On the role of phonons in intermediate valence compounds

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Résumé. — On a étudié l'influence des phonons sur le diagramme de phase pression-température (P, T) des terres rares ayant une valence intermédiaire. Nous montrons que les transitions 4f-5d causées par les phonons mènent à une valeur renormalisée $\tilde{V}$ de l'énergie d'hybridisation V et que cette valeur $\tilde{V}$ peut s'annuler et changer de signe. On montre ensuite que ce comportement de $\tilde{V}$ est une condition nécessaire pour un changement discontinu de l'occupation de l'état 4f. Le modèle décrit correctement la pente positive ($\mathrm{d}P/\mathrm{d}T > 0$) de la limite de la phase de valence intermédiaire, qui se termine par un point critique.

Abstract. — The influence of phonons on the pressure-temperature (P, T) phase diagram of intermediate valence compounds is investigated. It is shown that due to phonon induced 4f-5d interband transitions, the renormalized value $\tilde{V}$ of the hybridization energy V of 4f and conduction electrons may become zero and change its sign and that this is a necessary condition for a discontinuous change of the occupation of the 4f state. The model describes correctly the positive slope ($\mathrm{d}P/\mathrm{d}T > 0$) of the phase boundary of the mixed valence state which terminates in a critical point.

1. **Extended periodic Anderson model.** — The influence of phonons on the pressure-temperature (P, T) phase diagram of intermediate valence compounds has been calculated on the basis of the periodic Anderson model which was extended to include the interaction of 4f electrons and longitudinal optical phonons. The model Hamiltonian is then

$$\begin{aligned}\mathcal{H} = \sum_{k\sigma} \varepsilon_k\, d_{k\sigma}^+ d_{k\sigma} &+ \\ &+ \sum_{i\sigma} \left[E_0\, f_{i\sigma}^+ f_{i\sigma} + \frac{U}{2} f_{i\sigma}^+ f_{i\sigma} f_{i,-\sigma}^+ f_{i,-\sigma} \right] \\ &+ V \sum_{i\sigma} [f_{i\sigma}^+ d_{i\sigma} + H.c.] \\ &- \sum_{i\sigma} [g_1 f_{i\sigma}^+ f_{i\sigma} + g_2 (f_{i\sigma}^+ d_{i\sigma} + H.c.)]\, \varphi_i \\ &+ \sum_i \hbar\Omega (b_i^+ b_i + \tfrac{1}{2}) \qquad (1)\end{aligned}$$

with $\varphi_i = b_i + b_i^+$. The first three terms represent the periodic Anderson model. The g_1-electron phonon term is the usual density type of coupling of 4f electrons and phonons and leads to a weakly temperature dependent renormalization of the position E_0 of the 4f level with respect to the 5d band. It does not change the second order phase transition between the semiconducting and the intermediate valence phase [1]. The g_2-term induces 4f-5d interband transitions leading to a renormalized value $\tilde{V}$ of the hybridization energy V of 4f and 5d conduction electrons. These phonon effects are directly visible if we replace (1) by the Ersatz Hamiltonian :

$$\begin{aligned}\mathcal{H}_{\mathrm{HF}} = \sum_{k\sigma} \varepsilon_k\, d_{k\sigma}^+ d_{k\sigma} + \sum_{i\sigma} \tilde{E}_{i\sigma} f_{i\sigma}^+ f_{i\sigma} &+ \\ + \sum_{i\sigma} \tilde{V}_i [f_{i\sigma}^+ d_{i\sigma} + H.c.] & \\ + \sum_i \hbar\Omega ([b_i^+ - \langle b_i^+ \rangle][b_i - \langle b_i \rangle] + \tfrac{1}{2}) & \qquad (2)\end{aligned}$$

with

$$\tilde{E}_{i\sigma} = E_0 + U \langle n_{i,-\sigma}^{\mathrm{f}} \rangle - g_1 \langle \varphi_i \rangle \qquad (3)$$

$$\tilde{V}_i = V - g_2 \langle \varphi_i \rangle \qquad (4)$$

$$\langle \varphi_i \rangle = \sum_\sigma \left\{ \frac{2 g_1}{\hbar\Omega} \langle n_{i\sigma}^{\mathrm{f}} \rangle + \frac{2 g_2}{\hbar\Omega} \langle a_{i\sigma} \rangle \right\} \qquad (5)$$

$$\langle a_{i\sigma} \rangle = \langle f_{i\sigma}^+ d_{i\sigma} + H.c. \rangle . \qquad (6)$$

From (3) and (4) we see that for $g_2 = 0$ only the position E_0 of the 4f level is shifted whereas the hybridization constant remains unchanged. Since the shift is only weakly temperature dependent the results are qualitatively the same as those for the pure periodic Anderson model considered in [2]. Moreover, in the state of lowest free energy, no abrupt change of $\langle n^{\mathrm{f}} \rangle = \langle n_\uparrow^{\mathrm{f}} + n_\downarrow^{\mathrm{f}} \rangle$ or $\langle n_\uparrow^{\mathrm{f}} - n_\downarrow^{\mathrm{f}} \rangle$ is found in contrast to the results for the extended 1 impurity Anderson model [3].

For $g_1 \neq 0$ and $g_2 \neq 0$ the renormalized value $\tilde{V}$ may become zero and change its sign. It has been shown in [1] that this is a necessary condition for a discontinuous change of $\langle n^{\mathrm{f}} \rangle$ as function of T or E_0 (E_0 is here taken as the parameter which changes linearly with pressure, while a change of the occupation number $\langle n^{\mathrm{f}} \rangle$ is assumed to be proportional to a change of the lattice constant of the system) : the requirement $\tilde{V}_i = 0$ for a discontinuous change of $\langle n^{\mathrm{f}} \rangle$ is in higher order perturbation theory connected with a maximal softening of a phonon mode [1]. Moreover, approximating $\tilde{V}_i$ by a two center integral using a 6s or 5d and 4f wave function on neighbouring sites one can easily demonstrate that the integral changes sign when the distance between the centers is appropriately changed [4].

2. **The (*P*, *T*)-phase diagram.** — The self-consistent solutions for $\langle n^f_{i\sigma} \rangle$, $\langle a_{i\sigma} \rangle$ and the chemical potential μ determine the line of first order phase transition in the (E_0, T)-plane. Figure 1 and figure 2 show stable nonmagnetic and magnetic solutions of the extended periodic Anderson model. The term mixed valence is in this connection employed for the phase which has a remarkably lowered occupation number.

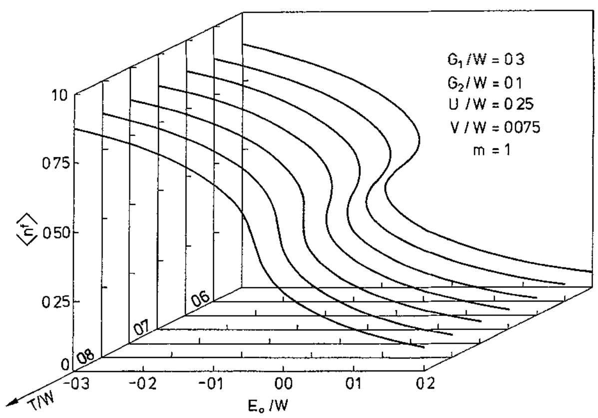

Fig. 1. — The disappearance of the first order phase transition of $\langle n^f \rangle$ as function of increasing temperature. W denotes the bandwidth, m is the number of electrons per site and $G_1 = 2\,g_1^2/\hbar\Omega$, $G_2 = 2\,g_2^2/\hbar\Omega$.

The behaviour of $\langle n^f \rangle (T)$ along the lines A and B is given in figure 3. This behaviour may be identified with the anomalous contraction of the phase along A and the anomalously large expansion of the intermediate valence phase along B. It agrees qualitatively with experimental data for the temperature dependent behaviour of the lattice constant in intermediate valence compounds [5].

We finally mention that the phase with the higher occupation of the 4f shell possesses the higher density of states (μ) due to the more pronounced f-character of the states in the vicinity of μ and hence possesses the higher entropy [6].

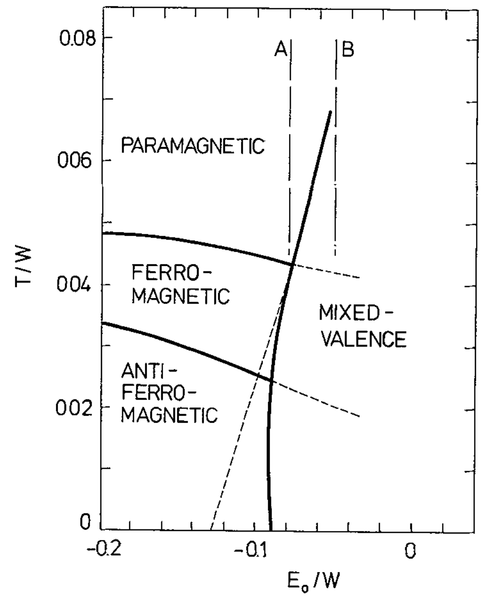

Fig. 2. — The (E_0, T)-phase diagram of the extended periodic Anderson model. The paramagnetic, ferromagnetic and antiferromagnetic phases are separated from the mixed valence phase by a line of first order phase transition. The dashed lines would be the continuation of the phase boundaries for the case that no magnetic ordering or no intermediate valence occurs. All parameter values are indicated in figure 1.

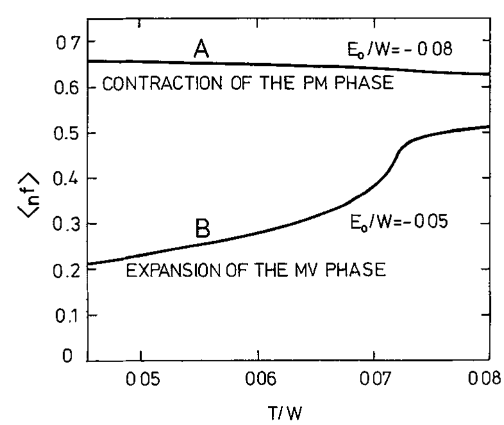

Fig. 3. — The anomalous behaviour of $\langle n^f \rangle$ as function of temperature along the lines A and B in figure 2.

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