

Theory of the Electronically Induced Crystallographic Transition. II

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A recently presented dynamic model concerning the electronically induced crystallographic transition is solved rigorously with higher-order terms in the distortion operator also taken into account.

There exist several theories concerning the metal-nonmetal transition (see review articles by Adler¹). One of these theories explains the metal-nonmetal transition in terms of the electronically induced crystallographic transition, which is thought to result from the competition between the lattice energy and the energy of the electrons. In its basic form, the theory is the following. Consider a one-dimensional crystal composed of two interpenetrating identical sublattices. With the assumption of one electron per lattice site, the system will behave like a metal according to band theory for the case that the system has a single periodicity, i.e., the distance between neighboring lattice sites is the same. This situation is defined to be nondistorted. Shifting both sublattices with respect to each other results into a splitting of the original bands, which leads to lower energy of the elec-

tron system but an increased lattice energy. The distorted system will behave like a semiconductor or an insulator depending on the magnitude of the energy gap. Supposing the lattice energy to be raised by an amount $\frac{1}{2}A\tau^2$, where τ denotes the shift of both sublattices with respect to each other, and taking into account only the original conduction band, we can write the Hamiltonian of the total system as²

$$H_N = \sum_{n=1}^{2N} \sum_{\sigma} \epsilon_n(\tau) c_{n,\sigma}^{\dagger} c_{n,\sigma} + \frac{1}{2}A\tau^2, \quad (1)$$

where $\epsilon_n(\tau)$ denotes the band structure in the distorted case and $2N$ the total number of energy levels. The operators $c_{n,\sigma}^{\dagger}$ and $c_{n,\sigma}$ are the well-known fermion creation and annihilation operators associated with the Bloch function $\varphi_n(x)|\sigma$ that has the periodicity of the distorted system. The free energy per electron of the total system is given by

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

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

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

Using the well-known thermodynamical argument that the free energy of a system assumes its lowest value in thermal equilibrium, the temperature dependence of τ is obtained by solving the transcendental equation

$$\frac{\partial f}{\partial \tau} = \frac{2}{N_0} \sum_{n=1}^{2N} \frac{d\epsilon_n}{d\tau} (1 + \exp\{\beta[\epsilon_n(\tau) - \mu]\})^{-1} + \frac{A}{N_0} \tau = 0. \quad (4)$$

The resulting function $\tau(\beta)$ contains the information concerning the eventual appearance of a phase transition and about the order of the phase transition.

In a recent paper³ we presented a dynamic theory of the electronically induced crystallographic transition. In this theory the distortion τ is conceived to be an operator. Adding the kinetic energy term $P^2/2M$ due to the relative motion of both sublattices with respect to each other, where $2M$ denotes

the total mass of a sublattice, we obtain the following Hamiltonian:

$$H_N = \sum_{n=1, \sigma}^{2N} \epsilon_n(\tau) c_{n, \sigma}^\dagger c_{n, \sigma} + \frac{P^2}{2M} + \frac{1}{2} A \tau^2. \quad (5)$$

P and τ are conjugate variables. The derivation of this Hamiltonian is based on the well-known adiabatic approximation of Born and Oppenheimer.⁴ The advantage of taking the distortion to be an operator is that the nature of the electron-lattice interaction is revealed and that the equilibrium value of the distortion can be obtained directly by means of quantum statistical mechanics without resorting to the minimization procedure. Taking into account only terms linear in τ it was shown by means of a unitary transformation that

the effect of the distortion can be described in terms of an effective electron-electron interaction. This interaction appears to be 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 purpose of this paper is to present the solution of the general case, where higher-order terms in τ also have to be taken into account. Changing to a second-quantized representation for the harmonic oscillator,

$$P = i(\hbar M \omega / 2)^{1/2} (b^\dagger - b), \quad (6)$$

$$\tau = (\hbar / 2M\omega)^{1/2} (b^\dagger + b),$$

where $\omega^2 = A/M$ and $[b, b^\dagger] = 1$, the Hamiltonian of the dynamic model reads

$$H_N = \sum_{n=1}^{2N} \sum_{\sigma} \sum_{k=0}^{\infty} \frac{\epsilon_n^{(k)}(0)}{k!} \left(\frac{\hbar}{2M\omega} \right)^{k/2} (b^\dagger + b)^k c_{n, \sigma}^\dagger c_{n, \sigma} + \hbar \omega (b^\dagger b + \frac{1}{2}). \quad (7)$$

$\epsilon_n^{(0)}(0)$ denotes the band structure in the nondistorted situation and $\epsilon_n^{(k)}(0) \equiv (d^k \epsilon_n / d\tau^k)_{\tau=0}$. Using the commutation relations for fermion and boson operators it follows that

$$[H_N - \mu N_e, c_{i, \sigma}^\dagger] = \sum_{k=0}^{\infty} \frac{\epsilon_i^{(k)}(0)}{k!} \left(\frac{\gamma}{\Omega} \right)^{k/2} (b^\dagger + b)^k c_{i, \sigma}^\dagger - \mu c_{i, \sigma}^\dagger, \quad (8a)$$

$$[H_N - \mu N_e, b^\dagger] = \hbar \omega b^\dagger + \left(\frac{\gamma}{\Omega} \right)^{1/2} \sum_{n=1, \sigma}^{2N} \sum_{k=1}^{\infty} \frac{\epsilon_n^{(k)}(0)}{(k-1)!} \left(\frac{\gamma}{\Omega} \right)^{(k-1)/2} (b^\dagger + b)^{k-1} c_{n, \sigma}^\dagger c_{n, \sigma}, \quad (8b)$$

where

$$\gamma / \Omega = \hbar / 2M\omega \text{ and } N_e = \sum_{n=1, \sigma}^{2N} c_{n, \sigma}^\dagger c_{n, \sigma}.$$

Besides M , N and N_0 also are proportional to Ω . Let us define

$$s = \lim_{\Omega \rightarrow \infty} b^\dagger / \sqrt{\Omega}. \quad (9)$$

Clearly this operator is a space average, i.e., it belongs to the center in a homogeneous representation.⁵ In the following it will be assumed that the thermodynamic-limit state is homogeneous and extremal invariant for space translations, i.e., s is a c number. This is not a serious limitation at all, because every homogeneous state can be decomposed into extremal ones. It also follows immediately that $\tau = 2\gamma^{1/2}s$ is a c number in the thermodynamic limit. This c number will be called $\langle \tau \rangle$. If we then take the thermodynamic limit, the equation of motion (8a) reads

$$\lim_{\Omega \rightarrow \infty} [H_N - \mu N_e, c_{i, \sigma}^\dagger] = [\epsilon_i(\langle \tau \rangle) - \mu] c_{i, \sigma}^\dagger. \quad (10)$$

Clearly, the Hamiltonian

$$H = \sum_{n, \sigma} [\epsilon_n(\langle \tau \rangle) - \mu] c_{n, \sigma}^\dagger c_{n, \sigma} \quad (11)$$

yields the correct time translation in the thermodynamic limit. This Hamiltonian gives rise to the

following time translation:

$$c_{l,\sigma}^\dagger(t) = c_{l,\sigma}^\dagger \exp\{-i[\epsilon_l(\langle\tau\rangle) - \mu]t\}. \quad (12)$$

Using the Kubo-Martin-Schwinger boundary condition⁶ it follows that

$$\langle c_{l,\sigma}^\dagger c_{l,\sigma} \rangle = (1 + \exp\{\beta[\epsilon_l(\langle\tau\rangle) - \mu]\})^{-1}. \quad (13)$$

The temperature dependence of $\langle\tau\rangle$ is determined by⁷

$$\lim_{\Omega \rightarrow \infty} \left[H_N - \mu N_e, \frac{b^\dagger}{\sqrt{\Omega}} \right] = 0 = \hbar\omega_S + \frac{\gamma^{1/2}}{\Omega} \sum_{n,\sigma} \frac{d\epsilon_n(\langle\tau\rangle)}{d\langle\tau\rangle} c_{n,\sigma}^\dagger c_{n,\sigma}. \quad (14)$$

Because the state is assumed to be homogeneous and extremal invariant for space translations, the operator

$$\lim_{\Omega \rightarrow \infty} \frac{1}{\Omega} \sum_{n,\sigma} \frac{d\epsilon_n(\langle\tau\rangle)}{d\langle\tau\rangle} c_{n,\sigma}^\dagger c_{n,\sigma}$$

is also a c number. After some trivial calculations it follows that relation (14) is the same as relation (4), which was obtained by the minimization procedure. The conclusion is obvious; The dynamic model is equivalent to the static model in the thermodynamic limit for the case that the state of the system is assumed to be homogeneous and extremal invariant for space translations. This results from the fact that both sublattices become infinitely heavy in the thermodynamic limit.

Although only a one-dimensional model is considered in this paper, the last result holds also for higher dimensional models. Further details concerning the calculations and the extension to higher dimensionality will be presented in a forthcoming paper.

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Photoemission Studies of the Oxidation of Strontium*

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The oxidation of strontium has been studied by ultraviolet photoelectron spectroscopy. Minimal oxidation produces a relatively sharp peak (width about 0.5 eV) in the energy distribution curves originating from a state 5.0 eV below the Fermi level; this state is seen to broaden strongly into a band as the O^{2-} concentration increases and $O^{2-}-O^{2-}$ overlap occurs. The metallic component of the emission appears to originate from a thin layer near the surface and is little affected by the oxidation.

It is well known that the alkaline-earth metals such as Sr react readily with gases such as oxygen, forming quite stable compounds.¹ The surfaces of these metals do not passivate as do those

of metals such as Al, and complete oxidation of typical samples occurs in air in relatively short times.¹ In this Letter we report on the study of changes in electronic structure of an Sr film dur-