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Electron-phonon coupling in mixed-valence systems

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The electron-phonon interaction in mixed-valence systems is modeled on the basis of an Anderson-like Hamiltonian that describes a cluster of one metallic rare-earth cation surrounded by six anions. Coupling between the electronic and phononic variables is introduced, keeping two different phonon modes: a breathing and an asymmetric mode. The first, related to the ionic radius, is treated exactly. The asymmetric mode, which determines the *sd-f* hybridization, is dealt with in the Born-Oppenheimer approximation. A variety of experimental results are adequately accounted for by this simple model, like the anomalous thermal expansion, the Debye-Waller factor, the phonon softening and broadening, and the charge-distance correlation.

I. INTRODUCTION

For around two decades the description and understanding of intermediate valence has attracted significant efforts.[1-3] However, several relevant issues remain to be solved, among them the full understanding of the electron-phonon interaction in fluctuating-valence systems.

The central objective of this paper is the study of phase transitions of mixed-valence systems like $\mathrm{Sm}_{1-x}M_x\mathrm{S}$, where M=Y,Th,Gd,... in general belong to the rare-earth (R) series. These systems exhibit a metal-insulator transition, characterized by an important variation of the cationic radius, when subject to changes in temperature, pressure, and/or dopant concentration.[4,5] In fact, the ionic radius of Sm changes from 1.14 (Å), in the insulating Sm^{2+} phase, to 0.96 (Å), in the metallic Sm^{3+} state. These large variations imply that the electron-phonon coupling plays a major role in the stabilization of the mixed-valence phase.

Several anomalous properties are associated with the latter. Among them we mention the following: (i) a negative thermal expansion coefficient for certain ranges of dopant concentration and temperature,[1,4,5] (ii) a reduction of the bulk compressibility modulus, as compared to other R chalcogenides,[1] (iii) an anomalous temperature dependence of the Debye-Waller factor,[6] (iv) a softening of the optical-phonon modes[7-9] (in particular, the LO phonons lie below the TO ones), (v) anomalous phonon broadening,[7,8] which is especially noticeable at the point L of the LO phonon branch, and (vi) negative values of the c_{12} elastic constant.[10]

Various models have been proposed to incorporate the electron-phonon interaction in the description and understanding of valence fluctuations. Some of them emphasize the coupling of the R valence to the symmetric breathing mode vibrations of the anions that surround it.[11-13] Others stress the role played by the lattice vibrations as the mechanism which induces the *sd-f* hybridization.[14,15] Phenomenological models have also been proposed to describe the lattice dynamics of these systems.[16] However, most of them have been solved by means of approximations[11,12,14] or in special limits.[13,15] Moreover, several important physical magnitudes have not been evaluated, especially at finite temperatures.

In this contribution we put forward a simple cluster model to investigate mixed valence systems, focusing on the electron-phonon interaction. Two types of phonon modes are considered: a symmetric breathing mode and an asymmetric one. The latter is analyzed in the Born-Oppenheimer approximation, and is the only term of the Hamiltonian not treated exactly. However, *a posteriori* its quantum character is retrieved. The energy eigenvalues and eigenstates are thus obtained and used to evaluate the thermodynamic averages of the magnitudes of physical interest.

While the symmetric mode belongs to the $\Gamma_1^+(\mathrm{Sm})$ representation, and is related to the point L of the LO branch, the asymmetric ones belong to the $\Gamma_{15}^-(\mathrm{Sm})$ representation, which is related to the point Γ of the same branch.[17] The reason to select the breathing mode for an exact treatment is that the physical magnitudes on which our interest is focused are predominantly related to the point L of the LO branch. They are the lattice parameter as a function of temperature,[1-4] the mean-square fluctuation of the anionic positions, the anomalous broadening and softening of the phonon frequencies at the point L of the LO branch,[7-9] and the dynamic correlation between the instantaneous valence and the anion-cation distance.[18]

This paper is organized as follows: After this introduction, in Sec. II, the model is presented in full detail, and solved as outlined above. In Sec. III our results are discussed in the light of the available experimental information. Finally, in Sec. IV conclusions are drawn and a brief summary is given.

II. MODEL AND SOLUTION

A. The Hamiltonian

In the formulation of our model we retain only the most essential physical ingredients. We do consider a single rare-earth (R) cation (Sm, for example) whose $4f$ states hybridize with the narrow sd conduction band of the host. Due to the strong coupling of the electrons with the lattice vibrations, we have to include the phonon field in our description. We retain two phonon modes: a breathing mode and an asymmetric oscillation. Both play significant and quite different roles, as we shall see shortly.

The model also has to embody the sd-f hybridization mechanism, which has been a subject of controversy. In fact, due to the different symmetries (opposite parity) of the sd and f orbitals, and since the cations are located at an inversion symmetry lattice site, a direct mixing of these orbitals is forbidden. To solve this difficulty Schweitzer[19] proposed many-body effects as the cause of the hybridization, while Lin and Falicov[20] employed first-neighbor mixing matrix elements. However, the asymmetric lattice vibrations constitute a very natural dynamic mechanism to induce the required instantaneous symmetry breaking.[14,15,17] On the other hand, the breathing mode, in which the six anions vibrate about the (R) ion preserving octahedral symmetry, is directly coupled to the cation valence.[17]

Thus, in the partial-wave representation, the Hamiltonian H can be written as

$$H = H_e + H_{\text{ph}} + H_{e\text{-ph}} \ , \tag{2.1}$$

where

$$H_e = \sum_k \varepsilon_k d_k^\dagger d_k + \sum_{\nu=1}^{N_f} E_f^0 f_\nu^\dagger f_\nu + U \sum_{\nu,\nu'=1}^{N_f} \hat{n}_{f\nu} \hat{n}_{f\nu'} \ , \tag{2.2}$$

$$H_{\text{ph}} = \hbar\omega_a a^\dagger a + \hbar\omega_b b^\dagger b \ , \tag{2.3}$$

$$H_{e\text{-ph}} = -G(b+b^\dagger) \sum_{\nu=1}^{N_f} E_f^0 f_\nu^\dagger f_\nu + \frac{1}{\sqrt{N}} \sum_{k,\nu} [V_0 + g(a+a^\dagger)](f_\nu^\dagger d_k + d_k^\dagger f_\nu) \ , \tag{2.4}$$

where $d_k^\dagger(d_k)$ and $f_\nu^\dagger(f_\nu)$ are fermion operators that create (destroy) electron states in the narrow s-d conduction band and in the f states, respectively. $k = (\mathbf{k}, \nu)$ is a collective index denoting both the wave vector $\mathbf{k}$ and the z component of the total angular momentum ν, ε_k denotes the energy of the band states, E_f^0 is the energy of the f-electron states localized on the R. The number operator is $\hat{n}_{f\nu} = f_\nu^\dagger f_\nu$, U is the on-site Coulomb repulsion between f electrons, and ω_a and ω_b are the frequencies of the asymmetric and the symmetric breathing oscillation modes, created by the boson operators $a^\dagger$ and $b^\dagger$, respectively. G is the coupling constant between the breathing mode and the number of f electrons[13] on the R, while V_0, which has its origin in the doping R impurities,[17] is the static hybridization term of the Anderson Hamiltonian.[21] The coupling constant g yields the magnitude of the mixing between band and localized f states, induced by the asymmetric phonon mode.[15,17]

It has been shown[13,15] that in the large-N_f limit, and for $U \longrightarrow \infty$, substantial simplifications do occur: electron-hole pairs and double f-electron transfer drop out of the treatment. Within this framework we incorporate an additional simplification: we assume the conduction band to be very narrow. Then our Hamiltonian reads

$$H = E_d d^\dagger d + [E_f^0 - G(b+b^\dagger)] f^\dagger f + \hbar\omega_a a^\dagger a + \hbar\omega_b b^\dagger b + [V_0 + g(a+a^\dagger)](f^\dagger d + d^\dagger f) \ , \tag{2.5}$$

where the state $f^\dagger|0\rangle$ represents, for example, a Sm^{2+} cation in the $4f^6$ state. $d^\dagger|0\rangle = \sum_k d_k^\dagger|0\rangle/\sqrt{N}$ represents a Sm^{3+} in a $4f^5$ state plus a conduction sd electron in a Wannier state centered around the cation. E_d is the energy eigenvalue of the atomic d state. In order to properly describe the insulating phase of SmS (with a cation Sm^{2+} configuration and no conduction electrons), we assume just one electron in our cluster. Since we limit our attention to an isolated cluster, fluctuations in the number of electrons are ruled out, as the conduction band is of zero width. On the other hand, and due to the absence of electronic orbital and spin degeneracy, it is possible to define just one asymmetric phonon mode capable of triggering the hybridization.

The Hamiltonian as written in Eq. (2.5) actually describes a R cation, of infinite mass, coupled through two distinct Einstein oscillator modes to six finite mass M_S sulphur atoms. The R ion can be found in only two possible electronic configurations (i.e., Sm^{2+} and Sm^{3+}).

B. Born-Oppenheimer approximation

In this paper we treat quantum mechanically the breathing mode, related to the operators b and $b^\dagger$. The asymmetric phonon mode, related to the f-d hybridization mechanism, is treated in the Born-Oppenheimer approximation, which has proved to be an adequate procedure in the low-temperature regime.[22] Thus, we replace the quantum operator $(a+a^\dagger)$ by a real classical displacement denoted by y. The rationale to proceed in this manner is that the physical magnitudes we evaluate in this paper are mainly related to the symmetric breathing mode; for example, the temperature variation of the lattice parameter. The latter is determined as the average value of the displacement associated with the breathing mode coordinate. Moreover, the softening and broadening of the phonon frequencies are especially relevant at the point L of the LO phonon branch, which is precisely associated to the breathing mode.[17] On the other hand, the main role of the asymmetric phonon mode, which is related to the point Γ of the LO branch, is to induce *sd-f* hybridization.[15]

Consequently, the Hamiltonian of Eq. (2.5) adopts the final form

$$H = b^\dagger b + [E_f^0 - G(b+b^\dagger)]f^\dagger f + (V_0 + gy)(f^\dagger d + d^\dagger f) + \frac{\hbar\omega_a}{4}y^2 \;, \tag{2.6}$$

where we have chosen $\hbar\omega_b = 1$ and $E_d = 0$ as the unit and origin of energy, respectively. The time-independent Schrödinger equation satisfied by H is

$$H|E\rangle = E|E\rangle \;. \tag{2.7}$$

The energy eigenvector $|E\rangle$ has fermionic and bosonic contributions, i.e., it belongs to the product space $H_e \otimes H_{\text{ph}}$. Thus we use[13] the most general form of a state, in our reduced Hilbert space, for the eigenvector

$$|E\rangle = \sum_n (\xi_n f^\dagger + \eta_n d^\dagger)|e\rangle \otimes |n\rangle \;, \tag{2.8}$$

where $|e\rangle$ denotes the vacuum of the electronic Hilbert space. The bosonic basis is defined by $b^\dagger b|n\rangle = n|n\rangle$, and consequently

$$|n\rangle = \frac{(b^\dagger)^n|0\rangle}{\sqrt{n!}} \;. \tag{2.9}$$

This way ξ_n and η_n are probability amplitudes for having the ion with an occupied f or d state, respectively, and n "bare" phononic excitations. Substitution of Eq. (2.9) into the eigenvalue equation, Eq. (2.7), leads to a typical three-term recursion relation[13,15]

$$(\varepsilon_n - E_f^0 - V^2/\varepsilon_n)\xi_n = -G(\sqrt{n}\,\xi_{n-1} + \sqrt{n+1}\,\xi_{n+1}) \;, \tag{2.10}$$

with

$$\eta_n = \frac{V}{\varepsilon_n}\xi_n \;, \tag{2.11}$$

and the definitions $\varepsilon_n \equiv E - \hbar\omega_b n$ and $V \equiv V_0 + gy$.

Eq. (2.10) is an eigenvalue equation, for the energies ε_n and eigenvectors ξ_n. The latter can be solved imposing the condition that $|\xi_{n+1}/\xi_n| \ll 1$, for $n \to \infty$ which is the requirement for the existence of a physical eigenfunction. More precisely, $\lim_{n\to\infty} |\xi_{n+1}/\xi_n| \approx G/(\hbar\omega_b\sqrt{n})$, as can be inferred from Eq. (2.10), *and* the condition that the sequence $\{\xi_n\}$ converges have to be simultaneously satisfied.

The close analogy between Eq. (2.11) and similar recursion relations derived in Refs. 13 and 15 is quite remarkable, since the latter were obtained for extended systems and not for a cluster calculation.

Once the energy spectrum and eigenfunctions have been obtained, following the procedure outlined above, the Helmholtz free energy F,

$$F(y) = -k_B T \ln \sum_\nu \exp[-\beta E_\nu(y)], \tag{2.12}$$

is evaluated as a function of the classical parameter y, associated with the asymmetric phonon mode. The Born-Oppenheimer approximation is generalized to finite temperatures, through the use of $F(y)$ as the potential energy for the breathing modes. After doing so we reintroduce the quantum nature of the variable y in the self-energy equation for the asymmetric phonon mode

$$[-\tfrac{1}{4}\hbar\omega_a(a - a^\dagger)^2 + F(a + a^\dagger)]\phi_j(y) = \varepsilon_j \phi_j(y) \;, \tag{2.13}$$

where we have reinserted $y = a + a^\dagger$ as a quantum operator acting on the asymmetric mode eigenfunction $\phi(y)$. Equation (2.13) is solved in the neighborhood of the absolute minimum of $F(y)$ using the harmonic approximation, to yield the probability distribution

$$\rho(y) = \frac{\sum_j |\phi_j(y)|^2 \exp(-\beta\varepsilon_j)}{\sum_j \exp(-\beta\varepsilon_j)} \;. \tag{2.14}$$

A well-known procedure[23] allows to carry out the summation above, in the harmonic approximation. It yields

$$\rho(y) = \exp[-\tilde{\beta}F(y)] \;, \tag{2.15}$$

where

$$\tilde{\beta} \equiv \frac{2}{\hbar\Omega}\tanh\left(\frac{\hbar\Omega}{2k_B T}\right) \;, \tag{2.16}$$

$$\hbar\Omega \equiv \left[2\left(\frac{\partial^2 F(y)}{\partial y^2}\right)_{y=y_0} \hbar\omega_a\right]^{1/2} \;. \tag{2.17}$$

Here y_0 denotes the absolute minimum of $F(y)$, while Ω is the oscillation frequency around that minimum. In the $k_B T \gg \hbar\Omega$ limit $\tilde{\beta} = (k_B T)^{-1}$ and Eqs. (2.15) and (2.16) become the classical expressions. In the opposite $T \to 0$ limit the "effective temperature" $(\tilde{\beta})^{-1} \to \hbar\Omega/2$, which corresponds to the zero-point fluctuation energy of the quantum oscillator.

In our adiabatic approximation the thermodynamic average of an operator A is denoted by $\langle A\rangle$ and given by

$$\langle A\rangle = \frac{1}{Q}\int_{-\infty}^{\infty} dy\,\rho(y) \times \sum_\nu \langle E_\nu(y)|A|E_\nu(y)\rangle e^{-\beta[E_\nu(y) - F(y)]} \;, \tag{2.18}$$

where the state $|E\rangle$ was defined in Eqs. (2.7) and (2.8), and

$$Q = \int_{-\infty}^{\infty} dy\,\rho(y) \;. \tag{2.19}$$

In (2.18) the y integral averages over the "slow" asymmetric modes, associated with the Γ point of the LO phonons,[15] while the quantum bracket yields a statistical average over the "fast" oscillations, which in this case correspond to the electronic and breathing modes.

C. Temperature dependence of the lattice parameter

An important physical magnitude is the lattice parameter and its temperature dependence. It is convenient to write this parameter $l(T)$ in terms of a nondimensional quantity $\lambda(T)$

$$l(T) = l_M + (l_I - l_M)\lambda(T) , \qquad (2.20)$$

which in turn can be written as a function of the phonon operators

$$\lambda(T) = \frac{\hbar\omega_b}{2G}\langle b + b^\dagger\rangle . \qquad (2.21)$$

Use of Eq. (2.5) and the Hellman-Feynman theorem allows us to prove that

$$\lambda(T) = \langle f^\dagger f\rangle \equiv n_f . \qquad (2.22)$$

The above relations are useful to test the accuracy of our numerical calculations, which turns out to be better than one part in 10^5. This linear relation between displacement from equilibrium and f-level occupation, known as Vegard's law, should hold for any model in which the valence is coupled linearly to the breathing modes, provided that the elastic energy is evaluated in the harmonic approximation.

D. System parameters

In order to obtain adequate estimates for the magnitude of the SmS system parameters a rough description of the interactions within the cluster, as well as its coupling to the rest of the lattice, is required. We put forward an analysis which implies several simplifications, since we only retain elastic interactions between first-neighbor Sm and S atoms, characterized by a Hooke constant K. Nevertheless the procedure is quite sound, since this nearest-neighbor interaction is at least one order of magnitude larger than the other elastic couplings, in actual R^{2+}S systems.[24]

The precise definition of our simplified model is as follows: The equilibrium elongation of each bond is defined as $l_I/2$ and $l_M/2$, for the Sm^{2+} and Sm^{3+} cations, respectively. The remainder of the lattice is simulated by six Sm cations, with an ionic radius $\langle R_{\text{ion}}\rangle = n_f R_I + (1-n_f)R_M$, where R_I and R_M are the Sm^{2+} and Sm^{3+} ionic radii, respectively. These cations play a "passive" role, which means that they have no electronic degrees of freedom and that their masses are infinite. They are disposed in a octahedral configuration around the central ("active") Sm, and at a distance l away. Their only role is to provide a suitable coordination for the six S anions. Within the context of an isolated cluster study we are only interested in the motion of the anions in the radial direction, relative to the central Sm. The position coordinate of an anion along the α axis, where $\alpha = x, y, z$ is given by $\frac{1}{2}\xi l + U_{\alpha\xi}$, while $\xi = +(-)$ denotes the anion to the right (left) of the central Sm.

Consequently, the elastic energy of the cluster can be written as

$$V_{\text{elas}} = \frac{K}{2}\sum_{\alpha\xi}\Big[\, f^\dagger f(\tfrac{1}{2}l + \xi U_{\alpha\xi} - \tfrac{1}{2}l_I)^2 + (1 - f^\dagger f)(\tfrac{1}{2}l + \xi U_{\alpha,\xi} - \tfrac{1}{2}l_M)^2 + (\tfrac{1}{2}l - \xi U_{\alpha,\xi} - \tfrac{1}{2}l_0)^2\Big] + \tfrac{1}{2}Pl^3 , \qquad (2.23)$$

where P represents the external hydrostatic pressure, $l_0 = l_M + n_f(l_I - l_M)$, and $l^3/2$ is a suitable choice for the cluster volume. We complete the cluster Hamiltonian by adding the electronic and anionic kinetic energies and the hybridization term. After a straightforward calculation we recast this Hamiltonian into the form given by Eq. (2.5), plus four oscillators decoupled from the electronic part and some constant terms that only depend on the lattice parameter l. The implementation of this new procedure yields explicit expressions for some parameters of the Hamiltonian in terms of well-known constants, and also gives some insight on the effect of pressure.

As a first obvious consequence of this analysis, the "bare" phonon frequencies become degenerate, and thus hereafter $\omega_a = \omega_b = \omega$, where ω is related to the Hooke constant K and the sulphur mass M_S by $\omega = \sqrt{2K/M_S}$. In actual systems, like $\mathrm{Sm_{0.75}Y_{0.25}S}$, the asymmetric phonon frequency ω_a (associated to the point Γ of the LO branch) and the symmetric frequency ω_b (point L of the same LO branch) differ[17,25] by less than 10%.

A rearrangement of Eq. (2.23) yields

$$G = \tfrac{1}{4}(l_I - l_M)\sqrt{3\hbar M_S\omega^3} \approx 3\hbar\omega \qquad (2.24)$$

for the coupling constant between the Sm valence and the breathing mode. The estimation of G above is obtained using the values $l_I - l_M = 0.36$ (Å) and $\hbar\omega \approx 0.031$ (eV), which corresponds to the phonon energy at point L of the LO branch, for a stable valent R^{2+}S system.[9]

The effect of pressure on the lattice parameter can also be obtained from relation (2.23), and is formally described by means of the following two equations:

$$l = l_0 - \frac{l^2}{2K}P \equiv l_0 - \frac{l}{3B_0}P , \qquad (2.25)$$

$$\frac{\partial E_f}{\partial P} = M_S\frac{\omega^2 l}{4B}(l_I - l_M) , \qquad (2.26)$$

where B is the bulk modulus for the actual system, while B_0 is the associated "bare" magnitude (say, the bulk modulus for a stable-valent R^{2+}S system).

Relation (2.25) is a generalization of Eqs. (2.20) and (2.22). However, the external pressure modifies the lattice parameter in two ways: first through the bare bulk modulus B_0, and second via the pressure shift of the f level, as obtained from Eq. (2.26). In fact, this shift generates a change in n_f, and the latter gives rise to a modification of l through a change in l_0. Consequently, the evaluation of the change in l due to the pressure shift of E_f implies a full solution of the dynamical problem. This way, pressure and lattice parameter are self-consistently coupled, in a highly nonlinear fashion, by means of Eqs. (2.25) and (2.26). The actual bulk modulus $B(P)$ and the f-level position $E_f(P)$ can only be obtained after this self-consistency is achieved. In addition, the actual f-level energy must be obtained by diagonalization of the Hamiltonian and, in general, turns out to be different to the bare parameter E_f.

If the f level is well below the Fermi energy, then the pressure does not modify the valence of the system, $n_f = 1$, and $B = B_0$. Thus relation (2.26) yields $(\partial E_f/\partial P) = \frac{3}{4}(l_I - l_M)l^2 \approx 6$ (meV/kbar). This last numerical estimate was obtained by using the known parameters[26] for the semiconducting R^{2+}S phase and is similar to the one observed in EuS, where a large enough gap of 1.6 (eV) does exist. In contrast, $(\partial E_f/\partial P) \approx 10$ (meV/kbar) for the (black) Sm^{2+}S system.[26] This disagreement is due to the fact that the SmS gap is very small and the system is very close to a valence transition. Thus, in the later case, the bare magnitudes of E_f and B_0 have no direct meaning, and a fully self-consistent solution of the problem is required. That analysis will be presented elsewhere; for the time being we omit a more extensive study of pressure effects.

As previously stated, the hybridization is due to the phonon-induced instantaneous dipole field. We carry out a rough estimate of this effect by using standard d and f orbitals. Their z angular-momentum component, and the degenerate Γ_{15}^- phonon are chosen according to the Wigner-Eckart theorem, to obtain

$$g(T) \approx c\frac{2^{10}e^2\sigma}{l^3}a_d\left(\frac{\sqrt{a_f a_d}}{a_d + a_f}\right)^9 \equiv g_0\left(\frac{l_I}{l(T)}\right)^3 , \tag{2.27}$$

where $\sigma = \sqrt{\hbar M_S \omega} \approx 0.06$ (Å) is associated to the zero-point vibration amplitude, c is a constant whose value may be estimated to be between 20 and 60, and a_f, a_d are the radii of the f atomic orbital and the s-d Wannier state, respectively. Using the estimates $4 < (a_d/a_f) < 6$ and $a_d \sim 1.2$ (Å), we obtain the approximate lower and upper bounds $\hbar\omega < g_0 < 2\hbar\omega$.

In Eq. (2.25) we also take into consideration the fact that the coupling constant g has a non-negligible dependence on the lattice parameter l, with g_0 being the insulating phase value. As l depends on T and on the parameters of the system, a self-consistent calculation for g is required for each temperature. Actually, our numerical computations do incorporate this self-consistency requirement, but our results turn out to be only slightly affected by this refinement.

In closing this subsection it is worth recalling that E_f^0 is shifted by $-G^2/\hbar\omega$, the polaronic correction.[27] Thus, it is convenient to redefine the f-level position $E_f^0 \rightarrow E_f = E_f^0 - G^2/\hbar\omega$. This way, the valence transition takes place when $E_f \approx 0$.

III. APPLICATION TO $\mathrm{Sm}_{1-x}R_x\mathrm{S}$ SYSTEMS

In this section we apply the formalism developed in the preceding one to the representative intermediate valence systems Sm$_{1-x}R_x$S, where R=Y,Th,Gd,....

The temperature dependence of several magnitudes of physical interest has been evaluated using the method described above. In our numerical computations we use $V_0 = 0$, $g_0 = 1.45$, and $G = 3.5$. These values are in agreement with our previous estimates, but a search has been made to narrow down on the appropriate range of g_0. The choice of $V_0 = 0$ is made in order to stress the effect of the dynamical hybridization.

In Fig. 1 we plot λ versus T, for a value of E_f below the Fermi level. Since we have chosen $E_d = 0$ in Eq. (2.5) as the origin of energies, in our cluster calculation the parameter E_f plays the same role as the distance of the f level to Fermi surface in an infinite system.[13,15] It is noticed that at low temperatures $\langle f^\dagger f\rangle \rightarrow 1$, which implies an insulating phase with only Sm^{2+} ions. The latter is quite natural, since we have chosen $E_f < 0$. For $k_B T \sim |E_f - E_d|$ the valence of the system stabilizes at an intermediate value ($\lambda \geq 0.5$). On the other hand, according to Eq. (2.21), these results provide information on the lattice parameter $l(T)$, which exhibits an anomalous negative thermal expansion for *increasing* temperatures, in agreement with experiment.[1-5]

In Fig. 2 we display the correlation function between metallic valence and Sm-S distance, given by

$$\lambda_d = \frac{\hbar\omega}{2G}\frac{\langle (b + b^\dagger)d^\dagger d\rangle}{\langle d^\dagger d\rangle} . \tag{3.1}$$

The above parameter gives a measure of the lattice response to valence fluctuations. When the latter fluctuates slowly the S atoms follow these valence changes

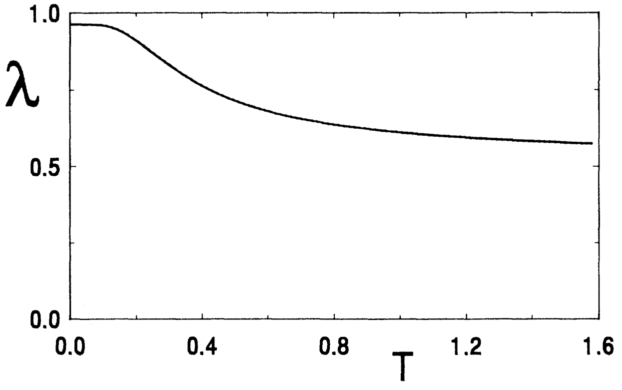

FIG. 1. Plot of λ vs T, for $E_f = -0.65$, $G = 3.5$, and $g_0 = 1.45$, all in the units $\hbar\omega = 1$ used throughout.

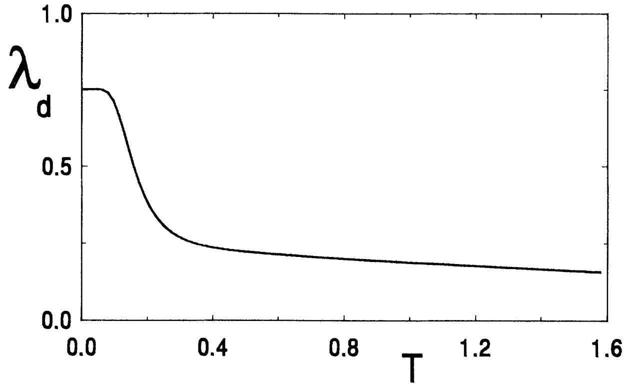

FIG. 2. Correlation function between metallic valence and Sm-S distance, λ_d vs T, for the same parameter values as Fig. 1.

in phase; thus, λ_d adopts the value that corresponds to the metallic phase ($\langle d^\dagger d\rangle = 1$) lattice parameter, that is $\lambda_d \approx 0$. But, when the valence fluctuates rapidly the S atoms are unable to respond fast enough and thus $\lambda_d \approx \lambda$, which implies that a static displacement sets in. However, when the f level lies below the d level, the adiabatic potential traps the f state, precluding breathing and mixing at very low temperatures. This behavior is observed in Fig. 2, for the same parameter values of the preceding figure, where it is seen that $\lambda_d \approx \lambda$ at low temperatures, while for intermediate temperatures λ_d tends to zero. The low-temperature result $\lambda_d \approx \lambda$ has been confirmed, within 30%, by extended x-ray-absorption fine-structure experiments[18] in $\mathrm{Sm}_{0.75}\mathrm{Y}_{0.25}\mathrm{S}$. However, the drift of λ_d towards zero at high T is yet to be corroborated experimentally.

For what follows it is useful to redefine the breathing phonon operators, choosing the equilibrium position $\Delta(T) = \langle b\rangle = \langle b^\dagger\rangle$ as the origin, say,

$$\gamma \equiv b - \Delta(T) \ , \tag{3.2}$$

with $\langle \gamma + \gamma^\dagger\rangle = 0$. In this notation the mean-square deviation of the anionic positions $\Delta\lambda$, which determines the Debye-Waller factor,[6] is written as

$$\Delta\lambda = \frac{\hbar\omega}{2G}\sqrt{\langle(\gamma+\gamma^\dagger)^2\rangle} \ . \tag{3.3}$$

In Fig. 3 plots of the temperature dependence of $\Delta\lambda$ are displayed. It is noticed that when E_f lies very close to the Fermi level [see Fig. 3(b)] an anomalous behavior is observed, which consists in a minimum of $\Delta\lambda$ versus T. When no valence fluctuations are present $\Delta\lambda$ is a monotonically growing function of T, while in the case at hand and when the temperatures are not too high, the fluctuations of the anionic positions are not solely due to thermal excitations but are dominated by the Sm valence fluctuations. As T increases the asymmetric vibration mode induces strong s-d hybridization, to which the ions are unable to respond dynamically, with the consequent decrease in $\Delta\lambda$. Finally, for high temperatures, thermal excitations become the dominant mechanism and drive a new increase of $\Delta\lambda$. Figure 3 also shows that this anomalous behavior disappears for larger values of $|E_f|$.

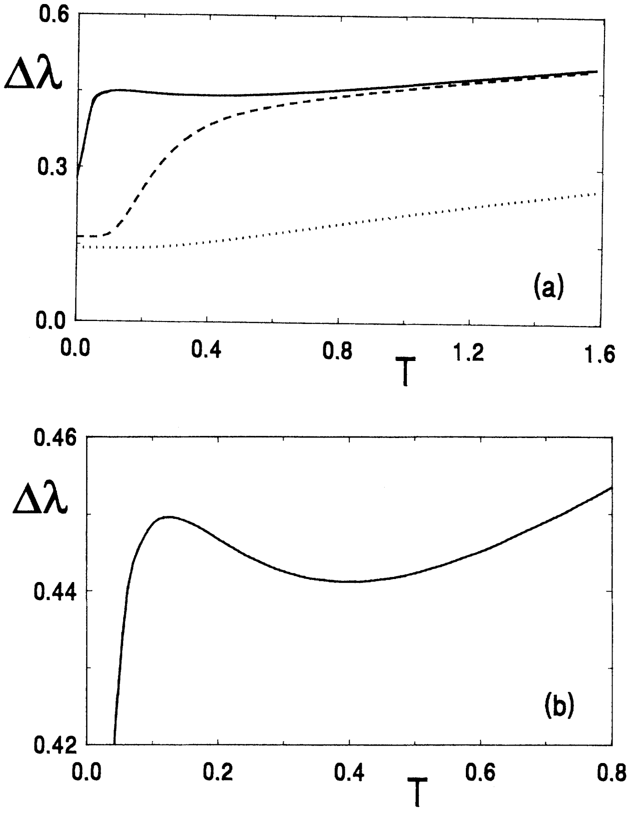

FIG. 3. Mean-square deviation of the anionic positions $\Delta\lambda$ vs T. In (a) the solid and dashed lines correspond to $E_f = -0.05$ and $E_f = -0.65$, respectively, and the other parameters as in previous figures. The dotted line corresponds to $G = 0$. (b) is an enlargement of the important features of the continuous curve in (a).

The contribution of the breathing mode to $\Delta\lambda$ is also clarified by the $G = 0$ (i.e., when the electron-phonon coupling is ignored) plot in Fig. 3. The small values of $\Delta\lambda$ confirm that valence fluctuations are the dominant feature in this regime.

The minimum of the mean vibration amplitude was observed experimentally in the $\mathrm{Sm}_{0.7}\mathrm{Y}_{0.3}\mathrm{S}$ system, through the measurement of the Debye-Waller factor, by Dernier *et al.*[6] The minimum of Fig. 3(b) corresponds to $\Delta\lambda \approx 0.08$ Å and to a temperature $0.4\hbar\omega$, both in good agreement with experiment.

We now consider the phonon softening, which in our treatment and for $T = 0$ is defined by

$$\begin{aligned} \hbar\Delta\omega &= \sum_\nu (E_{\mathrm{GS}} + \hbar\omega - E_\nu)\left|\frac{\langle\psi_\nu|(\gamma+\gamma^\dagger)|\psi_{\mathrm{GS}}\rangle}{\sqrt{\langle\psi_{\mathrm{GS}}|(\gamma+\gamma^\dagger)^2|\psi_{\mathrm{GS}}\rangle}}\right|^2 \\ &= E_{\mathrm{GS}} + \hbar\omega - \langle\phi|H|\phi\rangle \ , \end{aligned} \tag{3.4}$$

where $|\psi_{\rm GS}\rangle$ is the ground state of Eq. (2.5). The ket $|\phi\rangle = C(\gamma + \gamma^\dagger)|\psi_{\rm GS}\rangle$, where C is a normalization constant, represents the state generated by disturbing $|\psi_{\rm GS}\rangle$ with a probe that couples to the phonon field, for example, neutrons. Since the operator $\gamma^\dagger$ excites a purely vibrational mode, without center-of-mass displacement, $\langle\psi_{\rm GS}|\phi\rangle = 0$. Its average energy can be taken to be the energy required to create a phonon, thus justifying the definition given in Eq. (3.4) for the phonon softening.

The above expression for $\Delta\omega$ can be recast into

$$\frac{\Delta\omega}{\omega} = 1 - \left(\frac{\Delta\lambda_0}{\Delta\lambda}\right)^2 , \qquad (3.5)$$

where $\Delta\lambda_0$ is the zero-point vibration amplitude in the absence of electron-phonon coupling, i.e., when $G = 0$. The above expression is similar to a relation already derived, through approximations, by Kuroda and Bennemann.[12]

In Fig. 4 the softening $\Delta\omega$ is plotted as a function of E_f, for the static hybridization case $g = 0$. The value $V = 2$ corresponds to the average of the dynamic hybridization $V(y) = V_0 + gy$ for the parameter values used previously in Figs. 1, 2, and 3. However, the evaluation of the phonon softening is somewhat delicate, since one has to make sure that $\Delta\omega$ is associated to the creation of a phonon mode and not to an electronic transition. The sharp peak displayed by $\hbar\Delta\omega$ at the metal-insulator transition, i.e., for $E_f = 0$, constitutes a reassuring feature; moreover, its magnitude is in good agreement with experimental results[8,9] obtained for the $\mathrm{Sm}_{1-x}R_x\mathrm{S}$ family, which show up to 20% softening for the frequency associated to the point L of the LO phonon branch.

We also analyze the average

$$n_{\rm GS} = \langle\psi_{\rm GS}|\gamma^\dagger\gamma|\psi_{\rm GS}\rangle, \qquad (3.6)$$

which provides an indication of the number of breathing phonon states embodied in the ground state that cannot be eliminated by a translation of the origin. In Fig. 5 a plot of $n_{\rm GS}$ versus E_f is given for the same parameter values of the previous figure. Again a peak is present in the vicinity of the metal-insulator transition, which underscores the role played by the electron-phonon coupling in the valence mixing mechanism. Away from the peak $n_{\rm GS}$ is quite small, and thus the ground state can be basically described as a simple translation of the origin.

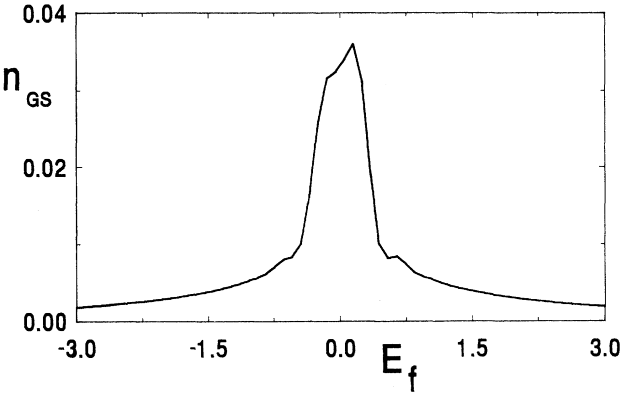

FIG. 5. Average number of phonons in the ground state $n_{\rm GS}$ vs E_f, at zero temperature and for $G = 3.5$ and $V = 2$.

In Fig. 6 the phonon linewidth Γ, of the breathing mode at zero temperature, is displayed for the same parameter values of the two preceding graphs. This linewidth is evaluated as the energy spread of the spectral decomposition of the state $|\phi\rangle$, defined after Eq. (3.4), and turns out to be

$$\Gamma = \frac{\hbar\omega}{\tilde{\Delta}}\sqrt{4n_{\rm GS}\tilde{\Delta} - (\tilde{\Delta} - 1)^2} , \qquad (3.7)$$

where

$$\tilde{\Delta} = \langle\psi_{\rm GS}|(\gamma + \gamma^\dagger)^2|\psi_{\rm GS}\rangle = \left(\frac{2G}{\hbar\omega}\Delta\lambda_{\rm GS}\right)^2 . \qquad (3.8)$$

Again, a large peak is observed in the vicinity of $E_f = 0$, which confirms a strong mixing of electron and phonon states near the transition. This mixing is significant only in this vicinity, which makes the mean field,[14] or coherent state,[11] approximations highly suspect in this neighborhood. Thus, an exact treatment of the electron-phonon

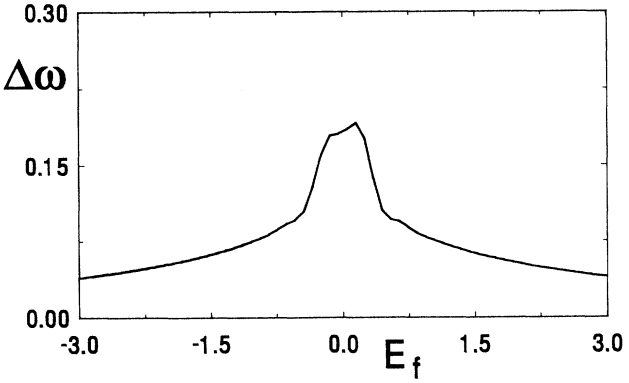

FIG. 4. Softening of the phonon mode $\Delta\omega$ vs E_f, at zero temperature and for $G = 3.5$ and $V = 2$.

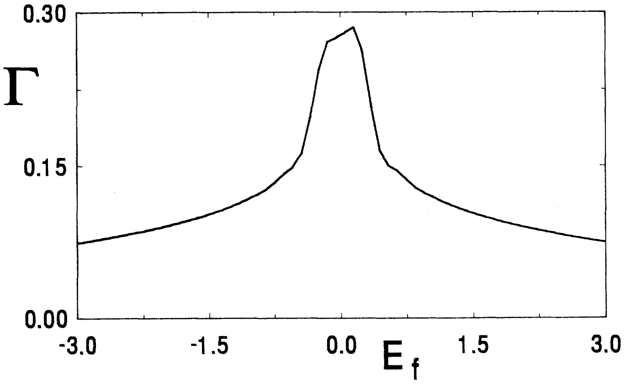

FIG. 6. Phonon linewidth Γ vs E_f, at zero temperature and for $G = 3.5$ and $V = 2$.

Hamiltonian of Eq. (2.4), as the one we presented above, is well justified in our case.

The peak in Fig. 6 reaches a maximum value of $\sim 0.2\hbar\omega$, again in good agreement with experiment. In actual systems, like $\mathrm{Sm}_{0.75}\mathrm{Y}_{0.25}\mathrm{S}$, a broadening of $\sim 25\%$ is observed.[7,8]

IV. SUMMARY AND CONCLUSION

A simplified treatment of mixed valence, concentrating on its interaction with the lattice, has been presented. The complexities of a system like $\mathrm{Sm}_{1-x}R_x\mathrm{S}$ were modelled by a seven atom cluster of one anion (Sm), surrounded by six S cations. Two types of phonon modes were included: a symmetric breathing mode, which was treated rigorously, and an asymmetric mode dealt with in the Born-Oppenheimer approximation. The first of these modes plays a key role in most of the experiments we focus our attention on, while the asymmetric one provides a dynamical *sd-f* hybridization mechanism.

In spite of the drastic simplifications that were made, and the approximation we have implemented to solve it, the results obtained provide an adequate description of the phenomenology and good agreement with the available experimental data, in view of which we believe to have used the essential physical elements and realistic values of the pertinent parameters. Of special interest is the existence of a minimum, and the magnitude of the low-temperature maximum, in the plot of $\Delta\lambda$ versus T of Fig. 3(b), which describes the temperature dependence of the Debye-Waller factor. To the best of our knowledge this is the first theoretical justification for this effect, observed experimentally long ago.[6] Moreover, this minimum is a consequence of dynamic hybridization and does not appear in a static hybridization treatment, since it is related to the increase of the frequency of the valence fluctuations and the lattice response to it.

Two exact results were rigorously derived, under the proviso that the electron-phonon coupling is linear: Eq. (2.22), known as Vegard's law, and Eq. (3.5), which relates phonon softening and zero-point fluctuations. They provide a test to check the linear coupling hypothesis in actual physical systems.

In conclusion, our simple model yields satisfactory agreement with experiment and a consistent understanding of the physics involved.

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