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SEMIPHENOMENOLOGICAL APPROACH TO THE PROBLEM OF DISCONTINUOUS CHANGE OF VALENCE *

J. Zieliński **
International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

Simple, semiphenomenological theory of the abrupt change of valence in SmS is presented. The phase transition and the softening of the phonon mode can be considered as being due to the partial decoupling of phonons from the electronic system.

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** Permanent address: Institite of Physics, Silesian University, Uniwersytecka 4, Katowice, Poland.

The electron-phonon coupling is believed to be the possible mechanism which enables the theoretical explanation of the pressure induced change of valence as observed experimentally in SmS [1-4]. The appearance of this type of phase transition within purely electronic models seems to be due to the approximations ([5-8] and references cited therein). Recently, the atomic limit of the extended Falicov-Kimball model [5,6] coupled to phonons has been considered [9]. It has been found that at least for some special choice of parameters the discontinuous change of the occupation number of f-level $\langle n^f \rangle$ as a function of its energy E (which parametrizes the pressure) can be considered as an exact result [9]. In Refs.1,2 and 9 the phonon induced hybridization is assumed to be of primary importance for the phase transition as leading to the renormalization of the hybridization parameter. The effective hybridization can change its sign which leads to the discontinuous change of valence [1,9]. However, the physical interpretation of the vanishing of hybridization is not clear [2]. It should be noted that in Refs.1, 2, 3 and 9 the d-electron-phonon interaction is not considered.

The aim of the present note is to propose the simple semiphenomenological theory of the abrupt change of valence. Let us take into account that the electron-phonon coupling constant is proportional to the overlap integral in tight-binding approximation [10,4]. Thus, one can neglect the d-electron-phonon interaction only in the case that there are no d electrons at all. However, if there is at least small admixture of d states at the site, the coupling of phonons with d electrons, g_d, can be of some importance, being comparable with g_f. Such a situation can take place in the vicinity of the phase transition in SmS and we suppose that the values of g_f and g_d should depend on the average occupation numbers $\langle n^f \rangle$ and $\langle n^d \rangle$ in some way which enables the change of the sign of $g_f - g_d$ in the vicinity of the transition.

Let us consider the atomic limit of the extended spinless Falicov-Kimball model including the interaction of phonons with both types of electrons. The second-quantized form of the Hamiltonian can be written as

$$H = \varepsilon n^d + E n^f + V(f^+ d + d^+ f) + G n^f n^d + g^d n^d (b^+ + b) + g_f n^f (b^+ + b) + \hbar\omega_0 b^+ b , \tag{1}$$

where f,d (f^+,d^+) denote the annihilation (creation) operators for f,d electron and b,b^+ are those for phonon. $n^{f,d}$ stands for the corresponding electron number operator and V,G are the hybridization and Coulomb repulsion parameters, respectively. The simple canonical transformation of the type used by other authors [4,11] leads to the equivalent Hamiltonian

$$\tilde{H} = e^{-S} H e^{S} \quad , \quad S = -\frac{g_d}{\hbar\omega_0} n^d (b^+ - b) - \frac{g_f}{\hbar\omega_0} n^f (b^+ - b) \quad , \tag{2}$$

where

$$\tilde{H} = \tilde{\varepsilon} n^d + \tilde{E} n^f + \tilde{G} n^f n^d + V\{d^+ f \exp[\frac{g_d - g_f}{\hbar\omega_0}(b^+ - b)] + h.c.\} , \tag{3}$$

$$\tilde{\varepsilon} = \varepsilon - \frac{g_d^2}{\hbar\omega_0} \quad , \quad \tilde{E} = E - \frac{g_f^2}{\hbar\omega_0} \quad , \quad \tilde{G} = G - \frac{2 g_d g_f}{\hbar\omega_0} . \tag{4}$$

Let us consider the second order terms with respect to the electron-phonon coupling and neglect the term linear in $b^+ - b$. This implies the quantitative modification only and is unimportant for qualitative discussion [9]. Then, the average number of f-electrons can be derived solving exactly the eigen problem ($\langle n^f \rangle + \langle n^d \rangle = 1$).

$$\langle n^f \rangle = \frac{1 + \frac{1}{2}[1 + \frac{\tilde{E} - \tilde{\varepsilon}}{\Delta}]\exp(\frac{1}{2}\beta(\tilde{G} - \Delta)) + \frac{1}{2}[1 - \frac{\tilde{E} - \tilde{\varepsilon}}{\Delta}]\exp(\frac{1}{2}\beta(\tilde{G} + \Delta))}{2 + \exp(\frac{1}{2}\beta(\tilde{G} - \Delta)) + \exp(\frac{1}{2}\beta(\tilde{G} + \Delta))} , \tag{5}$$

where

$$\Delta = \sqrt{(\tilde{E} - \tilde{\varepsilon})^2 + 4\tilde{V}^2} \quad , \quad \tilde{V} = V\left(1 - \frac{1}{2(\hbar\omega_0)^2}(g_d - g_f)^2 \operatorname{ctgh}\frac{\beta\hbar\omega_0}{2}\right) , \tag{6}$$

and $\beta = (kT)^{-1}$.

In order to perform the calculations we assume the dependence of $g_{f,d}$ on $\langle n^f \rangle$

$$g_d = gA(1 - \langle n^f \rangle)^x \quad , \quad g_f = g\langle n^f \rangle^x , \tag{7}$$

which seems to be quite general and g,A,x are parameters. Then (5) becomes an equation for $\langle n^f \rangle$. We have found that the special form of $g_d(g_f)$ is not of crucial importance for the appearance of the transition (three-fold solution of (5)) which is governed by the value of g and the change of sign of $g_d - g_f$. Due to the fact that $g_d - g_f$ appears in $\tilde{E} - \tilde{\varepsilon}_0$, the second order theory does not seem to be the serious restriction.

The results for some values of parameters are presented in Figs.1 and 2. The insertion in Fig.2b shows that the transition disappears with increasing temperature and its position shifts slightly towards higher pressure (E parametrizes the pressure), similarly to the results of Entel and Leder [1]. Let us mention that in our case the phase transition takes place for finite value of effective hybridization.

One can take the hopping term for d electrons into account. Up to the second order this term transforms as

$$\widetilde{\sum_{i,j} t_{ij} d_i^+ d_j} = \sum_{i,j} t_{ij} d_i^+ d_j \Big\{1 - \frac{g_d}{\hbar\omega_0}[(b_j^+ - b_j) - (b_i^+ - b_i)]$$

$$- \left(\frac{g_d}{\hbar\omega_0}\right)^2 (b_i^+ - b_i)(b_j^+ - b_j) + \frac{1}{2}\left(\frac{g_d}{\hbar\omega_0}\right)^2 [(b_j^+ - b_j)^2 + (b_i^+ - b_i)^2]\Big\} , \tag{8}$$

which within the second order (and linear in t_{ij}) theory leads to the modification of the band energy

$$\varepsilon_k \rightarrow \tilde{\varepsilon}_k \left(1 - \left(\frac{g_d}{\hbar\omega_0}\right)^2 \operatorname{ctgh}\frac{\beta\hbar\omega_0}{2}\right) . \tag{9}$$

The finite band width of d electrons decreases the tendency to an abrupt transition [7] but its appearance within the atomic limit will be in general transmitted to the periodic (finite band width) case. We shall not discuss this problem here due to the fact that the periodic model is no longer exactly solvable and some approximations must be introduced [5,6].

Let us mention that in the present approach the softening of the phonon mode [1,4] in the vicinity of the phase transition is connected with partial decoupling of phonons from the electronic system. This is realized by vanishing of $g_d - g_f$ in the local part (3) of the model periodic Hamiltonian.

In conclusion, it seems worthwhile to look for the microscopic justification of the dependence of local electron-phonon coupling constant on the average number of electrons of the lattice site.

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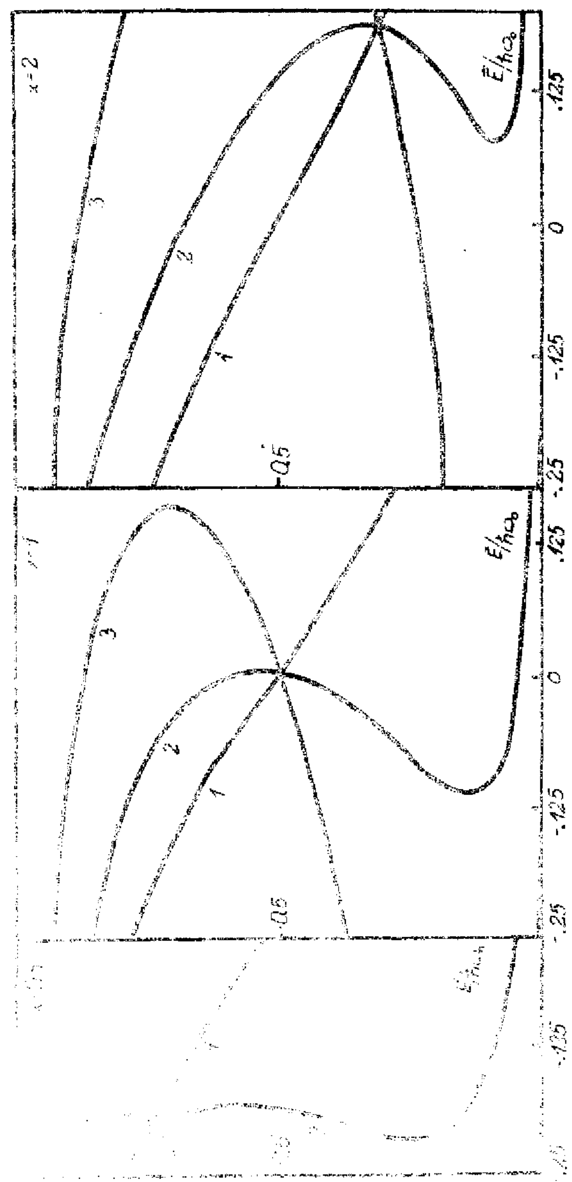

Fig.1 $\langle n^f \rangle$ as a function of E for T = 0, $g/\hbar\omega_0 = 0.5$, $v/\hbar\omega_0 = 0.3$. The numbers at the curves show the values of A (dimensionless). $\bar{E} = E + g^2/\hbar\omega_0 (A^2 - 1)$.

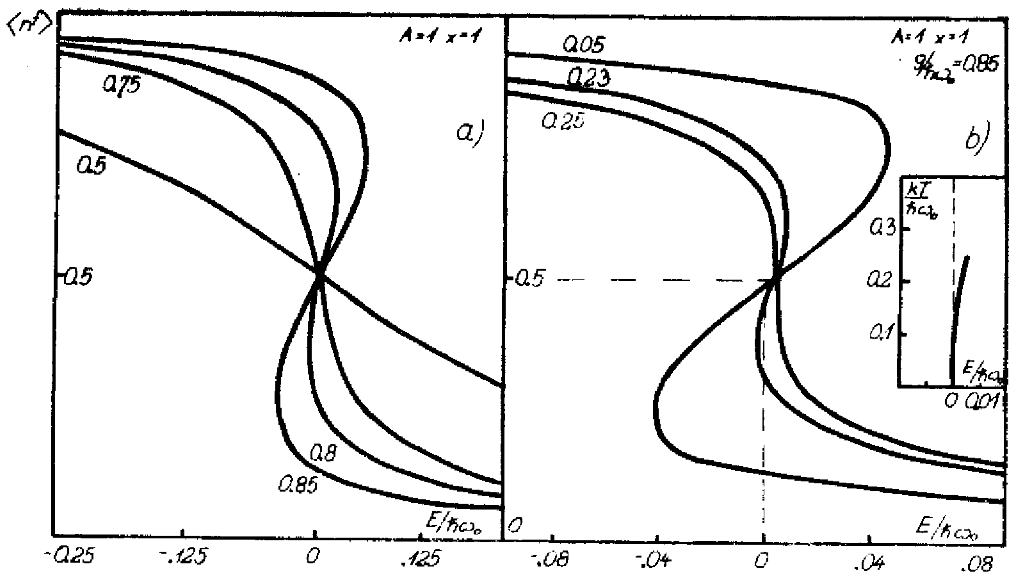

Fig.2 a) $\langle n^f \rangle$ as a function of E for different values of $g/\hbar\omega_0$ showed by the numbers at the curves T = 0, $v/\hbar\omega_0 = 0.3$.
b) $\langle n^f \rangle$ as a function of E for different temperatures $(kT/\hbar\omega_0)$, showed by the numbers at the curves, $v/\hbar\omega_0 = 0.3$, $G/h\omega_0 = 4.0$. In the insertion the phase boundary is presented.