PHYSICAL REVIEW B VOLUME 22, NUMBER 4 15 AUGUST 1980

Electron-phonon interaction in mixed-valence systems

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(Received 20 February 1980)

The importance of electron-phonon coupling in valence-fluctuation phenomena is discussed. It is shown that the electron-phonon renormalized d-f hybridization can account for the experimentally observed variation on the $4f$ width in some mixed-valence systems. A comparison is also made with previously obtained results.

It has been argued that the electron-phonon (EP) interaction plays an important role in the description of mixed-valence phenomena.[1] The significant variation of the ionic radii of a rare earth, when their electronic configurations change from $4f^n \rightleftarrows 4f^{n-1}$, is believed to excite the lattice degrees of freedom, and so the EP coupling is expected to be relevant. Experimental evidence can be found in a number of systems, e.g., softening of the longitudinal phonon modes in $\mathrm{Sm}_{0.75}\mathrm{Y}_{0.25}\mathrm{S}$.[2] This system also shows an anomalously broad longitudinal-optical mode in the same region where softening is stronger. These results have been interpreted as evidence of strong correlation between phonons and "valence fluctuation."[2]

Several theoretical works have appeared discussing the effects of the EP coupling on the renormalization of the purely electronic interactions.[1,3-8] The models discussed in these works show the importance of the EP contribution in the description of the mixed-valence systems by renormalizing the bare electronic interactions. The knowledge of these renormalizations modifies the validity of the range of the involved parameters giving a more realistic insight into the role of such renormalizations on the bare interactions, considered in pure electronic mixed-valence fluctuation models. Recently,[6] the effects of EP interaction were considered, using the canonical transformation method, within a one-site approximation. That work discussed the possibility of treating the proposed model Hamiltonian in the extreme limits pointed out by Sherrington and Riseborough,[1] namely, the static regime and the adiabatic one. Moreover, also considered was the possibility of including an intermediate regime depending on the approximations used to deal with the many-electron character of the effective Hamiltonian.

In the present work we intend to discuss the role of EP coupling in its most general form[5] using the displacement operator technique.[4] One starts from the following model Hamiltonian:

$$H = H^{\mathrm{el}} + H^{\mathrm{ph}} + H^{\mathrm{el-ph}}. \tag{1}$$

H^{el} stands for the pure electronic part of the Hamiltonian, which need not be specified at this point. H^{ph} describes the pure phononic contribution and is as usual written as

$$H^{\mathrm{ph}} = \sum_{\vec{q}} \hbar\omega_{\vec{q}} a_{\vec{q}}^{\dagger} a_{\vec{q}}, \tag{2}$$

where $a_{\vec{q}}$ $(a_{\vec{q}}^{\dagger})$ are annihilation (creation) phonon operators with wave vector $\vec{q}$ and energy ω.

$H^{\mathrm{el-ph}}$ represents a generalized electron-phonon interaction and is expressed by

$$H^{\mathrm{el-ph}} = \sum_{\vec{q}} A_{\vec{q}} (a_{\vec{q}} + a_{-\vec{q}}^{\dagger}) \tag{3}$$

with

$$A_{\vec{q}} = \sum_{\alpha,\beta} \sum_{\vec{k},\vec{q},\sigma} g_{\alpha\beta}^{\vec{k},\vec{q}} \alpha_{\vec{k}+\vec{q},\sigma}^{\dagger} \beta_{\vec{k},\sigma}. \tag{4}$$

Here $g_{\alpha\beta}^{\vec{k},\vec{q}}$ $(\alpha,\beta = f,d)$ denotes the EP couplings involving α- and β-like electrons and phonons with wave vector $\vec{q}$, whereas $\alpha_{\vec{k}\sigma}^{\dagger}, \alpha_{\vec{k}\sigma}$ $(\alpha = f,d)$ are the standard creation and annihilation fermion operators in Bloch states $\vec{k}$ with spin σ.

In order to decouple electrons and phonons, one defines the displacement operator

$$b_{\vec{q}}^{\dagger} = a_{\vec{q}}^{\dagger} + A_{\vec{q}}/\hbar\omega_{\vec{q}}. \tag{5}$$

So, the pure phononic and EP terms can be expressed as follows:

$$\begin{aligned} H^{\mathrm{ph}} + H^{\mathrm{el-ph}} &= \sum_{\vec{q}} \hbar\omega_{\vec{q}} \; b_{\vec{q}}^{\dagger} b_{\vec{q}} - \frac{A_{\vec{q}} A_{-\vec{q}}^{\dagger}}{\hbar\omega_{\vec{q}}} \\ &= \sum_{\vec{q}} \hbar\omega_{\vec{q}} b_{\vec{q}}^{\dagger} b_{\vec{q}} + H^{r}. \end{aligned} \tag{6}$$

Here H^r represents the correction to the pure electronic contribution H^{el} due to the EP coupling, i.e., the EP coupling is incorporated in the renormalized electron interactions mediated by phonons. H^r reads

$$\begin{aligned} H^{r} = - \sum_{\alpha,\beta,\alpha',\beta'} \sum_{\vec{k},\vec{q},\sigma,\vec{k}',\vec{q}',\sigma} \frac{g_{\alpha\beta}^{\vec{k},\vec{q}} g_{\alpha'\beta'}^{\vec{k}',\vec{q}'}}{h\omega_{\vec{q}}} \alpha_{\vec{k}+\vec{q},\sigma}^{\dagger} \\ \times \beta_{\vec{k},\sigma} \alpha'^{\dagger}_{\vec{k}'+\vec{q}',\sigma'} \beta'_{\vec{k}',\sigma'} \delta_{\vec{q},-\vec{q}'}. \end{aligned} \tag{7}$$

Notice that in Eq. (7) all possible renormalizations due to EP couplings are independent of the choice of the starting model electronic Hamiltonian H^{el}. Moreover, until now no approximation was performed to obtain H^r.

In the Wannier representation, the renormalized Hamiltonian

$$\tilde{H} = H^{\mathrm{el}} + H^r \tag{8}$$

is expressed by

$$\begin{aligned}\tilde{\tilde{H}} = {} & \sum_{i,\sigma} \tilde{\epsilon}_f n^f_{i\sigma} + \sum_{i,\sigma} \left\{ U_{ff} - \sum_{\vec{q}} \left[\left(\sum_{\vec{k}} g^{\vec{k},\vec{q}}_{ff} \right)^2 \Big/ \hbar\omega_{\vec{q}} \right] \right\} n^f_{i\sigma} n^f_{i\,-\sigma} + \sum_{l,j,\sigma} \tilde{T}_{lj} d^\dagger_{l\sigma} d_{j\sigma} \\ & + \sum_{l,\sigma} \left\{ U_{dd} - \sum_{\vec{q}} \left[\left(\sum_{\vec{k}} g^{\vec{k},\vec{q}}_{dd} \right)^2 \Big/ \hbar\omega_{\vec{q}} \right] \right\} n^d_{l\sigma} n^d_{l-\sigma} \\ & + \sum_{i,\sigma,\sigma'} \left(U_{df} - 2 \sum_{\vec{q}} \left\{ \left[\left(\sum_{\vec{k}} g^{\vec{k},\vec{q}}_{ff} \right) \left(\sum_{\vec{k}} g^{\vec{k},\vec{q}}_{dd} \right) + \left(\sum_{\vec{k}} g^{\vec{k},\vec{q}}_{fd} \right)^2 \delta_{\sigma\sigma'} \right] \Big/ \hbar\omega_{\vec{q}} \right\} n^d_{i\sigma} n^f_{i\sigma'} \right. \\ & + \sum_{i,j,\sigma} \left(V_{fd} f^\dagger_{i\sigma} d_{j\sigma} - \sum_{\vec{k},\vec{k}',\vec{q}} \sum_{\sigma'} \frac{1}{\hbar\omega_{\vec{q}}} g^{\vec{k}',-\vec{q}}_{fd} (g^{\vec{k},\vec{q}}_{ff} n^f_{i\sigma'} + g^{\vec{k},\vec{q}}_{dd} n^d_{i\sigma'}) \right. \\ & \qquad \left. \times \left(e^{i\vec{k}'\cdot(\vec{R}_i - \vec{R}_j)} f^\dagger_{i\sigma} d_{j\sigma} + e^{-i(\vec{k}'-\vec{q})\cdot(\vec{R}_i - \vec{R}_j)} d^\dagger_{j\sigma} f_{i\sigma} \right) \right) + \mathrm{H.c.},\end{aligned} \tag{9}$$

where

$$\tilde{\epsilon}_f = \epsilon_f - \sum_{\vec{q}} \left[\left(\sum_{\vec{k}} g^{\vec{k},\vec{q}}_{fd} \right)^2 \Big/ \hbar\omega_{\vec{q}} \right] \tag{10a}$$

and

$$\tilde{T}_{lj} = T_{lj} - \sum_{\vec{q}} \left[\left(\sum_{\vec{k}} g^{\vec{k},\vec{q}}_{fd} \right)^2 \delta_{lj}\delta_{li} \Big/ \hbar\omega_{\vec{q}} \right], \tag{10b}$$

T_{lj}, ϵ_f, V_{fd}, and $U_{\alpha\beta}$ ($\alpha, \beta = f, d$) being the hopping integral between l and j sites for d states, the f-level energy, f-d hybridization, and the Coulomb correlation between α- and β-like electrons, respectively.

From Eq. (9) one obtains the chosen pure-electronic Hamiltonian H^{el} if one sets $g_{\alpha\beta} = 0$. It should be mentioned that the electron renormalizations appearing in Eq. (9) were obtained from Eq. (7) under the following approximations:

(i) It is assumed that no hopping exists between f states; this is equivalent to defining an f-character Anderson lattice.

(ii) For the sake of simplicity, only pure local contributions for the renormalization between f-f, d-d, and d-f interactions which is compatible with the starting Hamiltonian H^{el} are kept, although in principle the renormalizations could affect nonlocal terms.

(iii) The bare d-f hybridization occurs only among next-neighbor sites since the symmetry of f and d states implies in zero local hybridization. Notice that the local occupation numbers present in the hybridization terms are referred to sites which could be occupied by f electrons.

At this point some comments concerning other works are worthwhile. Sherrington and Molnar[3] as well as Sherrington and Riseborough[1] considered that EP coupling through f electrons is at the origin of a polaronic effect. In Ref. 1, the authors used a unitary operator which exactly diagonalizes the EP coupling in the absence of d-f hybridization. Assuming a small d-f hybridization, the canonical transformation is performed using the same unitary operator as for zero hybridization. Then a perturbative calculation yields an EP-modified d-f hybridization thus arising the polaronic effect. Three points are to be considered.

(i) Although the final EP renormalized hybridization can be small enough in order to be compatible with the short $4f$ lifetime, it is not clear that the bare d-f hybridization is necessarily small as compared to the EP hybridization term.

(ii) Hewson and Newns[8] have shown for EP coupling through $4f$ electrons, the polaronic reduction condition is too strong to be achieved for mixed-valence compounds described within one-site model. For two coupled f sites, the width of the virtual bound state remains almost unaffected, the intersite transfer being reduced by the polaronic effect.

(iii) In the present work as well as in Entel *et al.*,[4] $f \rightleftharpoons d$ transitions in the presence of phonons are needed in order to enable a renormalization of the bare hybridization. That means that if $g_{fd} = 0$, the remaining $f \rightleftharpoons f$ and $d \rightleftharpoons d$ processes alone will not affect the V_{df} hybridization.

In Ref. 7, a generalized Anderson-type impurity model was studied, the EP coupling arising due to d-electronic states. In that work d-f hybridization was considered in the usual phenomenological way, namely: (i) acting at the impurity site and (ii) the matrix element $|V_{df}|^2$ was considered to be an effective parameter taking a constant value compatible with a reasonable $4f$ lifetime. This assumption leads to an almost constant $4f$ linewidth in the whole range of valence change. No mechanism was assumed to be responsible for possible narrowing effects due to the change of the hybridization parameter V_{df}. In the present work within a simple picture, is discussed the modification of the bare d-f hybridization through the effect of EP coupling. In order to compare the present results to those of Ref. 7, one considers the hybridization term in Eq. (9), under the Hartree-Fock approximation used in Ref. 7. The renormalized hybridization parameter turns out to be

$$\tilde{V}_{df} = V_{df} - G_{df}(G_{ff}\langle n^f\rangle + G_{dd}\langle n^d\rangle)\,. \tag{11}$$

Here, $G_{\alpha\alpha}(\alpha = d,f)$ denotes an average coupling

$$G_{\alpha\alpha} = G_{\alpha\alpha}^{\langle\vec{q}\rangle}\,, \tag{12a}$$

$$G_{df} = G_{df}^{\langle\vec{q}\rangle}\,, \tag{12b}$$

where the effective EP parameters $G_{\alpha\beta}^{\vec{q}}$ are defined as follows:

$$G_{\alpha\alpha}^{\vec{q}} = \sum_{\vec{k}'} \frac{1}{\sqrt{\hbar\omega_{\vec{q}}}}\, g_{\alpha\alpha}^{\vec{k}',\vec{q}}\,, \tag{13a}$$

$$G_{df}^{\vec{q}} = \sum_{\vec{k}'} \frac{Z}{\sqrt{\hbar\omega_{\vec{q}}}}\,(e^{i\vec{k}'\cdot\vec{R}_\delta} + e^{i(\vec{k}'-\vec{q})\cdot\vec{R}_\delta})\, g_{df}^{\vec{k}',-\vec{q}}\,, \tag{13b}$$

Z being the coordination number, $\vec{R}_\delta$ being the distance between next neighbors i and j sites, $\langle n^f\rangle$ and $\langle n^d\rangle$ being the total f- and d-occupation numbers, respectively.

Notice that this renormalized hybridization is essentially the same obtained in Ref. 6. However, the displacement operator technique circumvents some approximations used in the canonical transformation method. Moreover, the present treatment can explicitly account for the $\vec{k},\vec{q}$ dependence of the EP coupling.

In order to compare numerically the results obtained throughout this work with those of Ref. 7, one plots in Fig. 1 the behavior of the $4f$ width Δ_f against the concentration x for the pseudobinary intermetallic system $\mathrm{Eu}(A_{1-x}B_x)_2$; A and B standing for transition elements. The $4f$ width Δ_f was obtained by calculating the second moment of the density of states of the conduction electrons. For $x = 0$, the Eu valence is assumed to be 2+ whereas for $x = 1$ the Eu valence is assumed to be 3+. The dotted lines are the resulting widths arising from the constant mixing matrix element considered in Ref. 7. The full lines are self-consistently obtained under the physical approximations discussed above. One adopts the following choice for the parameters: $G_{df}G_{dd} = 0.25$ whereas $|V_{df}|^2$ assumes the values 0.2, 0.1, and 0.05 in order to obtain reasonable values for the f-level width Δ_f. Notice that one retains for the other parameters the same values used in Ref. 7. We emphasize that the transfer of a $4f$ electron to the conduction band changes the forces between atoms. Since the cohesive energy is to be ascribed to the conduction d states, we expect that the EP $d \rightleftarrows d$ coupling must be more relevant than the $f \rightleftarrows f$ one.[7] So we neglect in the numerical calculations the G^{ff} coupling appearing in Eq. (9).

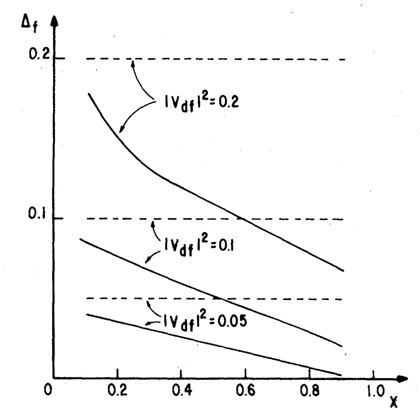

FIG. 1. Behavior of the $4f$ linewidth with the x concentration in the pseudobinary systems $\mathrm{Eu}(A_{1-x}B_x)_2$. The Eu valence state goes from 3+ (for $x = 0$) to 2+ (for $x = 1$). The full lines show the $4f$ linewidths obtained through an EP renormalized d-f hybridization for different values of $|V_{df}|^2$ [cf. Eq. (11) of the text]. For comparison, the dashed lines show the corresponding $4f$ linewidths calculated using the phenomenological constant d-f hybridizations as discussed in Ref. 7.

The tendency exhibited in Fig. 1 is in qualitative agreement with experimental results which one can infer from the work of Bauminger *et al.*[9] In that work, the Mössbauer measurements performed on $\mathrm{Eu(Rh_{1-x}Pt_x)_2}$, $(0 \leq x \leq 1)$ systems, reveal the following trend. When the concentration x increases, the d-occupation number increases accordingly, going from a one-line Mössbauer spectrum in $\mathrm{EuRh_2}$ (corresponding to fast fluctuations $\Delta_f^{(1)}$) to the appearance of two lines in $\mathrm{EuRh_{1.75}Pt_{0.25}}$ (corresponding to slow fluctuations $\Delta_f^{(2)}$) towards a one-line spectrum in $\mathrm{EuPt_2}$ (corresponding to a stable $4f$ configuration $\Delta_f^{(3)}$). So, we have $\Delta_f^{(1)} > \Delta_f^{(2)} > \Delta_f^{(3)}$, as indeed observed in Fig. 1. It should be pointed out that the renormalized hybridization $\tilde{V}_{df}$, which is at the origin of the narrowing mechanism, depends essentially on the simultaneous presence of the effective $f \rightleftarrows d$ and $d \rightleftarrows d$ EP coupling, contrary to the results obtained by other authors.[1,3,4] Furthermore the present approach generalizes the result obtained in Ref. 7, since the renormalized d-f hybridization, which is no longer a constant parameter, can account for the $4f$-width variation observed experimentally in some mixed-valence systems.[9]

The authors would like to thank Professor A. A. Gomes for valuable discussions and for a critical reading of the manuscript.

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