0q^2\,, \tag{2.13}$$

where R_n^0 denotes the equilibrium position in the nondistorted case.

In order to obtain the phonon energies the following Hamiltonian has to be diagonalized by means of a Bogoliubov-Valatin transformation:

$$H_{\mathrm{ph}}=\sum_i \frac{P_i^2}{2M}+\sum_i A_i\delta R_i+\frac{1}{2}\sum_{i,j} B_{ij}\delta R_i\delta R_j\,. \tag{2.14}$$

Because of the expansion around the new positions R_n^q, the term A_i does not equal zero. This term, however, is exactly canceled by the indirect ion-ion interaction via the electron gas. In case the indirect ion-ion interaction does not exist, the effect of A_i would simply be to cancel the increase in the static energy, i.e., to cancel the term $N_0B_0q^2$. In the case of nearest-neighbor interactions, the phonon spectrum reads

$$[\omega_q^{\pm}(k)]^2=\frac{1}{M}\,[C_1+C_2\pm(C_1{}^2+C_2{}^2+2C_1C_2\cos kd)^{1/2}]\,, \tag{2.15}$$

where

$$\frac{\partial^2 V(R_i^q-R_j^q)}{\partial R_i\partial R_j}=-C_1\,,\quad \frac{\partial^2 V(R_i^q-R_j^q)}{\partial R_i^2}=C_1$$

if

$$|R_i^q-R_j^q|=b_1=\frac{1-q}{2}\,d\,;$$

$$\frac{\partial^2 V(R_i^q-R_j^q)}{\partial R_i\partial R_j}=-C_2\,,\quad \frac{\partial^2 V(R_i^q-R_j^q)}{\partial R_i^2}=C_2$$

if

$$|R_i^q-R_j^q|=b_2=\frac{1+q}{2}\,d\,; \tag{2.16}$$

and

$$\frac{\partial^2 V(R_i^q-R_j^q)}{\partial R_i\partial R_j}=\frac{\partial^2 V(R_i^q-R_j^q)}{\partial R_i^2}=0,\quad \text{otherwise.}$$

The free energy per ion of the phonons is given by

$$F_{\mathrm{ph}}(q,T)=\frac{1}{2\pi\beta}\times\sum_{\sigma=+,-}\int_0^{\pi}\ln\{1-\exp[-\beta\hbar\omega_q^{\sigma}(kd)]\}\,d(kd). \tag{2.17}$$

In order to obtain the free energy per ion of the lattice the static term (2.13) has to be added to F_{ph}. Clearly the lattice favors a situation where the distortion is as small as possible.

III. RESULTS OF NUMERICAL CALCULATIONS

The free energy per ion reads

$$F(q,T)=F_{\mathrm{el}}(q,T)+F_{\mathrm{ph}}(q,T)+\frac{1}{2N_0}\sum_{i\neq j} V(R_i^0-R_j^0)+B_0q^2\,. \tag{3.1}$$

In order to study the eventual appearance of a phase transition the following quantity has to be considered:

$$\Delta F(q,T)=F(q,T)F(0,T)$$
$$=F_{\mathrm{el}}(q,T)-F_{\mathrm{el}}(0,T)+F_{\mathrm{ph}}(q,T)-F_{\mathrm{ph}}(0,T)+B_0q^2\,. \tag{3.2}$$

In this paper the following values of the parameters have been used:

$$x_0=6,\quad E_0=(\hbar^2/2md^2)\,x_0^2=+4\ \mathrm{eV}\,,$$

$$(C_0/2M)^{1/2}=10^{13}\ \mathrm{rad/sec},\quad B_0=8.5\ \mathrm{eV/ion}\,,$$

where it is assumed that $C_1=C_0+Dq$ and $C_2=C_0-Dq$. In Figs. 3(a) and 3(b) $\Delta F(q,T)$ has been plotted as a function of the distortion parameter q for, respectively, widely spread temperatures and for temperatures in the neighborhood of 384 °K. Using the well-known thermodynamical argument that the free energy of a system in thermal equilibrium assumes its lowest value, one may easily deduce from Figs. 3(a) and 3(b) the way in which the distortion parameter q depends on the temperature.

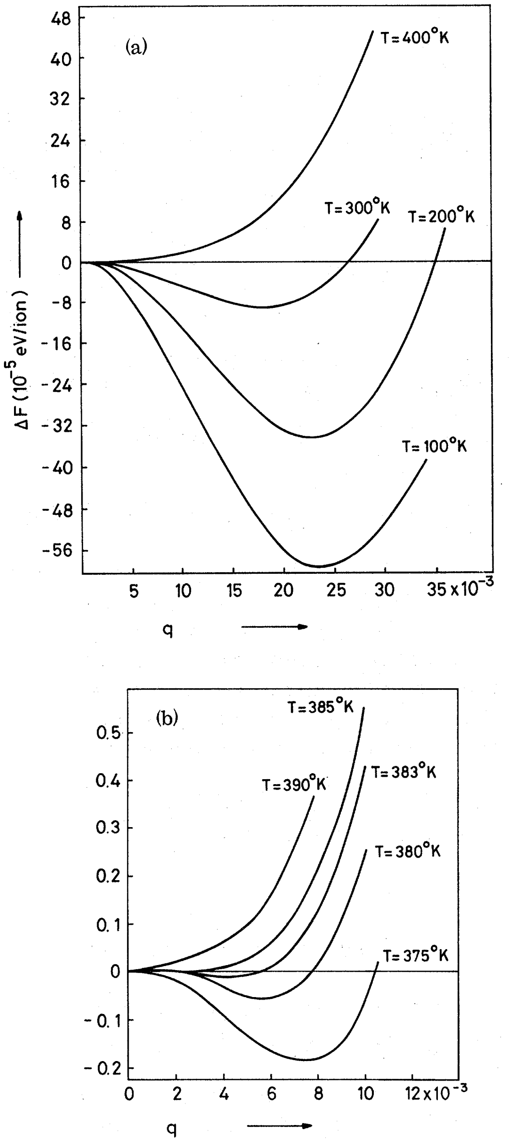

FIG. 3. (a) Change of the free energy as a function of q at several widely spread temperatures. (b) Change of the free energy as a function of q at temperatures around $T_c = 384$ °K.

A plot of this relation is presented in Fig. 4. It directly follows that the system exhibits a second-order phase transition at $T_c = 384$ °K. The periodicity of the system below T_c is different from the one above T_c.

In connection with these results the following remarks have to be made:

(i) The main contribution to the change in the free energy of the lattice is due to the term $B_0 q^2$. The free energy of the phonons can be neglected. This term only becomes important at large distortions. If D is of the order of C_0, the phonon free energy has to be taken into account at distortions of about 15% and higher.

(ii) In the relevant region of the distortion parameter q the gapwidth changes as $E_g = 4.9q$. The total bandwidth in this model is about 1.7 eV. The gap at zero temperature is 0.12 eV while the zero-temperature distortion is 2.4%. In this case the gap is much smaller than the bandwidth.

(iii) The transition temperature and the zero-temperature distortion depend strongly on the coefficient B_0. A value of $B_0 = 10$ eV/ion results in a transition temperature of about 200 °K and a zero-temperature distortion of about 1.2%, while a value of $B_0 = 5.5$ eV/ion gives rise to a transition temperature of about 1360 °K and a zero-temperature distortion of about 10%. This last case is shown in Fig. 5. Clearly the nature of the transition is not affected by the magnitude of B_0.

(iv) The same calculations were performed for a model with a bandwidth of about 0.2 eV. In this case the gap changes as $E_g = 1.9q$ in the relevant region of the distortion parameter q. It was found that this model exhibits a second-order phase transition as well.

IV. NARROW BAND LIMIT

The dispersion relation (2.5) can be approximately solved in an analytic way for large values of x_0, i.e., for narrow bands. For instance if x_0 is larger than 10, the bandwidth is smaller than 0.1 eV. Rewriting the dispersion relation (2.5) in the form

$$x = x_0 \pm [2x^2 e^{-x} \cos kd + 2x_0^2 e^{-x} \cosh qx - e^{-2x}(x + x_0)^2]^{1/2}, \quad (4.1)$$

it becomes obvious that in the narrow band limit (i.e., $x_0 \to \infty$, $qx_0 \to \infty$, $x \to x_0$) the electron levels are given by

$$E(k, q) = -E_0 \pm G[\tfrac{1}{2}(\cos kd + \cosh qx_0)]^{1/2}, \quad (4.2)$$

where $G = 4E_0 e^{-(1/2)x_0}$ and E_0 is the absolute value of E [defined in expression (2.4)] for $x = x_0$. It follows immediately from expression (4.2) that the original

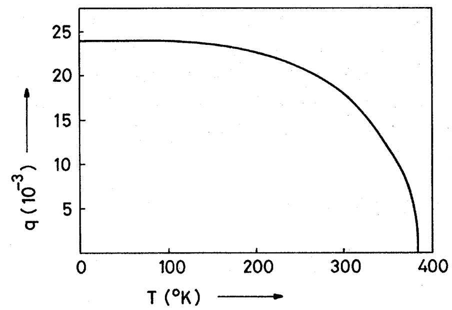

FIG. 4. Equilibrium value of q as a function of temperature.

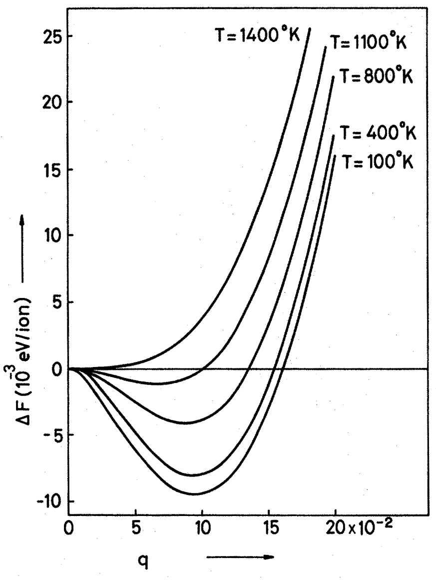

FIG. 5. Change of the free energy as a function of q at several temperatures for $B_0 = 5.5$ eV/ion.

band is split up by the distortion and that both subbands shift an equal amount in the narrow band limit. In the following, the thermodynamical behavior of the narrow band limit system is approximated by a two- and a four-level scheme.

A. Two-Level Scheme

In this scheme the energy levels of each subband are assumed to be melted together in one N_0-fold degenerate level. Taking $\cos kd = -1$, the energies of both levels are given by

$$E^+ = -E_0 + G \sinh \tfrac{1}{2} x_0 q \,,$$

$$E^- = -E_0 - G \sinh \tfrac{1}{2} x_0 q \,. \tag{4.3}$$

In this case the band-gap-to-bandwidth ratio is infinite, while the energy gap between both bands is approximately an exponential function of the distortion parameter q. The grand canonical partition function of this two-level system reads

$$Z = (1 + e^{-\beta(E^+ - \mu)})^{N_0} (1 + e^{-\beta(E^- - \mu)})^{N_0} \,, \tag{4.4}$$

where μ denotes the chemical potential or Fermi energy, which is determined by the number of electrons present. The thermodynamical potential Ω of the system is given by

$$\Omega = -(1/\beta) \ln Z = -(N_0/\beta) \ln(1 + e^{-\beta(E^+ - \mu)}) - (N_0/\beta) \ln(1 + e^{-\beta(E^- - \mu)}) \,. \tag{4.5}$$

In case there are $\overline{N}$ electrons present the chemical potential μ is determined by the relation

$$\overline{N} = -\frac{\partial \Omega}{\partial \mu} = N_0 [(1 + e^{\beta(E^+ - \mu)})^{-1} + (1 + e^{\beta(E^- - \mu)})^{-1}] \,. \tag{4.6}$$

It follows in a trivial way that the condition of one electron per ion, which is the case considered in this paper, results in a chemical potential μ which equals $\frac{1}{2}(E^+ + E^-) = -E_0$. Therefore, the free energy of the two-level system per ion is given by

$$F_{\mathrm{el}}(q, T) = -E_0 - (1/\beta) \ln[2 + 2\cosh(\beta G \sinh \tfrac{1}{2} x_0 q)] \,. \tag{4.7}$$

The total free energy per ion is obtained by adding to F_{el} the free energy per ion of the lattice. Neglecting the phonon contribution, the total free energy per ion reads

$$F(q, T) = F_{\mathrm{el}}(q, T) + \frac{1}{2N_0} \sum_{i \neq j} V(R_i^0 - R_j^0) + B_0 q^2 \,. \tag{4.8}$$

It should be stressed that this expression for the free energy only holds for small distortions. It is true that the electronic part is correct but the lattice contribution only behaves this way for small values of q. Assuming $q x_0 < 1$, the total free energy per ion reads for small values of q

$$F(q, T) = -E_0 - \frac{1}{\beta} \ln(2 + 2 \cosh \tfrac{1}{2} \beta G x_0 q) + \frac{1}{2N_0} \sum_{i \neq j} V(R_i^0 - R_j^0) + B_0 q^2 \,. \tag{4.9}$$

Minimizing expression (4. 9) with respect to q yields

$$\tfrac{1}{2} G x_0 \frac{\sinh \frac{1}{2} \beta G x_0 q}{1 + \cosh \frac{1}{2} \beta G x_0 q} = 2 B_0 q \,. \tag{4.10}$$

This transcendental equation has to be solved graphically. Above a certain temperature $T_c \neq 0$ only one solution is obtained, namely, $q = 0$. Below T_c, however, two solutions are obtained, namely, $q = 0$ and $q \neq 0$. It appears that $q \neq 0$ results in the lowest free energy. The $q \neq 0$ solution is a continuous function of the temperature and approaches $q = 0$ if T goes to T_c. Clearly the system exhibits a second-order phase transition. The transition temperature T_c is determined by

$$k T_c = \frac{G^2 x_0^2}{16 B_0} \,. \tag{4.11}$$

It follows immediately from expression (4. 10) by a self-consistency argument that there has to be a relation between the constants B_0, G, and x_0. This relation is given by

$$B_0 > \tfrac{1}{4} x_0^2 G \,. \tag{4.12}$$

The importance of the type of relation between B_0, G, and x_0 follows by noting that

$$-G\sinh\tfrac{1}{2}x_0q-\frac{\ln 4}{\beta}+B_0q^2$$

$$\leq F(q,T)+E_0-\frac{1}{2N_0}\sum_{i\neq j}V(R_i^0-R_j^0)$$

$$\leq -G\sinh\tfrac{1}{2}x_0q+B_0q^2. \tag{4.13}$$

It is immediately clear from this relation that if

$$B_0\leq\tfrac{1}{4}Gx_0\,, \tag{4.14}$$

both sublattices coincide undoubtedly at zero temperature, which is not a physical situation at all.

B. Four-Level Scheme

In this approximative scheme only four energy levels are considered, namely, the top and bottom levels of the upper and lower band. The top and bottom levels are chosen in order to incorporate the effect of the bandwidth. Assuming $qx_0<1$ the following four levels are obtained:

$$\begin{aligned}
E^+_{\text{top}}&=-E_0+G(1+\tfrac{1}{8}x_0^2q^2)\equiv E_1\,,\\
E^+_{\text{bot}}&=-E_0+\tfrac{1}{2}Gx_0q\equiv E_2\,,\\
E^-_{\text{top}}&=-E_0-\tfrac{1}{2}Gx_0q\equiv E_3\,,\\
E^-_{\text{bot}}&=-E_0-G(1+\tfrac{1}{8}x_0^2q^2)\equiv E_4\,.
\end{aligned} \tag{4.15}$$

Taking the degree of degeneracy of each of the levels to be $\frac{1}{2}N_0$, the grand canonical partition function of this four-level system reads

$$Z=\prod_{i=1}^{4}\left(1+e^{-\beta(E_i-\mu)}\right)^{N_0/2} \tag{4.16}$$

and the free energy per ion reads

$$F_{\text{el}}(q,T)=-E_0-(1/2\beta)\ln[2+2\cosh\beta G(1+\tfrac{1}{8}x_0^2q^2)]$$

$$-(1/2\beta)\ln[2+2\cosh\tfrac{1}{2}\beta Gx_0q]\,, \tag{4.17}$$

where it is assumed that there is one electron per ion present, i.e., $\mu=-E_0$. The total free energy per ion is obtained by adding to F_{el} the free energy per ion of the lattice. Neglecting the phonon contribution the following expression is obtained:

$$F(q,T)=F_{\text{el}}(q,T)+\frac{1}{2N_0}\sum_{i\neq j}V(R_i^0-R_j^0)+B_0q^2\,. \tag{4.18}$$

Minimizing expression (4.18) with respect to q yields

$$\tfrac{1}{8}Gx_0^2q\,\frac{\sinh\beta G(1+\frac{1}{8}x_0^2q^2)}{1+\cosh\beta G(1+\frac{1}{8}x_0^2q^2)}$$

$$+\tfrac{1}{4}Gx_0\,\frac{\sinh\frac{1}{2}\beta Gx_0q}{1+\cosh\frac{1}{2}\beta Gx_0q}=2B_0q\,. \tag{4.19}$$

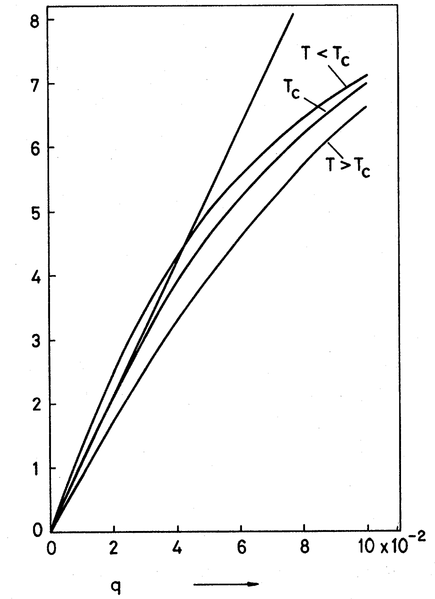

FIG. 6. Graphical solution of Eq. (4.19).

This transcendental equation has to be solved graphically as shown in Fig. 6. As in the previous case, the system exhibits a second-order phase transition. By a self-consistency argument it follows from (4.19) that

$$B_0>\tfrac{3}{16}Gx_0^2\,. \tag{4.20}$$

The transition temperature T_c is determined by

$$\tfrac{1}{8}Gx_0^2\,\frac{\sinh\beta_cG}{1+\cosh\beta_cG}+\tfrac{1}{16}\beta_cG^2x_0^2=2B_0\,. \tag{4.21}$$

Comparing this equation with expression (4.11) it follows that the transition temperature is lowered by taking the effect of the bandwidth into account.

An important difference between the four- and the two-level scheme is the fact that the band-gap-to-bandwidth ratio, which equals

$$4x_0q/(8+x_0^2q^2)\,, \tag{4.22}$$

is smaller than 1 instead of infinite.

V. DISCUSSION

The model, which is presented in this paper, exhibits a second-order phase transition. This phase transition is caused by the competition between the free energy of the electrons and the static repulsion term of the distorted lattice. Obviously this electronically induced crystallographic transition can be connected with the metal-nonmetal transition. It has to be remarked, however, that this model does not explain a sudden jump in the conductivity because the distortion parameter q is a continuous function of the temperature. The model only gives rise to a continuous change in the conductivity. This change may be rather strong near the transition temperature T_c because the occupancy of the energy levels in the upper band may strongly increase near T_c.

As has already been remarked, the underlying model was partially discussed by Adler and Brooks. They expressed the positions of the top of the valence and the bottom of conduction bands at $T=0$ in the following form:

$$\begin{aligned} E_v &= -E_0 - rE_g\ , \\ E_c &= -E_0 + (1-r)E_g\ , \qquad (5.1) \\ r &= \tfrac{1}{2}(1-\delta)\ , \end{aligned}$$

where $-E_0$ is the common energy of the band edges in the absence of distortion, E_g denotes the gap energy, and δ is a parameter which gives the deviation of the splitting from the symmetric case. In the narrow band approximation the Fermi energy for this system reads

$$\mu = \tfrac{1}{2}(E_c + E_v) = -E_0 + \tfrac{1}{2}\delta E_g\ . \qquad (5.2)$$

Clearly, the total free energy per ion of this system is given by

$$F = -E_0 + \tfrac{1}{2}\delta E_g - \frac{1}{\beta}\ln(2 + 2\cosh\tfrac{1}{2}\beta E_g) + \frac{1}{2N_0}\sum_{i\neq j} V(R_i^0 - R_j^0) + B_0 q^2\ . \qquad (5.3)$$

From this expression it follows immediately that if the product δE_g depends linearly on q the system exhibits a first-order phase transition. Taking δ to be a constant and E_g a linear function of q, Adler and Brooks arrived at the first mentioned result. In the narrow band limit discussed in Sec. IV it follows that the asymmetry parameter δ goes to zero in the case of δ potentials. This results in a second-order phase transition, which is in agreement with the Adler and Brooks $\delta = 0$ result. For narrow bands the asymptotic behavior of δ as a function of the distortion parameter q can be calculated. It follows that

$$\delta(q) = x_0 e^{-x_0/2}(\sinh\tfrac{1}{2}qx_0 - q\cosh\tfrac{1}{2}qx_0)\ , \qquad (5.4)$$

i.e., for small values of the distortion such that $qx_0 < 1$, δE_g will be proportional to q^2 resulting in a second-order phase transition. The numerical calculations presented in Sec. III also result in a second-order phase transition. In order to discuss that result in terms of the scheme mentioned above $\delta(q)$ was also calculated numerically. In Fig. 7 $\delta(q)$ is presented for the band structures given in Fig. 2. It appears that δ is a nearly linear function of q. This gives rise to a product δE_g consisting of quadratic and higher-order terms in the distortion parameter q, resulting again in a second-order phase transition.

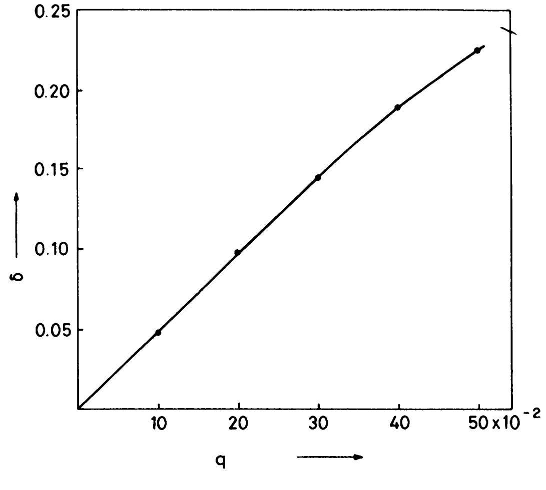

FIG. 7. The asymmetry parameter δ as a function of q in case $x_0 = 6$ and $E_0 = 4$ eV.

If the coefficient B_0 of the repulsive term in the lattice energy is too weak, both sublattices coincide at zero temperature. This case represents a highly unphysical situation. In order to bring about a proper phase transition, higher-order terms in the distortion parameter q have to be taken into account. In this way the lattice energy can be sufficiently increased in order to override the electronic terms and thus to obtain a proper competition between the electronic and lattice contribution.

Finally, it should be repeated that the electron-electron and electron-phonon interactions are ignored in the model under consideration and that the model is one dimensional. The effect of these interactions on the phase transition is unknown. What type of transition might occur in three-dimensional lattices is also unknown.

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Electrons in Crystals in a Finite-Range Electric Field[*]

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The problem of an electron in a finite-range constant electric field is treated; energy levels and eigenfunctions are calculated for the "empty crystal" and for a Mathieu-type model crystal. It is shown that the addition of boundary conditions may change the solution drastically. The influence of different boundary conditions on the eigenvalues and eigenfunctions is discussed and it is found that the former are relatively insensitive while the latter are sensitive to a change in boundary conditions. The result for the eigenvalues is shown to be consistent with an extension of the Born-Ledderman theorem to electronic states in finite crystals. The effective-mass approximation is shown to hold for this model even for moderate fields and use is made of it to explain the complex behavior of the wave functions near the bands' edges. All in all, a clear detailed picture, although limited in scope, is presented of properties of electrons in crystals under the influence of external electric fields.

I. INTRODUCTION

For many years the fundamental problem of a crystal in an external electric field has attracted much attention.[1] Some features of the issue, e.g., the behavior of the optical absorption in the presence of the field,[1-8] are still in dispute. For this effect, instead of a sharp absorption edge above the frequency connected with the band gap in the absence of the field, one gets an "exponential tail" of absorption in longer wavelengths, or smaller energies (the Franz-Keldish effect). Superposed on this absorption curve is a structure hitherto explained to be due to a "Stark ladder" effect. But the existence of the Stark ladder[4,8] and the details of the Franz-Keldish[7] effect are subjects far from being agreed upon. Several pictures have been suggested to describe this problem, but all of them treat the infinite crystal case in an infinite-range electric field.

In this paper we show how the introduction of boundaries into the problem influences the results obtained, bearing in mind that in physical reality the crystal's range and the range of the electric field are finite. We limit ourselves to the case of zero current and we treat the one-dimensional case as it contains the essential physical problem.

In Sec. II we treat analytically the case of an empty lattice in an electric field with appropriate boundary conditions. The energy eigenvalues and the eigenfunctions are calculated. For high energies the solutions have the known correct simple potential-well behavior. The applicability of this model to the case of a crystal in an applied electric field is discussed.

However, to get a more accurate picture (including the periodic potential and its effect), we have treated a model—a one-dimensional Mathieu-type finite crystal in an electric field—which incorporates enough real crystal properties to give us a clear picture of the main features, albeit only numerically. Changes in the energy distribution and in the eigenfunctions in the presence of the field are covered in detail, as well as side issues dealing with the finiteness of the crystal and with the influence of the boundary conditions. In Sec. III the problem is stated and discussed, and the different types of boundary conditions with which we deal are compared, using an extension of the Born-Ledderman (BL) theorem (Appendix D). The picture of the behavior of the crystal in the presence of the field is clarified using the numerical results. The decrease of the forbidden gap between two energy bands is shown as a function of the field. No Stark ladder is obtained in the energy spectrum. The two limiting cases of zero field and a strong field are considered and are shown to agree with the expected results. Wave functions for several field values are compared. In Sec. IV it is shown that for this finite model the effective-mass approximation (EMA) is really a very good approximation even for relatively high fields.

II. EMPTY LATTICE

Let us begin by solving the case of a semifree electron in an electric field; i.e., we take a potential well to represent the crystal (Fig. 1). The important point is the finite range of this well. The