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Theory of the Electronically Induced Crystallographic Transition

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An exactly solvable model is formulated for the electronically induced crystallographic transition. The model contains the essential and new feature that the distortion is conceived to be an operator. This entails a better understanding of the processes involved in this type of transition.

One of the possible explanations of the metal-nonmetal transition is in terms of the electronically induced crystallographic transition. This transition is thought to be a product of the competition between the lattice energy and the energy of the electrons. A crystalline distortion will split up the energy bands resulting in a lower energy of the electron system in case the original conduction band is partly filled, while the lattice energy is raised by the distortion. In this way a competition between the lattice and electronic energies is obtained.

This effect has been studied by Adler and Brooks.[1] Starting from a linear chain of δ potentials they obtained criteria for this type of transition. These criteria were applied to several models, e.g., a model in which the energy bands are spherical around the conduction- and valence-band edges. In most cases Adler and Brooks obtained a first-order phase transition. The case of a linear chain of one-dimensional δ potentials, however, always gives rise to a second-order phase transition as has been shown recently.[2] The effect was also studied by Labbé and Friedel.[3,4] Their three-dimensional model exhibits a first-order phase transition.

The theory of the electronically induced crystallographic transition as formulated up till now is a static theory; i.e., the electron-lattice interaction introduced by the distortion is described by a parameter. Minimization of the total free energy with respect to this distortion parameter yields the equilibrium value of the distorted system for a fixed temperature and also determines the order of the phase transition.

The purpose of this paper is to present a dynamic theory of the electronically induced crystallographic transition; i.e., the distortion is considered to be an operator.[5] The great advantage of this dynamic model with regard to the static model is that the equilibrium value of the distortion can be calculated directly by means of the methods of quantum statistical mechanics without resorting to the minimization procedure. This is significant because the real nature of the electron-lattice interaction, which is intro-

duced by the distortion, is revealed in this way. Because of mathematical simplicity this Letter will be concerned with the case of a one-dimensional crystal.

Consider a one-dimensional crystal composed of two interpenetrating sublattices. Shifting one sublattice with respect to the other distorts the electronic band structure of the crystal. In the following the case will be considered of one band, which is split up by the distortion into two sub-bands. Because the lattice energy is raised by an amount $\frac{1}{2}A\tau^2$, where τ denotes the shift of both sublattices with respect to each other, the Hamiltonian of the total system reads[2]

$$H=\sum_{n=1,\sigma}^{2N}\epsilon_n(\tau)c_{n,\sigma}{}^{\dagger}c_{n,\sigma}+\tfrac{1}{2}A\tau^2, \tag{1}$$

where $\epsilon_n(0)=\epsilon_n$ denotes the band structure in the nondistorted case and $2N$ the total number of energy levels within that band. The operators $c_{n,\sigma}{}^{\dagger}$ and $c_{n,\sigma}$ are the well-known fermion creation and annihilation operators associated with the Bloch function $\varphi_n(x)|\sigma\rangle$, which has the periodicity of the distorted system. The free energy of the total system reads

$$F=N_0\mu-\frac{2}{\beta}\sum_{n=1}^{2N}\ln(1+\exp\{\beta[\mu-\epsilon_n(\tau)]\})+\tfrac{1}{2}A\tau^2, \tag{2}$$

where N_0 denotes the total number of electrons present and μ the Fermi energy, which is determined by

$$N_0=2\sum_{n=1}^{2N}\frac{1}{1+\exp\{\beta[\epsilon_n(\tau)-\mu]\}^{-1}}. \tag{3}$$

The temperature dependence of τ is obtained by minimizing expression (2) with respect to τ. This function $\tau(\beta)$ decides about the eventual appearance of a phase transition and about the order of the phase transition.

In order to treat the electronically induced crystallographic transition in terms of a dynamic model, the distortion τ has to be conceived as a dynamical variable. An additional term, however, has to be incorporated into the Hamiltonian of the dynamic model. This term is the kinetic energy $P^2/2M$ due to the relative motion of both sublattices with respect to each other, where $2M$ denotes the total mass of a sublattice and it is assumed that both sublattices are identical. P and τ are conjugate variables. Expanding $\epsilon_n(\tau)$ aroung $\tau=0$ and assuming the distortion to be small, the following Hamiltonian has to be considered:

$$H=\sum_{n=1,\sigma}^{2N}\epsilon_n c_{n,\sigma}{}^{\dagger}c_{n,\sigma}-\tau\sum_{n=1,\sigma}^{N}v_n c_{n,\sigma}{}^{\dagger}c_{n,\sigma}+\tau\sum_{n=N+1,\sigma}^{2N}v_n c_{n,\sigma}{}^{\dagger}c_{n,\sigma}+\frac{P^2}{2M}+\tfrac{1}{2}A\tau^2, \tag{4}$$

where $v_n=(d\epsilon_n/d\tau)_{\tau=0}$ and the term

$$-\tau\sum_{n=1,\sigma}^{N}v_n c_{n,\sigma}{}^{\dagger}c_{n,\sigma}$$

is the electron-lattice interaction of the electrons situated in the lower sub-band, the minus sign arising from the fact that the band is shifted downwards, while the term

$$\tau\sum_{n=N+1}^{2N}v_n c_{n,\sigma}{}^{\dagger}c_{n,\sigma}$$

denotes the electron-lattice interaction of the electrons in the upper sub-band. Changing to a second quantized representation for the harmonic oscillator, the Hamiltonian of the dynamic model reads

$$H=\sum_{n=1,\sigma}^{2N}\epsilon_n c_{n,\sigma}{}^{\dagger}c_{n,\sigma}-\sum_{n=1,\sigma}^{N}w_n(b+b^{\dagger})c_{n,\sigma}{}^{\dagger}c_{n,\sigma}+\sum_{n=N+1,\sigma}^{2N}w_n(b+b^{\dagger})c_{n,\sigma}{}^{\dagger}c_{n,\sigma}+\omega(b^{\dagger}b+\tfrac{1}{2}), \tag{5}$$

where $w_n=v_n/(2M\omega)^{1/2}$ and $\omega^2=A/M$. Using the unitary transformation

$$\tilde{H}=\exp(-S)H\exp(S)=H+[H,S]+\frac{1}{2!}[[H,S],S]+\cdots, \tag{6}$$

where

$$S = -\sum_{n=1,\sigma}^{N} \frac{w_n}{\omega}(b - b^\dagger)c_{n,\sigma}{}^\dagger c_{n,\sigma} + \sum_{n=N+1,\sigma}^{2N} \frac{w_n}{\omega}(b - b^\dagger)c_{n,\sigma}{}^\dagger c_{n,\sigma}, \tag{7}$$

the following unitarily equivalent Hamiltonian is obtained:

$$\begin{aligned}\tilde{H} = {} & \sum_{n=1,\sigma}^{2N} \epsilon_n c_{n,\sigma}{}^\dagger c_{n,\sigma} - \frac{1}{2A}\sum_{n=1,\sigma_1}^{N}\sum_{m=1,\sigma_2}^{N} v_n v_m c_{n,\sigma_1}{}^\dagger c_{n,\sigma_1} c_{m,\sigma_2}{}^\dagger c_{m,\sigma_2} \\ & - \frac{1}{2A}\sum_{n=N+1,\sigma_1}^{2N}\sum_{m=N+1,\sigma_2}^{2N} v_n v_m c_{n,\sigma_1}{}^\dagger c_{n,\sigma_1} c_{m,\sigma_2}{}^\dagger c_{m,\sigma_2} \\ & + \frac{1}{A}\sum_{n=1,\sigma_1}^{N}\sum_{m=N+1,\sigma_2}^{2N} v_n v_m c_{n,\sigma_1}{}^\dagger c_{n,\sigma_1} c_{m,\sigma_2}{}^\dagger c_{m,\sigma_2} + \omega(b^\dagger b + \tfrac{1}{2}).\end{aligned} \tag{8}$$

It follows immediately from expression (8) that the effect of the distortion can be described in terms of an effective electron-electron interaction. This interaction is attractive for electrons situated in the same sub-band but repulsive and twice as strong in case both electrons are situated in different sub-bands. The mechanism of the phase transition now becomes clear. Electrons are thermally excited from the lower to the upper sub-band. In case there are practically no electrons present in the upper sub-band, a lot of energy is required in order to excite an electron from the lower to the upper sub-band. The more electrons are excited, however, the easier the next one can be excited. In this way a positive feedback is obtained and the scene is set for a phase transition.

The information concerning the order of the transition is obtained by calculating $\langle \tau \rangle$. After some calculations the following transcendental equation results:

$$\langle \tau \rangle = \frac{2}{A}\sum_{n=1}^{N} \frac{v_n}{1+\exp[\beta\{(\epsilon_n - \mu) - v_n\langle\tau\rangle\}]} - \frac{2}{A}\sum_{n=N+1}^{2N} \frac{v_n}{1+\exp[\beta\{(\epsilon_n - \mu) + v_n\langle\tau\rangle\}]}. \tag{9}$$

The Fermi energy μ is determined by

$$\sum_{n=1}^{N} \frac{1}{1+\exp[\beta\{(\epsilon_n - \mu) - v_n\langle\tau\rangle\}]} + \sum_{n=N+1}^{2N} \frac{1}{1+\exp[\beta\{(\epsilon_n - \mu) + v_n\langle\tau\rangle\}]} = \frac{N_0}{2}, \tag{10}$$

where N_0 denotes the total number of electrons present. The transcendental equation (9) has to be solved graphically. Above a certain temperature $T_c \neq 0$ only one solution exists, namely, $\langle\tau\rangle = 0$. Below T_c, however, more than one solution is obtained. In general a solution with $\langle\tau\rangle \neq 0$ results in the lowest free energy.

Obviously the dynamic model differs from the static model in the sense that the distortion is assumed to be an operator and that it contains an additional kinetic energy term due to the relative motion of both sublattices with respect to each other. Nevertheless both models give rise to the same transcendental equation. The dynamic model, however, gives more insight into the physical processes involved in order to arrive at this transcendental equation.

Finally it should be remarked that the dynamic model is exactly solvable and as such joins the small class of model Hamiltonians (like the BCS Hamiltonian in superconductivity[6]), which can be analyzed exactly and in every detail.

More details concerning the calculations and the extension to more dimensions will be presented in a forthcoming paper.

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