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Coupling between valence fluctuations and lattice vibrations in rare-earth chalcogenides

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A critical study of the interplay between *f-d* valence transitions and lattice vibrations in rare-earth chalcogenides is presented for a simplified electron-phonon coupling.

I. INTRODUCTION

During the last decade[1-4] mixed-valent systems of rare-earth materials have been studied intensively both experimentally and theoretically. Such systems exhibit an interesting behavior. However, so far no completely satisfying microscopic theory exists for the most essential physics of valence transitions. In the present study we would like to discuss a theory which takes into account the interplay between the valence fluctuations and the lattice vibrations in the mixed-valent systems.

Many experiments[5-8] and theories[9-18] have suggested already that the valence fluctuations and the lattice vibrations should interact strongly, because the former might induce local lattice distortions through the change in the ionic radii of relevant rare-earth ions. Therefore, one should study how this interaction affects the valence fluctuations as well as the lattice vibrations. Sherrington and Riseborough[14] have already studied this problem, but did not give any definite results. Our present study attempts to solve this problem by using simple models. We find these results: Firstly, the valence fluctuation is strongly suppressed by the local lattice distortion (polaron effect), if the lattice vibrations are much faster than the valence fluctuations. Then, the lattice vibrations are also not much affected. Secondly, phonon softening occurs but there are no large effects on the valence fluctuation if the lattice vibrations are much slower than the valence fluctuation. Thirdly, in the intermediate case, both valence fluctuations and lattice vibrations are changed due to their coupling. In particular, when both lattice vibrations and valence fluctuations have the same frequency, we find a very strong coupling between them and thus a drastic modification of the lattice vibrations (resonance effect).

In Sec. II, we propose a simplified Hamiltonian (including ionic-size effect) for the coupling between the valence fluctuations and the lattice vibrations. In Sec. III, we study the case in the semiconducting phase where only localized electrons are involved, while in Sec. IV we treat the case in the metallic phase where both localized and delocalized electrons are involved. Finally in Sec. V, we give a summary and some concluding remarks.

II. ELECTRON-LATTICE COUPLING (IONIC-SIZE EFFECTS)

Most of the rare-earth chalcogenides have NaCl-type structures and their lattice constants are given quite accurately by the sum of the ionic diameters of the rare-earth ion and the chalcogen ion. On the other hand, the ionic diameter of the rare-earth ion is intimately related to its valence, that is, the number of $4f$ electrons in the rare-earth ion. Smaller valence (i.e., a larger number of $4f$ electrons) means larger ionic diameter. Therefore, the fluctuating valence in a rare-earth ion directly causes a fluctuation in the ionic diameter. Furthermore, because of the strong Coulomb attraction among the rare-earth ion and its surrounding chalcogen ions it may induce local lattice distortion around the relevant rare-earth ion. Conversely the lattice vibration may seriously affect the valence fluctuation. Our aim in the present study is to investigate the essential features of this interplay between the valence fluctuation in the rare-earth ions and the lattice vibrations through the chalcogen ions. In the following we refer to SmS as a typical system just to simplify the terminology in the present study. The ionic radii of S^{2-}, Sm^{2+}, and Sm^{3+} ions are given by 1.84, 1.14, and 0.96 Å, respectively. Note, that the difference in the ionic radii of the two kinds of Sm ions is nearly 20% of the radius of the Sm^{3+} ion. The electronic configurations of Sm^{2+} and Sm^{3+} ions are characterized by $(4f)^6$ and $(4f)^5$, respectively. When an Sm ion changes its valence from Sm^{2+} to Sm^{3+}, it releases a localized $4f$ electron as a delocalized $5d$ electron. Hence we may use the average number $\bar{n}_d$ of $5d$ electrons per Sm atom to represent the average atomic concentration of Sm^{3+} ions in the system,

$$\bar{n}_d \equiv N(\mathrm{Sm}^{3+})/[N(\mathrm{Sm}^{3+})+N(\mathrm{Sm}^{2+})],$$

where $N(\mathrm{Sm}^{3+})$ and $N(\mathrm{Sm}^{2+})$ are the numbers of

Sm^{3+} and Sm^{2+} ions, respectively.

As regards the interplay between the valence fluctuation and the lattice vibration, S ions may be supposed to play a predominant role, because an S ion has nearly five times smaller atomic mass than that of an Sm ion. Therefore, throughout the present study we neglect the effects of the finiteness of the Sm-ions atomic mass for the sake of simplicity. Since an Sm^{3+} ion has a smaller ionic diameter than an Sm^{2+} ion as noted above, when a Sm ion changes its valence from Sm^{2+} to Sm^{3+}, the *S* ions surrounding the relevant Sm ion must contract towards the Sm ion. Then, the repulsive interactions among the S-ions core electrons and the Sm-ions core electrons might just balance the attractive Coulomb interaction among the S ions and the Sm ions. On the other hand, when an Sm ion changes its valence from Sm^{3+} to Sm^{2+}, the situation is reversed. Then, the S ions surrounding the Sm ion must be pushed away from the Sm ion. The most essential part of these processes can be described by the following simple electron-phonon interaction:

$$H_{e\text{-ph}} = -\sum_{\vec{R}_s,\,\alpha} g\,\frac{\vec{a}_\alpha\cdot\vec{u}(\vec{R}_s)}{a}\,[\,n_f(\vec{R}_s+\vec{a}_\alpha)-\bar{n}_f\,]\;. \tag{2.1}$$

Note, g should also include Coulomb contributions proportional to $\langle i/\nabla V_s/i\rangle$. In Eq. (2.1) $\vec{R}_s$ runs over all of the S-ion sites, $\vec{a}_\alpha(\alpha=\pm 1,\ \pm 2,\ \pm 3)$ denotes the unit lattice vector of magnitude a (a is the lattice constant) pointing to the nearest neighbors of an S ion, $\vec{u}_s(\vec{R}_s)$ is the displacement vector of the S ion at lattice point $\vec{R}_s$, $n_f(\vec{R})$ is the number operator of $4f$ electrons at the Sm ion at lattice site $\vec{R}$, and $\bar{n}_f$ is the average number of $4f$ electrons per Sm ion throughout the sample. Since only the difference $[n_f(\vec{R})-\bar{n}_f]$ is relevant, we may simply set $n_f(\vec{R})=1$ if the Sm ion at $\vec{R}$ is divalent and $n_f(\vec{R})=0$ if the Sm ion is trivalent, while $\bar{n}_f=1-\bar{n}_d$. Now, as is usually done, we rewrite Eq. (2.1) in terms of electron operators (f, d, etc.) and phonon (Einstein phonon in the present case) operators. Then,

$$H_{e\text{-ph}} = \sum_{\vec{R}_s,\,\alpha} g_\alpha[\,n_f(\vec{R}_s+\vec{a}_\alpha)-\bar{n}_f\,][\,b^\dagger_\alpha(\vec{R}_s)+b_\alpha(\vec{R}_s)\,]\,, \tag{2.2}$$

where $g_\alpha=(\hbar/2\omega_0 M_s)^{1/2} g\,\mathrm{sgn}(\alpha)$ and M_s is the atomic mass of an S ion. The phonon operator is defined by

$$\vec{u}(\vec{R}_s)=\left(\frac{\hbar}{2\omega_0 M_s}\right)^{1/2}\sum_{\alpha}\,[\,b^\dagger_\alpha(\vec{R}_s)+b_\alpha(\vec{R}_s)\,]\,\frac{\vec{a}_\alpha}{a}\,,$$

together with $b^\dagger_\alpha(\vec{R}_s)\equiv b^\dagger_{-\alpha}(\vec{R}_s)$ and $b_\alpha(\vec{R}_s)\equiv b_{-\alpha}(\vec{R}_s)$. The harmonic term in the phonon Hamiltonian is given by

$$H_{\mathrm{ph}}=\sum_{\vec{R}_s,\,\alpha}\tfrac{1}{2}\hbar\,\omega_0[\,b^\dagger_\alpha(\vec{R}_s)b_\alpha(\vec{R}_s)+\tfrac{1}{2}]\,. \tag{2.3}$$

III. SIMPLE MODEL ASSUMING LOCALIZED *d* ELECTRONS

First, we investigate the case $\bar{n}_d \ll 1$, which is supposed to be a extreme case realized in the semiconducting phase. Then the Sm ions are mostly in the Sm^{2+} state and only occasionally excited to the Sm^{3+} state through the f-d hybridization mechanism. Consequently, we may regard Sm^{3+} ions as isolated excited states of Sm ions just like impurities dissolved in the Sm^{2+} matrix, and neglect in lowest approximation the interaction among Sm^{3+} ions.[19] When a Sm ion changes its valence from Sm^{2+} to Sm^{3+}, it must release a localized f electron as a delocalized d electron. The d electron can move to other Sm ion sites because of the delocalized nature of the d wave function. However, it cannot move completely away from the Sm^{3+}-ion site from which it has been released because of the strong Coulomb attraction between the d electron and the f hole left

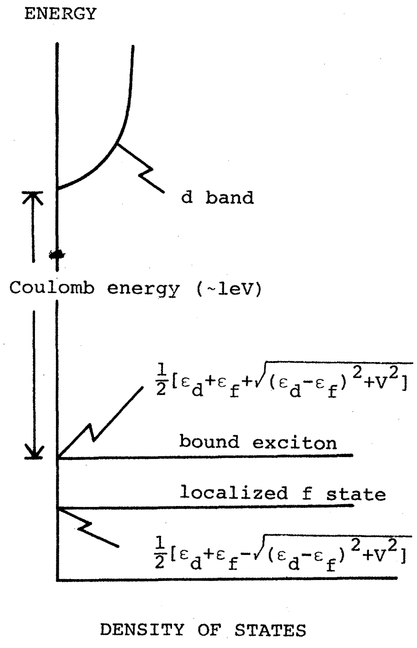

FIG. 1. Illustration of the electronic configuration in the semiconducting phase described by Eq. (3.1) in which the electron-phonon interaction is neglected. Only the localized f states are occupied by electrons in the ground state. The characteristic frequency of the valence fluctuation is given by the larger of $(\epsilon_d-\epsilon_f)/\hbar$ and $V/\hbar$. In the present study we assume $(\epsilon_d-\epsilon_f)\gg V$, i.e., $\bar{n}_d \ll 1$.

behind in the Sm^{3+} ion. Actually, a bound exciton is formed whose binding energy is of the order of the Coulomb energy, which is significantly larger than the relevant energies involved in the present problem. Thus, we may neglect the explicit effects of the band character of the d electrons,[20] although implicit band effects are included in the formation of the exciton. Thus, neglecting band effects, the simplest form of the effective Hamiltonian for the present problem may be given by

$$H = H_f + H_d + H_{fd} + H_{\mathrm{ph}} + H_{e\text{-ph}} \quad , \tag{3.1}$$

with

$$H_f \equiv \sum_{\vec{\mathrm{R}}_m} \epsilon_f n_f(\vec{\mathrm{R}}_m) \ ,$$

$$H_d \equiv \sum_{\vec{\mathrm{R}}_m} \epsilon_d n_d(\vec{\mathrm{R}}_m) \ ,$$

$$H_{fd} \equiv \sum_{\vec{\mathrm{R}}_m} [Vf^\dagger(\vec{\mathrm{R}}_m) d(\vec{\mathrm{R}}_m) + \mathrm{H.c.}] ,$$

where H_{ph} and $H_{e\text{-ph}}$ are given in Eqs. (2.3) and (2.2). Here, R_m runs over all of the Sm sites. We use $n_f(\vec{\mathrm{R}}_m) + n_d(\vec{\mathrm{R}}_m) = 1$. As far as the present problem is concerned, the spin degeneracy of the electron is not relevant, and hence we do not use explicitly spin indices. The electronic configuration described by Eq. (3.1) in which the electron-phonon interaction is neglected is illustrated in Fig. 1.

Since we wish to treat the electron-phonon interaction $H_{e\text{-ph}}$ as exactly as possible, we treat $H_{e\text{-ph}}$ by using the canonical transformation method rather than the perturbation method. The canonical transformation[14] which diagonalizes the electron-phonon interaction $H_{e\text{-ph}}$ is given by e^D with

$$D = \sum_{\vec{\mathrm{R}}_s, \alpha} \frac{g_\alpha}{\omega_0} [n_f(\vec{\mathrm{R}}_s + \vec{\mathrm{a}}_\alpha) - \bar{n}_f][b_\alpha^\dagger(\vec{\mathrm{R}}_s) - b_\alpha(\vec{\mathrm{R}}_s)] .$$

Then, the transformed Hamiltonian $\tilde{H} = e^{-D} H e^D$ is given by

$$\tilde{H} = \tilde{H}_f + \tilde{H}_{fd} + \tilde{H} \ .$$

with

$$\tilde{H}_f = H_f - \sum_{\vec{\mathrm{R}}_s} \omega_0 \left(\sum_\alpha \frac{g_\alpha}{\omega_0} [n_f(\vec{\mathrm{R}}_s + \vec{\mathrm{a}}_\alpha) - \bar{n}_f] \right)^2 ,$$

$$\tilde{H}_d = H_d ,$$

$$H_{fd} = \sum_{\vec{\mathrm{R}}_m} \left[Vf^\dagger(\vec{\mathrm{R}}_m) d(\vec{\mathrm{R}}_m) \exp\left(\sum_\alpha \frac{g_\alpha}{\omega_0} [b^\dagger(\vec{\mathrm{R}}_m + \vec{\mathrm{a}}_\alpha) - b(\vec{\mathrm{R}}_m + \vec{\mathrm{a}}_\alpha)] \right) + \mathrm{H.c.} \right] ,$$

$$\tilde{H}_{\mathrm{ph}} = H_{\mathrm{ph}} \ . \tag{3.2}$$

Now $\tilde{H}_{fd}$ is taken into account perturbationally. With the help of the ordinary Green's-function technique,[21] we calculate the average f-electron number $\bar{n}_f = \langle n_f(\vec{\mathrm{R}}_m) \rangle$, the ground-state energy $E_0 = \langle \tilde{H} \rangle$, the renormalized phonon energy $\tilde{\omega}_0$, and the mean-square displacement of S ions $\langle u^2(\vec{\mathrm{R}}_s) \rangle$. Here, $\langle A \rangle$ means the expectation value of A for the true ground state of $\tilde{H}$. Since the explicit procedure of the calculation is quite straightforward, we only give the final results which are exact up to $O(V^2)$:

$$\bar{n}_d \simeq \sum_{n=0}^{\infty} \left(\frac{\eta^{2n}}{n!} \right) \frac{|\tilde{V}|^2}{(\epsilon_d - \tilde{\epsilon}_f + n\omega_0)^2} \ , \tag{3.3}$$

$$E_0 \simeq \epsilon_f + \tfrac{1}{2}\omega_0 - \sum_{n=0}^{\infty} \left(\frac{\eta^{2n}}{n!} \right) \frac{|\tilde{V}|^2}{\epsilon_d - \tilde{\epsilon}_f + n\omega_0} \ , \tag{3.4}$$

$$\tilde{\omega}_0 \simeq \omega_0 \left[1 - \frac{|\tilde{V}|^2}{\omega_0} \sum_{n=0}^{\infty} \left(\frac{\eta^{2n+2}}{n!} \right) \left(\frac{1}{\epsilon_d - \tilde{\epsilon}_f + n\omega_0 - \tilde{\omega}_0} + \frac{1}{\epsilon_d - \tilde{\epsilon}_f + n\omega_0 + \tilde{\omega}_0} - \frac{2}{\epsilon_d - \tilde{\epsilon}_f + n\omega_0} \right) \right] , \tag{3.5}$$

$$\langle u^2\rangle \simeq \frac{3\hbar}{2\omega_0 M_s}\left[1+|\tilde{V}|^2\sum_{n=0}^{\infty}\left(\frac{\eta^{2n+2}}{n!}\right)\left(\frac{4}{(\epsilon_d-\tilde{\epsilon}_f+n\omega_0)^2}+\frac{2}{[\epsilon_d-\tilde{\epsilon}_f+(n+1)\omega_0]^2}-\frac{6}{(\epsilon_d-\tilde{\epsilon}_f+n\omega_0)[\epsilon_d-\tilde{\epsilon}_f+(n+1)\omega_0]}\right)\right], \tag{3.6}$$

with

$$\eta^2 \equiv \sum_{\alpha}\left(\frac{g_\alpha}{\omega_0}\right)^2,$$

$$|\tilde{V}|^2 \equiv |V|^2 e^{-\eta^2}, \tag{3.7}$$

$$\tilde{\epsilon}_f \equiv \epsilon_f + (2\bar{n}_f - 1)\eta^2\omega_0 .$$

In deriving these results, we have assumed $(\epsilon_d - \tilde{\epsilon}_f) > 0$, which is consistent with the condition $\bar{n}_d = 1 - \bar{n}_f \ll 1$. Here, it should be noted that every bare vertex V is renormalized to $\tilde{V}$ due to an arbitrary number of phonon-closed loops attached to it. This is essentially due to the local lattice distortion. The n summation in the above equations gives the exchange process between two adjacent vertices. In calculating the renormalized phonon energy $\tilde{\omega}_0$, we have used, for the phonon Green's function, the form[21]

$$D(\omega) = -i\int dt \langle T\,[[b^\dagger(t) - b(t)],[b(0) - b^\dagger(0)]]\rangle \times e^{i\omega t}, \tag{3.8}$$

where $b^\dagger(\vec{R}_s, t)$ and $b(\vec{R}_s, t)$ are the Heisenberg representation of $b^\dagger(\vec{R}_s)$ and $b(\vec{R}_s)$, respectively. The renormalized phonon frequency $\tilde{\omega}_0$ is given by the pole of $D(\omega)$, whose formal expression is given by

$$D(\omega) = D_0(\omega)[1 - \Pi(\omega)D_0(\omega)]^{-1}, \tag{3.9}$$

with

$$D_0(\omega) = 2\,\omega_0(\omega^2 - \omega_0^2 + i\delta)^{-1},$$

where $\Pi(\omega)$ is the phonon self-energy whose typical diagrams are illustrated in Fig. 2.

Now we discuss these results in some limiting cases. First, we assume $(\epsilon_d - \tilde{\epsilon}_f) \gg \omega$. Then Eqs. (3.3)–(3.6) simplify as follows:

$$\bar{n}_d \simeq \frac{|V|^2}{(\epsilon_d - \tilde{\epsilon}_f)^2}, \tag{3.10}$$

$$E_0 \simeq \epsilon_f - \frac{\omega_0}{2} - (\epsilon_d - \epsilon_f)\bar{n}_d, \tag{3.11}$$

$$\tilde{\omega}_0 \simeq \omega_0\left[1 - 2\eta^2\left(\frac{\omega_0}{\epsilon_d - \tilde{\epsilon}_f}\right)\bar{n}_d\right], \tag{3.12}$$

$$\langle u_s^2\rangle \simeq \frac{3\hbar}{2\omega_0 M_s}\left(1 + 2\eta^2\frac{\omega_0}{\epsilon_d - \tilde{\epsilon}_f}\bar{n}_d\right). \tag{3.13}$$

To be consistent with the condition[20] $\bar{n}_d \ll 1$, we must have $[|V|^2/(\epsilon_d - \tilde{\epsilon}_f)^2] \ll 1$. Note, the polaron factor in $\tilde{V}$ is completely canceled by the contributions from the terms including the multiphonon exchange between the two adjacent vertices. So we have the bare vertex V in Eq. (3.10). Note, the valence fluctuation makes the phonon softer through the electron-phonon interactions, see Eq. (3.12). Also note, the correction to $\langle u_s^2\rangle$ due to the electron-phonon interaction may be regarded fully due to the phonon softening. Equation (3.13) results from Eq. (3.12) if $\langle u_s^2\rangle$ is given by $(3\hbar/2\tilde{\omega}_0 M_s)$. Secondly, we assume $\omega_0 \gg (\epsilon_d - \tilde{\epsilon}_f) > 0$. Then, we find

$$\bar{n}_d \simeq \frac{|\tilde{V}|^2}{(\epsilon_d - \tilde{\epsilon}_f)^2}, \tag{3.14}$$

$$E_0 \simeq \epsilon_f + \frac{\omega_0}{2} - (\epsilon_d - \epsilon_f)\bar{n}_d, \tag{3.15}$$

$$\tilde{\omega}_0 \simeq \omega_0\left(1 + (2 - \eta^2)\,\eta^2\,\frac{\epsilon_d - \tilde{\epsilon}_f}{\omega_0}\,\bar{n}_d\right), \tag{3.16}$$

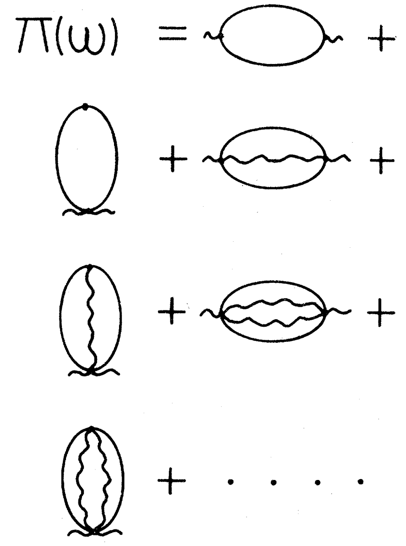

FIG. 2. Typical diagrams for the phonon self-energy. The solid lines denote f- or d-electron propagator and the wavy lines denote unperturbed phonon propagator $D_0(\omega)$. The vertices denote the renormalized f-d mixing interaction $\tilde{V}$.

and

$$\langle u_s^2 \rangle \simeq \frac{3\hbar}{2\omega_0 M_s} (1+4\eta^2 \bar{n}_d) . \tag{3.17}$$

To be consistent with the assumption[20] $\bar{n}_d \ll 1$, we must have $[\,|\tilde{V}|^2/(\epsilon_d - \tilde{\epsilon}_f)^2] \ll 1$. In this case, we note that the multiphonon exchange is not important and hence we have $\tilde{V}$ in Eq. (3.14). Also, note the valence fluctuation makes the phonon harder for $\eta^2 < 2$ and softer for $\eta^2 > 2$. We can estimate η^2 approximately by using the relation

$$\eta^2 \simeq \frac{N_{\mathrm{NN}}}{8} [R(\mathrm{Sm}^{2+}) - R(\mathrm{Sm}^{3+})]^2 / \langle u_s^2 \rangle_0 , \tag{3.18}$$

which is derived in the Appendix. Here, $R(M)$ is the ionic diameter of the ion M and N_{NN} is the number of the nearest neighbors of an S ion. By using the experimental data,[4] $R(\mathrm{Sm}^{2+}) \simeq 1.14$ Å, $R(\mathrm{Sm}^{3+}) \simeq 0.96$ Å, and $N_{\mathrm{NN}} = 6$ together with[6] $[\langle u^2(R_s) \rangle_0]^{1/2} \simeq 0.07$ Å we find $\eta^2 \simeq 5$. Although we cannot take this number for η^2 too seriously because of the crudeness involved in the formula (3.18), we still feel that it is unlikely to find the phonon hardening due to the valence fluctuation in a real system. Finally note, the correction in $\langle u_s^2 \rangle$ is essentially independent of the phonon softening or hardening.[22] Actually this correction results from the random motion of an S ion following the changes in ionic sizes of its neighboring Sm ions induced by the valence fluctuation. Thirdly, we assume $\omega_0 \simeq \epsilon_d - \tilde{\epsilon}_f$. Then we have to execute the n summation in Eqs. (3.3), (3.4), and (3.6) to obtain the values of $\bar{n}_d$, E_0, and $\langle u_s^2 \rangle$. Most interesting is the calculation of $\tilde{\omega}_0$. Note, the first term in the second set of large parentheses in Eq. (3.5) will be divergent if we take $\tilde{\omega}_0 = \epsilon_d - \tilde{\epsilon}_f \simeq \omega_0$ with $n = 0$. Therefore, we cannot replace $\tilde{\omega}_0$ in Eq. (3.5) simply by ω_0, as is done in usual perturbation procedure. Solving Eq. (3.5) with respect to $\tilde{\omega}_0$ we find

$$\tilde{\omega}_0 \simeq \omega_0 \left(1 \pm \eta \frac{|\tilde{V}|}{\omega_0} \right), \quad \epsilon_d - \tilde{\epsilon}_f \simeq \omega_0 , \tag{3.19}$$

where the sign ± corresponds to the sign of $(\omega_0 - \epsilon_d + \tilde{\epsilon}_f)$. This is the result due to the resonantlike coupling effect between the phonon and the valence fluctuations. One should note again that, although we do have a nonperturbative modification of the phonon frequency, we do not find a singular behavior of other physical quantities such as $\bar{n}_d$, E_0, and $\langle u_s^2 \rangle$. The anomalous softening of the optical-zone boundary phonons observed in SmS at low pressure can be explained with the present model by assuming that $(\epsilon_d - \tilde{\epsilon}_f) \gtrsim \omega_0$.

IV. SIMPLE MODEL ASSUMING DELOCALIZED *d* ELECTRONS

If $\bar{n}_f \equiv 1 - \bar{n}_d \ll 1$, then all of the Sm ions are mostly in the Sm^{3+} state and very occasionally excited to the Sm^{2+} state through the *f*-*d* hybridization mechanism. This is supposed to be an extreme case realized in the metallic phase. Again, we may neglect the interaction among excited Sm^{2+} states. In the present case, we have the delocalized *d* electrons in the ground-state Sm^{3+} configuration of the Sm ion. The *d* electrons are occasionally trapped by the Sm ion to become bound *f* electrons. This physical model is most simply described by the following Hamiltonian:

$$H = H_f + H_d + H_{fd} + H_{\mathrm{ph}} + H_{e\text{-ph}} \tag{4.1}$$

where H_f, H_{ph}, and $H_{e\text{-ph}}$ are given in Eq. (3.1). H_d is given by

$$H_d = \sum_{\vec{k},\sigma} \epsilon_k d^\dagger_{\vec{k}\sigma} d_{\vec{k}\sigma}$$

and

$$H_{fd} = \sum_{\vec{R}_m} \sum_{\vec{k},\sigma} [V f^\dagger(\vec{R}_m) d_{\vec{k},\sigma} + \mathrm{H.c.}] .$$

Here, ϵ_k is the band energy of the *d* electrons. Note that we use a spin-nonconserving interaction H_{fd} because we are not interested in the spin degeneracy of the *f* states in the present study, but we need to take explicit account of the spin degeneracy of the *d* states in order to avoid unphysical occurrence of the excitonic state. The electronic configuration described by (4.1) in which the electron-phonon interaction is neglected is illustrated in Fig. 3. Now we can follow the procedure similar to that taken in the previous section. We apply the polaron transformation to H to obtain the effective Hamiltonian

$$\tilde{H} = \tilde{H}_f + \tilde{H}_d + \tilde{H}_{fd} + \tilde{H}_{\mathrm{ph}} , \tag{4.2}$$

where $\tilde{H}_d = H_d$,

$$\tilde{H}_{fd} = \sum_{\vec{R}_m} \sum_{\vec{k},\sigma} \left[V f^\dagger(\vec{R}_m) d_{\vec{k},\sigma} \exp\left(\sum_\alpha \frac{g_\alpha}{\omega_0} [b^\dagger(\vec{R}_m + \vec{a}_\alpha) - b(\vec{R}_m + \vec{a}_\alpha)] \right) + \mathrm{H.c.} \right] ,$$

and $\tilde{H}_f$ and $\tilde{H}_{\mathrm{ph}}$ are given in Eq. (3.2). We can use a perturbation expansion with respect to V to calculate various physical quantities. For practical purpose, we may reasonably assume that the density of the d states is given by a constant ρ_0 within the range of the energy of our present interest. Then, the average number of the f electrons $\bar{n}_f$, the shift ΔE_0 of the ground-state energy E_0 due to including $\tilde{H}_{fd}$, the renormalized phonon frequency $\tilde{\omega}_0$, and the mean-square displacement $\langle u^2(\vec{R}_s)\rangle$ are given up to $O(V^2)$ by

$$\bar{n}_f \simeq 2|\tilde{V}|^2\rho_0 \sum_{n=0}^{\infty} \frac{\eta^{2n}}{n!} \frac{1}{n\omega_0+\tilde{\epsilon}_f-\mu}\,, \tag{4.3}$$

$$\Delta E_0 \equiv E_0 - \rho_0 D^2 - \tfrac{1}{2}\omega_0 \simeq -\rho_0|\tilde{V}|^2 \sum_{n=0}^{\infty} \frac{\eta^{2n}}{n!} \ln\left|\frac{D}{n\omega_0+\tilde{\epsilon}_f-\mu}\right|\,, \tag{4.4}$$

$$\begin{aligned}\tilde{\omega}_0 \simeq \omega_0\Bigg[1+\frac{2\rho_0|\tilde{V}|^2}{\omega_0}\sum_{n=0}^{\infty}\frac{\eta^{2n+2}}{n!}\Bigg(\ln\left|\frac{\tilde{\epsilon}_f-\mu+n\omega_0-\tilde{\omega}_0}{\tilde{\epsilon}_f-\mu+n\omega_0}\right| + \ln\left|\frac{\tilde{\epsilon}_f-\mu+n\omega_0+\tilde{\omega}_0}{\tilde{\epsilon}_f-\mu+n\omega_0}\right| \\ - i\pi\theta(\tilde{\epsilon}_f-\mu+n\omega_0-\tilde{\omega}_0)\Bigg)\Bigg]\,,\end{aligned} \tag{4.5}$$

$$\langle u_s^2\rangle \simeq \frac{3\hbar}{2\omega_0 M_s}\left[1+2\rho_0|\tilde{V}|^2\sum_{n=0}^{\infty}\frac{\eta^{2n+2}}{n!}\left(\frac{2}{\tilde{\epsilon}_f-\mu+(n+1)\omega_0}+\frac{4}{\tilde{\epsilon}_f-\mu+n\omega_0}-\frac{6}{\omega_0}\ln\left|\frac{\tilde{\epsilon}_f-\mu+(n+1)\omega_0}{\tilde{\epsilon}_f-\mu+n\omega_0}\right|\right)\right]. \tag{4.6}$$

Here, $\tilde{\epsilon}_f$, η^2, and $|\tilde{V}|^2$ are given in Eq. (3.7). μ and D are the Fermi energy and half of the d band width, respectively. In deriving these results we have used the assumption $(\tilde{\epsilon}_f-\mu)/D \ll 1$, $(\omega_0/D) \ll 1$, together with $\tilde{\epsilon}_f - \mu > 0$ and have kept the lowest-order terms in each expression. For $\tilde{\epsilon}_f - \mu \gg \omega_0$, Eqs. (4.3)–(4.5) simplify as follows:

$$\bar{n}_f \simeq 2\rho_0|V|^2 \frac{1}{\tilde{\epsilon}_f-\mu}\,, \tag{4.7}$$

$$\Delta E_0 \simeq -\tfrac{1}{2}(\tilde{\epsilon}_f-\mu)\ln\left(\frac{D}{\tilde{\epsilon}_f-\mu}\right)\bar{n}_f\,, \tag{4.8}$$

$$\tilde{\omega}_0 \simeq \omega_0\left(1-2\eta^2\frac{\omega_0}{\tilde{\epsilon}_f-\mu}\bar{n}_f\right), \tag{4.9}$$

$$\langle u_s^2\rangle \simeq \frac{3\hbar}{2\omega_0 M_s}\left(1+2\eta^2\frac{\omega_0}{\tilde{\epsilon}_f-\mu}\bar{n}_f\right). \tag{4.10}$$

Note, that these results are essentially the same as those given in Eqs. (3.10)–(3.13), where $\bar{n}_d$ and $(\epsilon_d - \tilde{\epsilon}_f)$ are replaced by $\bar{n}_f$ and $\tilde{\epsilon}_f - \mu$, respectively. For $\omega_0 \gg \tilde{\epsilon}_f - \mu > 0$, we find

$$\bar{n}_f \simeq 2\rho_0|\tilde{V}|^2/(\tilde{\epsilon}_f-\mu)\,, \tag{4.11}$$

$$\Delta E_0 \simeq -\tfrac{1}{2}(\epsilon_f-\mu)\ln\left|\frac{D}{\tilde{\epsilon}_f-\mu}\right|\bar{n}_f\,, \tag{4.12}$$

$$\begin{aligned}\tilde{\omega}_0 \simeq \omega_0\Bigg[1+\Bigg((2-\eta^2)\eta^2\frac{(\tilde{\epsilon}_f-\mu)}{\omega_0}\ln\left|\frac{\omega_0}{\tilde{\epsilon}_f-\mu}\right| \\ - i\pi\eta^2\frac{(\tilde{\epsilon}_f-\mu)}{\omega_0}\Bigg)\bar{n}_f\Bigg]\,,\end{aligned} \tag{4.13}$$

$$\langle u_s^2\rangle \simeq \frac{3\hbar}{2\omega_0 M_s}(1+4\eta^2\bar{n}_f)\,. \tag{4.14}$$

Again, these are essentially the same results as those given in the previous section, see Eqs. (3.14)–(3.17). The only modification is the lifetime effect in $\tilde{\omega}_0$.

As is clear from this, all the results given here are essentially the same as those given in the previous section. Therefore, previous remarks

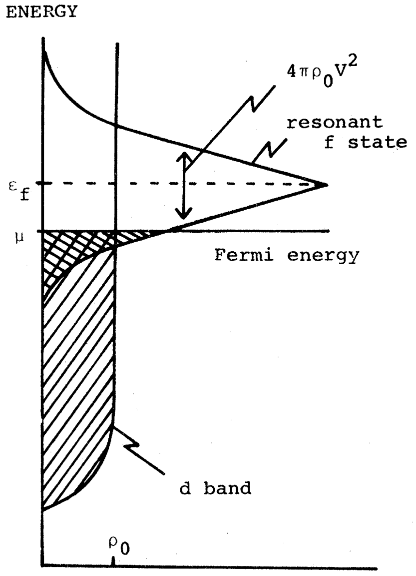

FIG. 3. Illustration of the electronic configuration in the metallic phase described by Eq. (4.1) in which the electron-phonon interaction is neglected. Only the states in the shaded areas both of the d band and the resonant f states are occupied by electrons in the ground state. The characteristic frequency of the valence fluctuation is given by the larger of $(\epsilon_f-\mu)/\hbar$ and $\rho_0 V^2/\hbar$. In the present study we assume $(\epsilon_f-\mu) \gg \rho_0 V^2$, i.e., $\bar{n}_f \ll 1$.

are also relevant here. However, the situation is different for the result for $\tilde{\omega}_0$ in the limit $\omega_0 \simeq \tilde{\epsilon}_f - \mu$. Although we have a singular term in Eq. (4.5) for $n = 0$ and $\tilde{\omega}_0 \simeq \omega_0$, implying that we must solve (4.5) with respect to $\tilde{\omega}_0$ again, the result is not as singular as that given in Eq. (3.19). One obtains

$$\tilde{\omega}_0 \simeq \omega_0(1+\gamma) \ , \tag{4.15}$$

with

$$\gamma \simeq \gamma_0(\ln\gamma_0 + \ln|\ln\gamma_0| + \cdots)$$

and

$$\gamma_0 \equiv \rho_0 |\tilde{V}|^2 \eta^2/\omega_0 .$$

A typical example for the present case may be[5-8] $\mathrm{Sm}_{1-x}Y_x\mathrm{S}$ with $x \gtrsim 0.2$ at room temperature. In order to make a critical comparison of the present results with experiments[5-8] we also have to include the lattice vibrations of the Sm ions explicity.[23] But the general physical situation is well explained by the present model assuming that $\tilde{\epsilon}_f - \mu \gtrsim \omega_0$.

V. CONCLUSION

So far we have investigated the essential features of the interplay between the valence fluctuations and the lattice vibrations by using a simple-model Hamiltonian. The interaction between them includes the ionic-size effect. The latter may be dominant and is most simply described by the electron-phonon interaction given in Eq. (2.12). For simplicity we neglected the lattice vibration of Sm ions.

The essential results of our study are summarized as follows: In a simplified physical model we view the system with $\bar{n}_d \ll 1$ as a system with a few Sm^{3+} ions in an Sm^{2+}-rich system. The case $\bar{n}_f \ll 1$ is viewed correspondingly. We have then calculated the ground-state energy E_0, the renormalized phonon energy $\tilde{\omega}_0$, and the mean-square displacement of S ions $\langle u^2(\vec{R}_s)\rangle$ to first order in the impurity-ion concentration x rigorously. Here, x is defined by $x = \bar{n}_d$ if $\bar{n}_d \ll 1$ and by $x = \bar{n}_f$ for $\bar{n}_f \ll 1$. The results simplify in some limiting cases. If the characteristic electron energy $\Delta\epsilon$ [which is $(\epsilon_d - \tilde{\epsilon}_f)$ or $(\tilde{\epsilon}_f - \mu)$, respectively] is much larger than the characteristic phonon-energy ω_0, the electron-phonon interaction corrections are small, of the relative order of $O(\eta^2(\omega_0/\Delta\epsilon)x)$. The shift $\Delta\omega_0$ in the phonon energy due to the electron-phonon interaction is always negative. The renormalized phonon becomes softer proportionally to the impurity-ion concentration x. The corrections to $\langle u^2(\vec{R}_s)\rangle$ seem to be simply due to the phonon-softening effects. On the other hand, when $\Delta\epsilon \ll \omega_0$, then drastic effects result from the electron-phonon interaction. The matrix element for the f-d hybridization is reduced by the polaron factor of $O(e^{-\eta^2})$. The shift $\Delta\omega_0$ in the phonon energy can be positive or negative depending on the sign of $(\eta^2 - 2)$. The correction to $\langle u^2(R_s)\rangle$ is $O(\eta^2 x)$, which is significantly larger than that expected from the modification in the phonon energy.[22] When $\Delta\epsilon \simeq \omega_0$, we find singular modifications in the phonon frequency [see Eqs. (3.18) and (4.14)], which cannot be expressed simply by the perturbation expansion in x, while we do not find anything singular in other physical quantities.

These results are applicable only to cases with $\bar{n}_d \ll 1$ or $\bar{n}_f \ll 1$ in the strict sense of the approximation used. So it makes sense for the semiconducting phase, because to our best knowledge most of the mixed-valent materials seem to have $\bar{n}_d \ll 1$ in the semiconducting phase. On the other hand, this is not the case for the metallic phase. We have to include higher-order terms in power of $\bar{n}_f$ in order to discuss the more realistic cases.

One of the conventional ways to extend the present study in such direction is to replace the unperturbed f Green's function $G_f^{(0)}(\epsilon) \equiv (\epsilon - \tilde{\epsilon}_f + \mu + i\delta)^{-1}$ used in the above calculations by the renormalized one $G_f^{(1)}(\epsilon) \equiv [\epsilon - \tilde{\epsilon}_f + \mu + \Sigma_f^{(1)}(\epsilon)]^{-1}$, where the self-energy is given by

$$\Sigma_f^{(1)}(\epsilon) \equiv \sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{g}{\omega_0}\right)^{2n} \times \sum_{\vec{k}} \frac{|V|^2}{\epsilon - \epsilon_{\vec{k}} + \mu - n\omega_0 + i\delta\,\mathrm{sgn}(\epsilon_{\vec{k}} - \mu)} \ .$$

which simplifies as

$$\Sigma_f^{(1)}(\epsilon) \simeq \begin{cases} -i\Delta\,\mathrm{sgn}(\epsilon - \mu) & (\text{for } |\epsilon - \mu| \gg \omega_0) \\ -i\tilde{\Delta}\,\mathrm{sgn}(\epsilon - \mu) & (\text{for } \omega_0 \gg |\epsilon - \mu|) \ , \end{cases}$$

with $\Delta \equiv 2\pi\rho_0|V|^2$ and $\tilde{\Delta} \equiv 2\pi\rho_0|\tilde{V}|^2$. This approximation[24] is to neglect the vertex corrections due to the multiphonon exchange processes, which are negligible in the both limits of $[(\tilde{\epsilon}_f - \mu)^2 + \Delta^2]^{1/2} \gg \omega_0$ and of $\omega_0 \gg [(\tilde{\epsilon}_f - \mu)^2 + \tilde{\Delta}^2]^{1/2}$. Thus we can also calculate $\bar{n}_f$, E_0, $\tilde{\omega}_0$, and $\langle u_s^2\rangle$ rigorously in these limits. The details of such calculations and the results will be published separately,[24] but the qualitative feature of the results is summarized in brief as follows: When $(\tilde{\epsilon}_f - \mu)^2 + \Delta^2 \gg \omega_0^2$, $\bar{n}_f$ is given by $\cos^{-1}\{(\tilde{\epsilon}_f - \mu)/[(\tilde{\epsilon}_f - \mu)^2 + \Delta^2]^{1/2}\}/\pi$ and the energy $(\tilde{\epsilon}_f - \mu)$ and $\bar{n}_f$ appearing in Eqs. (4.8)–(4.10) are replaced by $[(\tilde{\epsilon}_f - \mu)^2 + \Delta^2]^{1/2}$ and $\sin(\pi\bar{n}_f)/\pi$, respectively. When $\omega_0^2 \gg (\tilde{\epsilon}_f - \mu)^2 + \tilde{\Delta}^2$, $\bar{n}_f$ is given by $\cos^{-1}\{(\tilde{\epsilon}_f - \mu)/[(\tilde{\epsilon}_f - \mu)^2 + \tilde{\Delta}^2]^{1/2}\}$, and the energy $(\tilde{\epsilon}_f - \mu)$ and $\bar{n}_f$ appearing in Eqs. (4.12)–(4.14) are replaced by $[(\tilde{\epsilon}_f - \mu)^2 + \tilde{\Delta}^2]^{1/2}$ and $\sin(\pi \bar{n}_f)/\pi$, respectively. Hence, we note that the results given in the present study can be used not only for cases with $x \ll 1$, but also for cases with more realistic values of x by regarding $(\Delta\epsilon/\hbar)$ as the characteristic frequency of valence fluctuation as far as the semiquantitative studies are concerned.

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APPENDIX: DERIVATION OF EQ. (3.18)

If the electron-phonon interaction, Eq. (2.1), would result dominantly from the ionic-size effect, then we can relate the coupling constant g to the difference between the ionic diameter of an Sm^{2+} ion and that of an Sm^{3+} ion. Let us look at a pair of neighboring S^{2-} ion and Sm ion located at sites $\vec{R}_s$ and $\vec{R}_s + \vec{a}_\alpha$, respectively. Then the displacement u of the S ion is a function $u(n_f)$ of the number n_f of f electrons in the Sm ion. We may regard the difference $\langle \Delta u \rangle \equiv |u(1) - u(0)|$ as the difference between the ionic diameters $\Delta R \equiv [R(\mathrm{Sm}^{2+}) - R(\mathrm{Sm}^{3+})]$. Then,

$$g \simeq \tfrac{1}{2} M_s \omega_0^2 \Delta R \ . \tag{A1}$$

On the otherhand, $M_s \omega_0$ is related to the mean-square displacement $\langle u_s^2 \rangle_0$ in the zero-point oscillation by the relation

$$M_s \omega_0 = \tfrac{1}{2} \langle u_s^2 \rangle_0 \ . \tag{A2}$$

Using these results, we find the result (3.18). Note, this estimate of g neglects contributions resulting from the conventional electron-lattice coupling.

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