

Electron-phonon interaction in systems with unstable valency

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A theory is developed of electronic-vibrational interaction in rare-earth (RE) semiconductors with stable and intermediate valencies. A microscopic substantiation is proposed for the model of adiabatic charge density deformations that are related to local excitations (excitons) in RE-ion f shells. It is shown that the strong softening of the modes by excitonic instability of RE semiconductors to a transition into a state with intermediate valency leads to a substantial renormalization and damping of the phonons in a phase with intermediate valency. The calculated dispersion of the renormalization and damping agrees well with experiment.

1. INTRODUCTION

Notwithstanding the noticeable progress in calculations of the phonon spectra of crystals containing atoms with unfilled d and f shells (see, e.g., Ref. 1), the theory of electron-phonon interaction in these systems is still quite far from completion. The difficulties encountered are due primarily to the dual role of the $d(f)$ electrons in the formation of the phonon spectrum. On the one hand, these electrons can be regarded as belonging to the core and as such are described by different variants of the deformed-ion model² or by the deformed-cluster model.⁴ In theories of this type, which are as a rule phenomenological, it is assumed that the shell electrons become *adiabatically* attuned to the ion displacements, and the role of the “nonadiabatic” electron-phonon interaction in the formation of the phonon spectrum is small. On the other hand, the electron spectra of both metallic and nonmetallic compounds of $d(f)$ elements contain bands brought about by direct or indirect overlap of the $d(f)$ shells, and in many theories^{5,6} the contribution of these electrons to the formation of the phonon spectrum is described, in analogy with the contribution of normal electrons in wide bands, on the basis of the Fröhlich Hamiltonian for *nonadiabatic* electron-phonon interaction. Since the $d(f)$ bands are frequently quite narrow, the logic of this approach suggests a substantial nonadiabaticity of ion interaction with d and f electrons, and hence a large contribution of the electron-phonon interaction to the renormalization of the phonon spectrum. Both approaches, despite the evident disparity of the initial premises, yield in many cases a relatively fair description of the phonon spectra (if enough fitting parameters are used), so that the question of the role of electron-phonon interaction in the formation of the vibrational spectrum remains actually open.

It must be added that the microscopic character of the description of the electron-phonon interaction with the aid of a Fröhlich Hamiltonian is to a certain degree illusory. It is well known that the procedure of “derivation” of the Fröhlich Hamiltonian admits of a definite leeway in the choice of the bare phonons, and the prescription for a consistent description of the electron-phonon interaction with the aid of this Hamiltonian, developed in its day for simple metals,^{7,8} requires introduction into the Fröhlich Hamiltonian of “adiabatic” phonons whose dynamic matrix contains an adiabatic part of the electron-phonon interaction. Only the slow electronic excitations, which take no part in the formation of the adiabatic potential relief for the ion motion, con-

tribute to the true electron-phonon interaction. Depending on the width of the d or f band, many various regimes of electron interaction with the ion subsystem are possible, ranging from almost adiabatic (for broad bands) to substantially retarded (for extremely narrow bands). In the latter case, however, the narrowness of the bands means strong localization of the $d(f)$ electrons in the atomic shells, and this leads in turn to replacement of the “fast” translational degrees of freedom typical of good metals by fast atomic excitations, as in nonconducting crystals with strongly polarizable shells.

The question of the degree of nonadiabaticity of the electron interaction is particularly pressing for systems with unstable valency of the $d(f)$ shells). The reason is that valency fluctuations, connected at first glance with intra-atomic degrees of freedom, are characterized in these systems by times 10^{-12} – 10^{-13} s, close to the vibration period of the lattice ions. This suggests a strong nonadiabaticity of the electronic-vibrational system and an important role of polaron effect in the very cause of the intermediate valency (see, e.g., the review by Khomskii⁹). Attempts were made in the theory of electron-phonon interaction in systems with intermediate valency (IV) to describe the phonon spectrum both in a phenomenological model of deformable clusters,^{10,11} and with the aid of a Fröhlich Hamiltonian.¹² The problem was solved in these papers, however, without allowance for the specific features of a semiconductor with IV and without an understanding of the nature of its ground state, in fact within the framework of a two-band model of the metal.

In this paper we propose a procedure for a consistent separation of the adiabatic phonons in rare earth (RE) semiconductors with unfilled cation f shells, present a microscopic substantiation of the model of deformed crystals as applied to these systems, and separate, on the basis of comparison with experimental data, the adiabatic and nonadiabatic contributions of the f shells to the formation of the phonon spectrum of samarium sulfide in the normal semiconducting state and in the intermediate valency phase.

2. ELECTRON-PHONON INTERACTION IN RE SEMICONDUCTORS WITH STABLE VALENCY

Rare-earth chalcogenides are systems for which the problems of the procedure of formation of adiabatic phonons, formulated in the Introduction, are fully relevant. Indeed, in these systems the RE f levels, which form the upper

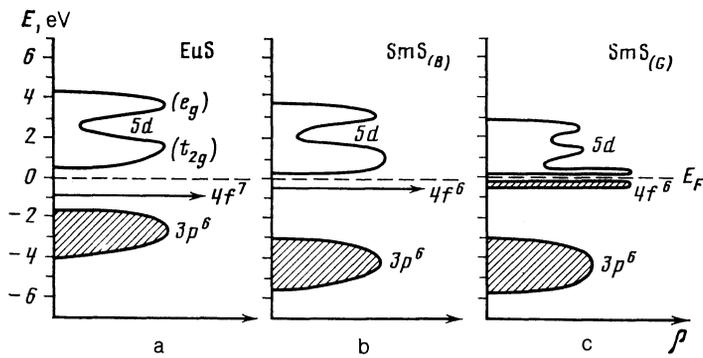


FIG. 1. Electronic density of states

very narrow valence band, land in the usual semiconductor gap between the valence band due to p -shells of the chalcogen ions and the conduction band genetically related to the unfilled d shells of the RE ions. This narrow band can be located deep inside the gap (europium chalcogenides) or near the bottom of the conduction band (samarium chalcogenides). In the latter case, under pressure or when doped with trivalent RE elements, a phase transition from a normal semiconductor to a semiconductor with IV takes place (see Ref. 9). We have thus a standard system with extremely narrow filled f bands a broad band gap (for example, EuS), a narrow-band semiconductor with a narrow band gap (the "black" phase of $\text{SmS}_{(B)}$), and a semiconductor with extremely narrow forbidden band (50–70 K) and a valence band made up of f -shells of RE ions in the IV state (the "gold" phase of $\text{SmS}_{(G)}$). Figure 1 shows schematically the electronic spectra of these systems, and Fig. 2 the corresponding phonon spectra.¹⁾

We see that the phonon spectrum differs substantially from the standard EuS spectrum even in the "black" $\text{SmS}_{(B)}$; the entire LO mode is substantially softened. The LO mode in the "gold" phase $\text{SmS}_{(G)}$ turns out to be lower than the TO mode in the entire Brillouin zone. In addition, the LA mode is substantially softened along [111]. We shall attempt below to separate the adiabatic and nonadiabatic contributions to the renormalization of the phonon spectra of RE semiconductors with NaCl structure, by comparing the electron and phonon spectra shown in Fig. 1 and 2 with the present notions concerning the nature of the IV phase in samarium chalcogenide.

Let us formulate the procedure of separating the adia-

batic phonons for systems in which there exist, beside the band degrees of freedom, also specific intra-atomic degrees connected with the virtual excitations in the unfilled f -shells of atoms of one of the sublattices. The traditional procedure of separating electronic and vibrational variables^{7,8} is implemented for the electron-ion Hamiltonian written in the form

$$H\{\mathbf{r}, \mathbf{R}\} = H_i\{\mathbf{R}\} + H_{ei}\{\mathbf{r}, \mathbf{R}\} + H_e\{\mathbf{r}\}, \quad (2.1)$$

where $\{\mathbf{R}\}$ and $\{\mathbf{r}\}$ are the aggregates of the ion and electron coordinates. The wave function of the electron-ion system is expanded in the set of adiabatic basis functions

$$\Psi\{\mathbf{r}, \mathbf{R}\} = \sum_p \Phi_p\{\mathbf{R}\} \psi_p\{\mathbf{r}, \mathbf{R}\}, \quad (2.2)$$

where $\psi_p\{\mathbf{r}, \mathbf{R}\}$ is the wave function of the electron subsystem at fixed positions of the ions, and $\Phi_p\{\mathbf{R}\}$ is the wave function of the vibrational subsystem corresponding to a given set p of electron quantum numbers. In the theory of simple metals the basis ψ_p is chosen to be the Bloch wave functions of the conduction electrons. In the case of RE semiconductors it is necessary to include in the basis $|p\rangle$, besides pairs comprising a conduction-band electron and a valence-band hole, also localized f -shell excitations—states of the Frenkel-exciton type, which determine the polarizability of the RE ions.

Expanding Φ_p in (2.2) in terms of the adiabatic vibrational functions:

$$\Phi_p\{\mathbf{R}\} = \sum_{\beta} \xi_{p\beta} \chi_{p\beta}\{\mathbf{R}\}, \quad (2.3)$$

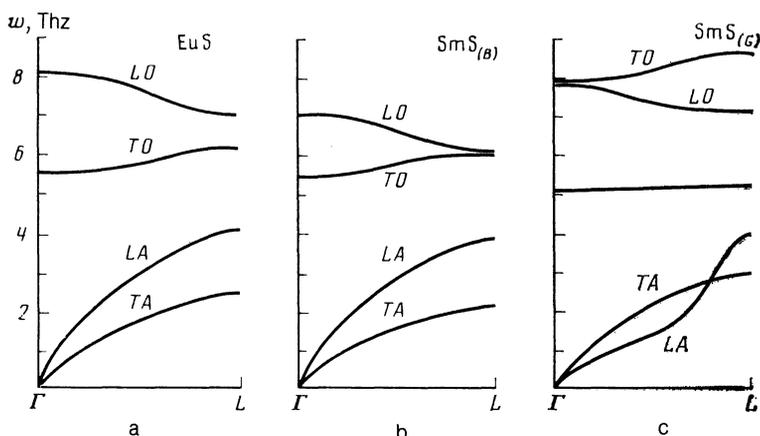


FIG. 2. Phonon spectra.

we obtain an equation for the ground state of the system (cf. Ref. 7)

$$\sum_{\beta} \xi_{0\beta} [H_i\{\mathbf{R}\} + E_0\{\mathbf{R}\} - E] \psi_0\{\mathbf{r}, \mathbf{R}\} \chi_{0\beta}\{\mathbf{R}\} = -\hat{C}_R \sum_{p\beta} \psi_p\{\mathbf{r}, \mathbf{R}\} \chi_{p\beta}\{\mathbf{R}\}, \quad (2.4)$$

where $E_0\{\mathbf{R}\}$ is the crystal energy in the ground state with a filled valence band described by the electronic wave function $\psi_0\{\mathbf{r}, \mathbf{R}\}$. The right-hand side of (2.4) contains corrections to the wave functions for the nonadiabaticity of the ground state whose operator is of the known form

$$\hat{C}_R \psi_p\{\mathbf{r}, \mathbf{R}\} = -\sum_j \frac{1}{M_j} \nabla_j \psi_p\{\mathbf{r}, \mathbf{R}\} \nabla_j - \frac{1}{2} \sum_j \frac{1}{M_j} \nabla_j^2 \psi_p\{\mathbf{r}, \mathbf{R}\} \quad (2.5)$$

(the summation is over the lattice sites). The equation for the adiabatic-phonon spectrum is obtained by discarding the right-hand side of (2.4):

$$(H_i\{\mathbf{R}\} - \Delta E_0\{\mathbf{R}\}) \chi_{0\beta}\{\mathbf{R}\} = E_{0\beta} \chi_{0\beta}\{\mathbf{R}\}, \quad (2.6)$$

where ΔE_0 is the electron-energy part that depends on the ion displacements $\mathbf{u}_j = \mathbf{R}_j - \mathbf{R}_{j0}$ and determines the electronic contribution to the strength matrix

$$\Delta E = E_0\{\mathbf{R}\} - E_0\{\mathbf{R}_0\} = \sum_p \sum_{jj'} \sum_{xx'} \frac{\langle 0 | \nabla_{\mathbf{R}_j} H_{ei} | p \rangle \langle p | \nabla_{\mathbf{R}_j'} H_{ei} | 0 \rangle}{E_0 - E_p} u_j^x u_{j'}^{x'}. \quad (2.7)$$

The matrix K has the standard adiabatic-theory form^{4,8}

$$K(\mathbf{R}_j - \mathbf{R}_{j'}) = \frac{\partial^2 U_{i-i}}{\partial \mathbf{R}_{j0} \partial \mathbf{R}_{j'0}} + \left\langle 0 \left| \frac{\partial H_{ei}(r)}{\partial \mathbf{R}_{j0}} \chi(\mathbf{r}, \mathbf{r}') \frac{\partial H_{ei}(r')}{\partial \mathbf{R}_{j'0}} \right| 0 \right\rangle, \quad (2.8)$$

where $\chi(\mathbf{r}, \mathbf{r}')$ is the electronic-subsystem linear-response function and enters in the right-hand side of (2.7), while $|0\rangle$ is the ground state of the system.

The non-adiabaticity of the electron-ion system leads to mixing of the adiabatic vibrational modes, and we obtain for the coefficients $\xi_{p\beta}$ in (2.3) the system of equations

$$(E - E_{p\alpha}^{an}) \xi_{p\alpha} = \sum_{p'\beta} C_{pp'}^{\alpha\beta} \xi_{p'\beta}, \quad (2.9)$$

where $C_{pp'}^{\alpha\beta}$ are matrix elements of the nonadiabaticity operator:

$$C_{pp'}^{\alpha\beta} = A_{pp'}^{\alpha\beta} + B_{pp'}^{\alpha\beta}, \quad (2.10)$$

$$A_{pp'}^{\alpha\beta} = \sum_j \frac{1}{M_j} \frac{\langle p | \nabla_{\mathbf{R}_j} H_{ei} | p' \rangle}{E_{p'} - E_p} \langle \chi_{0\alpha} | \nabla_{\mathbf{R}_j} | \chi_{0\beta} \rangle,$$

$$B_{pp'}^{\alpha\beta} = \sum_{j''} \frac{1}{2M_j} \frac{\langle p | \nabla_{\mathbf{R}_j} H_{ei} | p'' \rangle \langle p'' | \nabla_{\mathbf{R}_j} H_{ei} | p' \rangle}{(E_p - E_{p''})(E_{p''} - E_{p'})}$$

(see Ref. 7). The corrections to the phonon energy are given in lowest-order perturbation theory by

$$\Delta E_{0\alpha} = B_{00}^{\alpha\alpha} + \sum_{p\beta} \frac{|A_{0p}^{\alpha\beta}|^2}{E_{0\alpha} - E_{p\beta}}. \quad (2.11)$$

The contribution of these corrections to the phonon frequencies are known⁷ to be small in terms of the parameter $[\hbar\omega_{ph}/(E_0 - E_p)]^2$ compared with the contribution of (2.7).

Let us thus consider the adiabatic contribution of the electronic states of an RE semiconductor to the renormalization of the phonon spectrum, choosing the states $|p\rangle$ in (2.7) to be a continuum of free electron-hole pairs:

$$|b_{\mathbf{k}, \mathbf{q}}\rangle = b_{c, \mathbf{k}+\mathbf{q}}^{\dagger} b_{v, \mathbf{k}} |0\rangle = N^{-1} \sum_{jm} b_{c, j+\mathbf{m}}^{\dagger} b_{v, j} |0\rangle \exp\{-i\mathbf{q}\mathbf{R}_j - i(\mathbf{k}+\mathbf{q})\mathbf{R}_m\} \quad (2.12)$$

and excitonic excitations that have in the general case an intermediate radius

$$|B_{\mathbf{q}}\rangle = N^{-1/2} \sum_{jm} F(\mathbf{m}) b_{c, j+\mathbf{m}}^{\dagger} b_{v, j} |0\rangle \exp(i\mathbf{q}\mathbf{R}_j). \quad (2.13)$$

Here $F(\mathbf{m})$ is the envelope of the exciton wave function, while b_c and b_v are the electron second-quantization operators in the conduction and valence bands.

Substituting (2.12) and (2.13) in (2.7) we obtain in the usual manner the contributions made to the renormalization of the vibrational energy by the band and excitonic excitations $\Delta E_{0\alpha}^{(band)}$ and $\Delta E_{0\alpha}^{(ex)}$:

$$\Delta E_{0\alpha}^{(band)} = \sum_{\mathbf{k}\mathbf{q}\alpha'} \frac{(T_{\mathbf{k}\mathbf{q}}^{\alpha\alpha'}) \cdot T_{\mathbf{k}\mathbf{q}}^{\alpha\alpha'}}{E_{0\alpha} - E_{p, \alpha'}(\mathbf{k}, \mathbf{q})}, \quad (2.14a)$$

where

$$T_{\mathbf{k}\mathbf{q}}^{n_{\mathbf{q}\alpha}, n_{\mathbf{q}\alpha} \pm 1} = \left[\frac{\hbar}{2N\omega_{\mathbf{q}\alpha}} \left(n_{\mathbf{q}\alpha} \pm \frac{1}{2} + \frac{1}{2} \right) \right]^{1/2} \times \sum_{\mathbf{m}} \exp\{-i(\mathbf{k} + \mathbf{q})\mathbf{R}_m\} Q_{\mathbf{q}\alpha}(\mathbf{R}_m), \quad (2.15a)$$

$$Q_{\mathbf{q}\alpha}(\mathbf{R}_m) = \int d^3\mathbf{r} \varphi_{\alpha}(\mathbf{r}) P_{\mathbf{q}\alpha}(\mathbf{r}) \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_m), \quad (2.16)$$

$$P_{\mathbf{q}\alpha}(\mathbf{r}) = -\sum_{\mathbf{t}} M_{\mathbf{t}}^{-1/2} \exp(i\mathbf{q}\mathbf{R}_{\mathbf{t}}) \mathbf{e}_{\mathbf{q}\alpha}^{\mathbf{t}} \nabla_{\mathbf{r}} V(\mathbf{r} - \mathbf{R}_{\mathbf{t}}), \quad \mathbf{R}_{\mathbf{t}} = \mathbf{R}_{\mathbf{t}} + \rho_{\mathbf{t}}, \quad (2.17)$$

$\mathbf{e}_{\mathbf{q}\alpha}^{\mathbf{t}}$ are the phonon-polarization vectors, $n_{\mathbf{q}\alpha}$ are the phonon occupation numbers, and t is the sublattice index. For the exciton contribution we get

$$\Delta E_{0\alpha}^{(ex)} = \sum_{\mathbf{q}\alpha'} \frac{(T_{\mathbf{q}}^{\alpha\alpha'}) \cdot T_{\mathbf{q}}^{\alpha\alpha'}}{E_{0\alpha} - E_{ex, \alpha'}(\mathbf{q})}, \quad (2.14b)$$

$$T_{\mathbf{q}}^{n_{\mathbf{q}\alpha}, n_{\mathbf{q}\alpha} \pm 1} = \left[\frac{\hbar}{2\omega_{\mathbf{q}\alpha}} \left(n_{\mathbf{q}\alpha} \pm \frac{1}{2} + \frac{1}{2} \right) \right]^{1/2} \times \sum_{\mathbf{m}} Q_{\mathbf{q}\alpha}(\mathbf{R}_m) F(\mathbf{m}). \quad (2.15b)$$

The excited-state energies in the denominators of (2.14a) and (2.14b) are of the form

$$E_{p\alpha}(\mathbf{k}, \mathbf{q}) = \varepsilon_{\mathbf{k}+\mathbf{q}}^c - \varepsilon_{\mathbf{k}}^v \pm \hbar\omega_{\mathbf{q}\alpha} + E_{0\alpha}, \quad (2.18a)$$

$$E_{ex, \alpha'}(\mathbf{q}) = E_{ex}(\mathbf{q}) \pm \hbar\omega_{\mathbf{q}\alpha} + E_{0\alpha}, \quad (2.18b)$$

where $E_{ex}(\mathbf{q})$ is the exciton energy. Finally, varying (2.14a) and (2.14b) over the phonon occupation numbers, we ob-

tain expressions for the renormalization of the phonon modes:

$$\delta^{band}(\hbar\omega_{q\alpha})^2 = -2\hbar^2 \sum_{mm'} Q_{q\alpha}^*(\mathbf{R}_m) Q_{q\alpha}(\mathbf{R}_{m'}) \times \frac{1}{N} \sum_{\mathbf{k}} \exp\{i(\mathbf{k}+\mathbf{q})(\mathbf{R}_m-\mathbf{R}_{m'})\} \times \frac{\varepsilon_{\mathbf{k}+\mathbf{q}}^c - \varepsilon_{\mathbf{k}}^v}{(\varepsilon_{\mathbf{k}+\mathbf{q}}^c - \varepsilon_{\mathbf{k}}^v)^2 - (\hbar\omega_{q\alpha})^2}, \quad (2.19a)$$

$$\delta^{ex}(\hbar\omega_{q\alpha})^2 = -2\hbar^2 \left| \sum_{\mathbf{m}} Q_{q\alpha}(\mathbf{R}_m) F(\mathbf{m}) \right|^2 \frac{E_{ex}(\mathbf{q})}{E_{ex}^2(\mathbf{q}) - (\hbar\omega_{q\alpha})^2}. \quad (2.19b)$$

One of the tasks of the present paper is a microscopic substantiation of the choice of the adiabatic electronic variables—local charge density distortions (CDD) for the model of deformed clusters^{3,4}; this is why we have changed over to the site representation in the matrix elements of (2.15). The excitonic excitations describe in our systems the contribution from the distortions of the RE-ion f shells, therefore their interaction with the normal lattice modes can be easily interpreted in terms of intraatomic transitions; a totally symmetric displacement Γ_1 of the lattice atoms—the breathing mode—should correspond to monopole f - f excitations of the RE-element shells, atomic transitions with $\Delta l = 1$ (f - d transitions) determine the dipole response of the shells to displacements with point symmetry Γ_{15} , etc. The fact that the excitons actually have an intermediate radius (2.13) complicates the picture somewhat and, as will be shown below, leads to observable effects in the renormalization and damping of the phonons. The contribution from the interband transitions can also be reduced to local CDD, at least in the nearest-neighbor approximation for linear combinations of the atomic orbitals.

Returning to the question of the differences between the phonon spectra of EuS and SmS_(B), we see that for all the similarity of the properties of these systems they differ precisely in the excitation energies of the electrons from the unfilled f shells. The optical spectra of the EuS and SmS_(B) undergo transitions $f_j^n \rightarrow f_j^{n-1} b_{ck}$ with ionization of these shells when one of the electrons goes off to the conduction band, and also transitions $f_j^n \rightarrow f_j^{n-1} d_j$ with excitation of the f shells themselves. These transitions contribute to (2.18a) and (2.18b), respectively, the threshold energy Δ for a zero-phonon transition of type (2.18a) being 1.12 eV in EuS and 0.23 eV in SmS_(B), while the energy $E_{ex}(0)$ of the optical transition of type (2.18b) is ≈ 2.4 eV in EuS and 0.6–0.8 eV in SmS_(B).^{16,17}

These data suggest that the principal mechanism that softens the phonon spectrum of SmS_(B) compared with EuS is connected with the increase of the adiabatic contribution of the dipole deformations of the RE-element electron shells. Let us find the corresponding contributions to the renormalizations of the longitudinal phonon modes. To this end we must know the form, in the site approximation, of the electron wave functions in the conduction and valence bands. It is known that there is no direct overlap between the f shells of RE ions in sulfides, and the finite width of the valence band (Fig. 1b) is due only to indirect overlap via the d shells (con-

duction-band states). It is convenient to take this overlap into account from the very beginning,^{18,19} choosing as the initial “atomic” functions linear combinations of f and d orbitals which diagonalize the one-electron Hamiltonian of a self-consistent field with filled valence band and empty conduction band

$$H_{band} = \sum_{\mathbf{k}\alpha\sigma} \varepsilon_{\mathbf{k}}^a b_{\mathbf{k}\alpha\sigma}^\dagger b_{\mathbf{k}\alpha\sigma}, \quad a=v, c, \quad (2.20)$$

where

$$\varepsilon_{\mathbf{k}}^{v,c} = \frac{1}{2}(\varepsilon_{d\mathbf{k}} + \varepsilon_f) \mp \frac{1}{4}[(\varepsilon_{d\mathbf{k}} - \varepsilon_f)^2 + 4|V_{fd}(\mathbf{k})|^2]^{1/2}, \\ b_{\mathbf{k}v\sigma} = b_{f\sigma} \cos \varphi + b_{d\mathbf{k}\sigma} \sin \varphi, \quad \text{tg } 2\varphi = 2V_{fd}(\mathbf{k})/(\varepsilon_{d\mathbf{k}} - \varepsilon_f), \quad (2.21) \\ b_{\mathbf{k}c\sigma} = -b_{d\mathbf{k}\sigma} \cos \varphi + b_{f\sigma} \sin \varphi,$$

$\varepsilon_{d\mathbf{k}}$ is the conduction band without allowance for fd hybridization, while $b_{f\sigma}$ and $b_{d\mathbf{k}\sigma}$ are the second-quantization operators of the initial f and d states. The hybridization is characterized by a matrix element that is off-diagonal relative to the site

$$V_{fd}(\mathbf{k}) = \sum_{\mathbf{m}} V_{fd}(\mathbf{m}) \exp\{i\mathbf{k}\mathbf{R}_m\}, \quad (2.22)$$

$$V_{fd}(\mathbf{m}) = (\mathbf{j}+\mathbf{m}, d|V|\mathbf{j}, f) = V_{\chi}(\mathbf{m}),$$

$$|\chi(\mathbf{m})| = 1, \quad \chi(-\mathbf{m}) = -\chi(\mathbf{m}).$$

In the lowest order in V , the correct linear combinations of the f and d orbitals take the form

$$\psi_v(\mathbf{r}-\mathbf{R}_0) = A\psi_f(\mathbf{r}-\mathbf{R}_0) - G_0 V \sum_{\mathbf{m}} \chi^*(\mathbf{m}) \psi_d(\mathbf{r}-\mathbf{R}_0-\mathbf{R}_m), \quad (2.23a)$$

$$\psi_c(\mathbf{r}-\mathbf{R}_0) = A\psi_d(\mathbf{r}-\mathbf{R}_0) - G_0 V \sum_{\mathbf{m}} \chi(\mathbf{m}) \psi_f(\mathbf{r}-\mathbf{R}_0-\mathbf{R}_m). \quad (2.23b)$$

Here A is a normalization factor defined in the nearest-neighbor approximation by the condition $A^2 + 12|VG_0|^2 = 1$. The projection operators $\chi(\mathbf{m})$ select linear neighboring-site wave-function combinations that correspond to a given point-group representation.²⁾ In (2.23) are introduced the lattice Green's functions

$$G_0 = N^{-1} \sum_{\mathbf{k}} (\varepsilon_{d\mathbf{k}} - \varepsilon_f)^{-1}, \quad (2.24)$$

which can be estimated at $D^{-1} \ln|D/\Delta|$, where D is the width of the conduction band and Δ is the band gap for not too small Δ .

To obtain the wave function of a “dipole” exciton with an electron in an excited state of point symmetry T_{2g} it is necessary to take a linear combination of conduction-band orbitals (2.23b) with envelopes $F(\mathbf{m})$ in (2.13). Under conditions of weak hybridization, however, it suffices to retain in it only the central term $\sim F(0)$. As a result, the contribution from the dipole CDD of the f -shells to the renormalization of the phonon spectra takes the form

$$\delta^{\Gamma_{15}}(\hbar\omega_{q\alpha})^2 = -2\hbar^2 \frac{|Q_{q\alpha}^{\Gamma_{15}}(0)F(0)|^2 E_{ex}^{\Gamma_{15}}(\mathbf{q})}{|E_{ex}^{\Gamma_{15}}(\mathbf{q})|^2 - (\hbar\omega_{q\alpha})^2} \\ \approx -2\hbar^2 \frac{|I_{q\alpha}^{\Gamma_{15}} R_q^{\Gamma_{15}}|^2}{E_{ex}^{\Gamma_{15}}(0)} = \lambda_{\alpha}^{\Gamma_{15}} \Phi^{\Gamma_{15}}(\mathbf{q}, \omega_{q\alpha}). \quad (2.25)$$

We have neglected in the last equation the dispersion of the exciton band and separated in the coupling constant the contribution of the "local" CDD $I_{q\alpha}^{\Gamma_{15}}$, which can be identified with the corresponding parameter of the dipole deformation of the shell in the Bilz-Allen adiabatic theory.^{3,4} We have also separated the additional factor $R_q^{\Gamma_{15}}$ connected with the nonfinite character of the interaction, i.e., with the spatial extent of the LCAO (2.23) that describe the states of the conduction and valence bands:

$$I_{q\alpha}^{\Gamma_{15}} = \int d^3r \psi_j^*(\mathbf{r}) P_{q\alpha}^{\Gamma_{15}}(\mathbf{r}) \psi_d(\mathbf{r}), \quad (2.26a)$$

$$R_q^{\Gamma_{15}} = F(0) [A^2 + (VG_0)^2 S(\mathbf{q})], \quad S(\mathbf{q}) = \sum_{\mathbf{m}}^{(nn)} \cos \mathbf{q}\mathbf{R}_m. \quad (2.26b)$$

The summation in the structure factor $S(\mathbf{q})$ is over the nearest neighbors in the cation sublattice.

Thus, the phonon-spectrum renormalization dispersion determined by the form factor $\Phi^\Gamma(\mathbf{q}, \omega_{q\alpha})$ in (2.25), in which are gathered all the factors that depend on the wave vector \mathbf{q} , is produced by the standard contribution Φ_0^Γ of the localized CDD model, a contribution that depends only on the type of lattice and symmetry of the mode Γ , and by the additional factor Φ_1^Γ that modulates this dependence:

$$\Phi^\Gamma(\mathbf{q}, \omega_{q\alpha}) = \Phi_0^\Gamma(\mathbf{q}, \omega_{q\alpha}) \Phi_1^\Gamma(\mathbf{q}, \omega_{q\alpha}). \quad (2.27)$$

In the specific case considered this dependence is due to the nonpointlike character of the CDD, and in the general case it can receive a substantial contribution also for the singularities of the dispersion of the exciton or electron excitations in the denominators of expressions (2.19), for example the Kohn or Van Hove singularities in the band spectrum (2.19a).

The standard form factors of the localized DCC model are analytically calculated in the Appendix for symmetric directions of the Brillouin zone. Also calculated there are the additional corrections for the non-pointlike character of the CDD. In $\text{SmS}_{(B)}$, where the fd hybridization effects are weak, we have $VG_0 \sim V/D \ll 1$ and these corrections are insignificant. To the same accuracy, $o(V^2/D^2)$, we can neglect also the band contribution (2.19a), which does not contain the terms with $\mathbf{R}_m = \mathbf{R}_{m'} = 0$ already accounted for in the form of localized exciton modes. The interband transitions that contribute to the phonon renormalizations are thus simultaneously also nondiagonal with respect to the lattice sites.

The form factor $\Phi_0^{\Gamma_{15}}(\mathbf{q}, \omega_{q\alpha})$ for the CDD dipole mode, calculated from Eqs. (A.9), is shown in Fig. 3a. It is seen that the dipole contribution to $\Delta(\hbar\omega_{q,LO})^2$ can cause a noticeable renormalization of this mode near the points Γ and X , but vanish at the L -point. The corrections for the covalency, as already mentioned, are small and do not alter the phonon dispersion in symmetric directions (see Fig. 3b). We see thus that the experimentally observed softening of the LO mode along the Γ - L line (Fig. 2) cannot be attributed to a single CDD dipole mode and it is necessary to take into account the contribution of the totally symmetric mode (Refs. 10, 11).

To separate this mode from the spectrum of the adiabatic electronic excitations we use the same procedure as in the

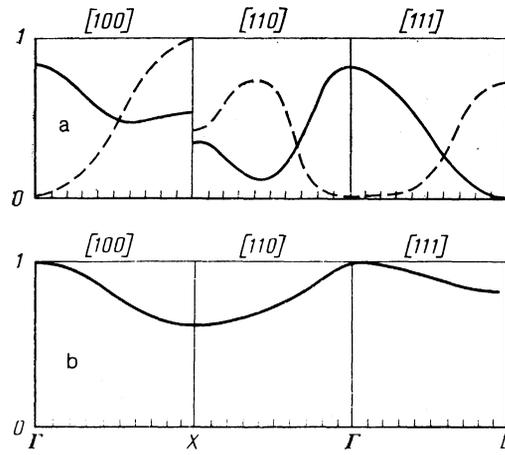


FIG. 3. Dipole-mode form factors in relative units (N is the scale factor): a) standard contribution $\Phi_0^{\Gamma_{15}}(\mathbf{q}, \omega_{q\alpha})$ (N ; solid lines— $\alpha = LO$, $N = 1$; dashed— $\alpha = LA$, $N = 5$; b) correction $|R_q^{\Gamma_{15}}|^2$ ($A^2 = 0.9$).

case of the Γ_{15}^- mode, i.e., we describe the main contribution to the CDD in terms of exciton transitions. To describe the interaction with a totally symmetric vibration breathing mode we must construct a "monopole" exciton that has the same symmetry as the ground state and describes the totally symmetric deformations of the RE ion f shells. Clearly, it is utterly insufficient to take into account only the contribution made to these deformations by the monopole intra-atomic transitions $4f^n \rightarrow nf$, $n = 5, 6, \dots$ in the Sm ion shells, since the corresponding excitations are too hard and hardly change insignificantly EuS to $\text{SmS}_{(B)}$. As noted already by Stevenson,²⁰ however, for an RE semiconductor with an electron spectrum of the type shown in Fig. 1 it is always possible to construct an exciton state having the same symmetry as the ground state, in which one of the f -shell electrons goes over to a weakly bound orbit that captures the nearest coordination spheres. In the case of the Sm ($f_{7F_0}^6$) ion, the excited state can be represented in the form^{19b}

$$\psi_{ex}^{7F_0}(\mathbf{q})_i = 2^{-1/2} \sum_{\mathbf{m}j\sigma} F_q^{7F_0/2}(\mathbf{m}) b_{c, j+\mathbf{m}, \sigma}^+ b_{v, j} |f_j^6, {}^7F_0\rangle \exp(i\mathbf{q}\mathbf{R}_j), \quad (2.28)$$

where $F_q^{7F_0/2}(\mathbf{m})$ is the envelope of an exciton wave function whose symmetry properties are such that it generates a linear combination of d -orbitals \tilde{b}_j that are transformed in accordance with the irreducible representation $\gamma_{5/2}$ of a binary rotation group, for which

$$\Gamma({}^6H_{5/2}) \gamma_{5/2} = \Gamma({}^7F_0), \quad (2.29)$$

${}^6H_{5/2}$ and 7F_0 are the atomic terms of the Sm ion in the respective configurations f^5 and f^6 ; in the cubic group they go over into Γ_{7^-} and Γ_{1^+} , so that $\gamma_{5/2}$ should be transformed into the Γ_{7u} state formed by the t_{2g} and e_g orbitals of the conduction band. The term of (2.28) diagonal in \mathbf{m} is, naturally, absent.

Experimental observation of such monopole excitons is difficult, since the corresponding optical transition is forbidden. If, however, they are regarded as intermediate-radius excitons,^{19a} the excitation energy for them should not differ noticeably from the energy of the edge of the $f^6 \rightarrow f^5 b_{kc}$ interband transitions. The energy difference of monopole excitations in EuS and $\text{SmS}_{(B)}$ is then approximately equal to Δ , so

that a noticeable enhancement of the monopole mode is to be expected in $\text{SmS}_{(B)}$.

Monopole excitons in $\text{SmS}_{(B)}$ can be regarded as fast compared with the lattice vibrations, $\hbar\omega_{LO}/\Delta_{ex} \approx 0.15$, and their contribution to the phonon spectrum can be taken into account in the form of the renormalization (2.19b). The exciton-excitation matrix element contains then, in the case of monopole lattice distortion, only integrals that are off-diagonal in lattice site, of form

$$F(\mathbf{m}) \int d^3\mathbf{r} \psi_c^*(\mathbf{r}-\mathbf{R}_{l+m}) P_{q\alpha}^{\Gamma_1}(\mathbf{r}-\mathbf{R}_{l+m}) \psi_v(\mathbf{r}-\mathbf{R}_l).$$

Substituting here ψ_c and ψ_v from (2.23) and putting approximately

$$\int d^3\mathbf{r} \psi_d^*(\mathbf{r}) P_{q\alpha}^{\Gamma_1}(\mathbf{r}) \psi_d(\mathbf{r}) \approx \int d^3\mathbf{r} \psi_f^*(\mathbf{r}) P_{q\alpha}^{\Gamma_1} \psi_f(\mathbf{r}) \equiv I_{q\alpha}^{\Gamma_1}, \quad (2.30)$$

we obtain an equation similar to (2.25):

$$\delta_{ex}^{\Gamma_1}(\hbar\omega_{q\alpha})^2 = -2\hbar^2 \frac{|I_{q\alpha}^{\Gamma_1}|^2 |R_q^{\Gamma_1}|^2}{\Delta_{ex}(0)} \equiv \lambda_{\alpha}^{\Gamma_1} \Phi^{\Gamma_1}(\mathbf{q}, \omega_{q\alpha}), \quad (2.31)$$

where the covalent form factor is

$$R_q^{\Gamma_1} = F_1 [12 - S(\mathbf{q})] AVG_0, \quad F_1 = |F(\mathbf{m})|. \quad (2.32)$$

The form factors of this renormalization for the standard CDD model and the covalent corrections $R_q^{\Gamma_1}$ are calculated in the Appendix [Eqs. (A.8) and (A.10)] and are shown in Fig. 4.

A comparison of Figs. 3a and 4a shows that the monopole form factor $|I_{q\alpha}^{\Gamma_1}|$ is large precisely in those parts of the Brillouin zone in which the dipole form factor $|I_{q\alpha}^{\Gamma_{15}}|^2$ is small, i.e., in the vicinity of the point L . The joint action of the modes Γ_{15}^+ and Γ_{15}^- ensures thus a renormalization of the LO mode of the spectrum in the entire Brillouin zone.

Experiment (Fig. 2) shows that the LA mode of the spectrum, in contrast to the LO mode in $\text{SmS}_{(B)}$ is practically not renormalized compared with EuS . The contribution of the CDD modes to the renormalization of the LA phonons in the vicinity of the L point on the face of the Brillouin zone is small from general considerations, since the phonons in question correspond to motion of the ions predominantly from the heavy-cation sublattice.¹³ Therefore the renormalization from the dipole distortions of the f shell of the Sm ions, whose form factor is large just in the vicinity of the L point (Fig. 3a), turns out to be small. As for the mode Γ_{15}^+ , the maximum of the renormalization form factor, which is in the vicinity of the point $[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$ for the $LA[\xi, \xi, \xi]$ photons, there exists here a specific mechanism for mutual cancellation of the monopole and dipole shell distortions.

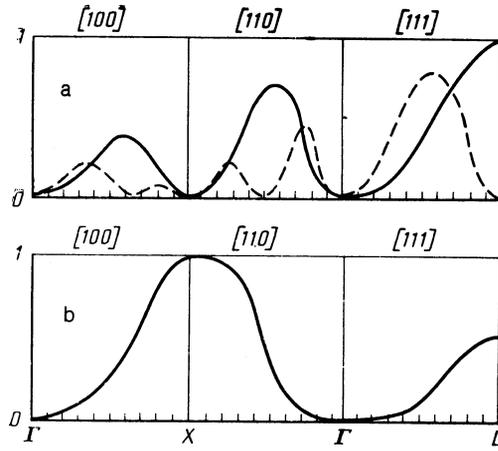


FIG. 4. Form factors of fully symmetric mode, in relative units (see Fig. 3 for the symbols): a) $\Phi_0^{\Gamma_1}(\mathbf{q}, \omega_{q\alpha})N$; solid lines: $\alpha = LO, N = 1$, dashed— $\alpha = LA, N = 15$; b) $|R_q^{\Gamma_1}|^2$.

As shown in Ref. 21, the renormalization $\Delta^{\Gamma_1^+}(\omega_{q,LA})^2$ is due primarily to the interaction of the Sm ion shells in the cation sublattice with the neighboring Sm ions in the same sublattice, the corresponding coupling constant being of the same sign, $g_0 g_1 > 0$ (see Fig. 5). This is possible, for example, if it is assumed that the constant g_0 describes an ion-shell interaction, and the constant g_1 a shell-shell interaction. Then, as seen from Fig. 5, when the nearest neighbor C_1 of a given cation C_0 is displaced, the contribution from the displacement of the C_1 ion to the monopole deformation of the C_0 ion is offset by the dipole distortion of the shell of this ion.

The foregoing calculation can be regarded as a microscopic confirmation of the applicability of the deformed-cluster model to the description of the semiconductor phase of narrow-band and narrow-gap RE semiconductors. It has been found that the contribution of the "exciton" degrees of freedom to the CDD explains the principal effect—the softening of the longitudinal optical modes. The band component of the renormalization contributes to the dipole mode of the CDD. For the monopole mode, the band correction to the phonon frequencies, obtained under the same assumptions as in (2.31), is of the form

$$\delta_{band}^{\Gamma_1}(\hbar\omega_{q\alpha})^2 \approx -2\hbar^2 |I_{q\alpha}^{\Gamma_1}|^2 |R_{q,band}^{\Gamma_1}|^2 \chi_q(0), \quad (2.33)$$

where

$$R_{q,band}^{\Gamma_1} = AVG_0 \left[\sum_{\mathbf{m}}^{(nn)} (1 - \cos \mathbf{qR}_m)^2 \right]^{1/2},$$

$$\chi_q(0) = N^{-1} \sum_{\mathbf{k}} \frac{1}{\epsilon_{\mathbf{k}+\mathbf{q}}^c - \epsilon_{\mathbf{k}}^v} \equiv G_0. \quad (2.34)$$

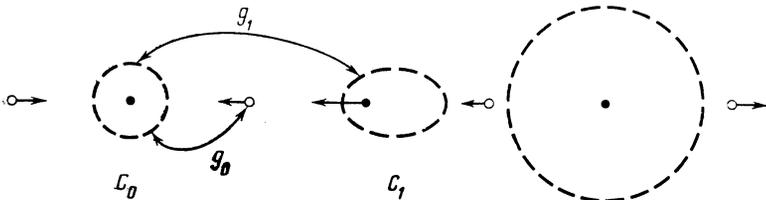


FIG. 5. Displacements of the S ions (O) and Sm ions with deformed shell (\bullet with dashed oval) for $LA[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$.

The ratio of the band and exciton corrections is determined by the parameter $\Delta_{\text{ex}}^{\Gamma_1} G_0 \approx \Delta_{\text{ex}}^{\Gamma_1} / D \ll 1$, and the dispersion of the form factor $R_{\mathbf{q}, \text{band}}^{\Gamma_1}$ hardly differs from that of the exciton form factor.

3. ELECTRON-PHONON INTERACTION IN RE SEMICONDUCTORS WITH INTERMEDIATE VALENCY

In the description of the electronic contribution to the phonon spectrum of $\text{SmS}_{(B)}$ in the “normal” phase, the use of exciton variables can be regarded as a convenient method for a microscopic derivation of the CDD model parameters. When it comes to the “gold” phase $\text{SmS}_{(G)}$ with intermediate valency, however, the exciton degrees of freedom assume the principal role. According to Refs. 19 and 20, the cause of the onset of IV is exciton instability, and the ground state of $\text{SmS}_{(G)}$ is the result of mixing of singlet states 7F_0 of $\text{Sm}(f^6)$ ions with exciton states of the same symmetry, i.e., precisely with those $f^5\bar{b}$ excitons (2.28) which are assumed in our theory to be responsible for the monopole relaxation of the samariumcation f shells.

The main effect in the $\text{SmS}_{(G)}$ spectrum is the strong softening of the LA mode in the $[111]$ direction and the abrupt increase of the phonon damping.^{14,15} In the vicinity of the point $[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$ the softening of the LA mode compared with $\text{SmS}_{(B)}$ is 15%, and the damping increases from 0.35 THz to 0.55 THz. Interaction of the breathing mode with the monopole relaxation of the f shells is traditionally regarded to be the cause of phonon renormalization and damping,^{11,12} but in the microscopic approach¹² the authors start out from an EPI Hamiltonian of the Fröhlich type with local valence fluctuations of the type $f_j d_j^+$, which agrees poorly with the assumed total symmetry of the phonon mode. A more reasonable explanation for $\text{Sm}_{1-x}\text{Y}_x\text{S}$ was offered in Ref. 21 within the framework of a two-band metal, but the microscopic nature of the nonadiabatic EPI in the real superconducting situation of $\text{SmS}_{(G)}$ remains unclear.

Within the framework of the exciton CDD mechanism, a natural explanation is obtained both for the enhancement of the contribution of the totally symmetric mode Γ_1^+ to the renormalization of the LA phonons, and for the increase of the electron-ion interaction adiabaticity responsible for their damping. The wave function of an Sm ion in a site \mathbf{m} and in an IV state is

$$\psi_{\mathbf{m},g} = \cos \theta |f_{\mathbf{m}}^6, {}^7F_0\rangle + \sin \theta |f_{\mathbf{m}}^5 ({}^6H_{5/2}) b_{\mathbf{m},\Gamma_1^+}, {}^7F_0\rangle, \quad (3.1)$$

where the symbol $b_{\Gamma_1^+, \mathbf{m}}^+$ denotes a combination of electron-hole pairs centered on the site \mathbf{m} , in (2.28), and θ is a variational parameter that determines the intermediate valency, $\sin^2 \theta \approx 0.7$ for $\text{SmS}_{(G)}$. Clearly for such a ground state we can construct an exciton of the same symmetry—the anti-binding combination

$$\psi_{\mathbf{m},ex} = \cos \theta |f_{\mathbf{m}}^5 b_{\mathbf{m}}^+, {}^7F_0\rangle - \sin \theta |f_{\mathbf{m}}^6, {}^7F_0\rangle. \quad (3.2)$$

It appears that just these states were recorded as f - f transitions of 20 meV energy in the optical measurements of Trawaglini and Wachter.²² This assumption is in accord with both the anomalously smallness of the transition energy on the scale of intracenter atomic terms, and the giant oscillator strength for this transition, which exceeds by 6 orders the usual value for intra-atomic f - f transitions. It seems natural to relate the enhancement of the renormalization of the

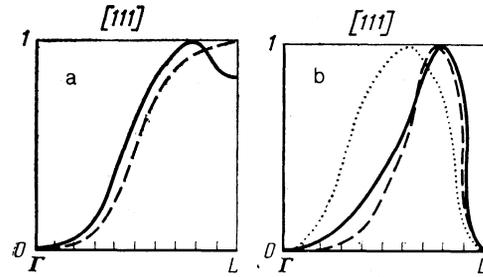


FIG. 6. Form factors of “gold” phase: a) covalent form factor $|R_{\mathbf{q}}^{\Gamma_1^+}|^2$ for $A^2 = 0.8$ (dashed curve) and $A^2 = 0.6$ (solid line); b) shift of the squared phonon frequencies: experiment (solid line, CDD model (dotted) and CDD model with allowance for $R_{\mathbf{q}}^{\Gamma_1^+}$ (dashed).

LA -phonon mode in $\text{SmS}_{(G)}$ compared with $\text{SmS}_{(B)}$ precisely with these RE-cation valence-shell monopole excitations that are features of the IV phase.

In the zeroth approximation in the nonadiabaticity operator we obtain from (2.14b) the already known expression (2.19b) for the renormalization of a spectrum in which the covalent form factor changes:

$$R_{\mathbf{q}}^{\Gamma_1^+} = F_1^2 (12 - S(\mathbf{q})) \left\{ A^2 \frac{\sin 2\theta}{2} + \frac{A |V| G_0}{F_1} \cos 2\theta + (VG_0)^2 S(\mathbf{q}) \sin \theta \cos \theta \right\}. \quad (3.3)$$

Figure 6a shows the calculated $R_{\mathbf{q}}^{\Gamma_1^+}$ for the $[111]$ direction. In the calculation we have approximately assumed the exciton wave function to be localized on the nearest sites, $F_1 \approx 1/\sqrt{12}$, thereby simplifying greatly the calculations while retaining the main qualitative features of the renormalization dispersion. The value $\sin^2 \theta = 0.7$ corresponds to the experimental valence of $\text{SmS}_{(G)}$. The deviation of A^2 from unity is determined by the fd -hybridization degree, which is larger in $\text{SmS}_{(G)}$ than in $\text{SmS}_{(B)}$. However, band calculations for the “metallic” state of $\text{SmS}_{(G)}$, carried out without allowance for multiparticle effects,²⁴ show that even in $\text{SmS}_{(G)}$ the factor A^2 does not differ too much from unity. Figure 6a shows form factors calculated for $A^2 = 0.6$ and 0.8. It can be seen that the collective factor $R_{\mathbf{q}}^{\Gamma_1^+}$ serves to shift the maximum of the LA -phonon renormalization frequency away from the middle of the ΓL line towards larger \mathbf{q} . The total form factor $\Phi^{\Gamma_1^+}(\mathbf{q}, \omega_{\mathbf{q}, LA})$ (2.27) for the “gold” phase is shown in Fig. 6b together with the experimental phonon-frequency shifts determined from the data of Ref. 14 by separating the contribution of the hard ions (A.6). It is assumed here that the entire renormalization is connected with the CDD by the Γ_1^+ mode. Allowance for the renormalization simplifies substantially the agreement with experiment compared with the standard form factor $\Phi_0^{\Gamma_1^+}$ (A.9), whose contribution to the renormalization is shown by the dotted line. In principle, the shift of the renormalization maximum of the $\text{SmS}_{(G)}$ LA phonons can be obtained also by adding the dipole CDD mode Γ_{15}^- (Ref. 11). This procedure, however, yields a 15% softening of the spectrum also at the L point (see Fig. 3 of Ref. 11), contrary to experiment.

The dispersion of the damping of the LA phonons in the $[111]$ direction is usually attributed to a nonadiabatic contribution from electronic deformation modes.^{10,21} In our model, the damping is, of course, explained by the nonadiabaticity of the exciton renormalization and by the substantial role of the covalent form factor $R_q^{\Gamma_1^+}$. With allowance for the nonadiabatic corrections (2.11), the covalent form factor becomes

$$|R_q^{\Gamma_1^+}|^2 \left(1 + \frac{\omega_{q,LA}^2}{\Delta_{ex}^2}\right) \quad (3.4)$$

(cf. Ref. 7). The damping γ at finite temperatures is controlled by the same symmetry factors and agrees well with experiment.¹⁰

It was noted in Ref. 10 that dipole processes are faster than monopole ones, although no phenomenological explanation could be given for this circumstance. From our point of view, there are actually no grounds for assuming that the interaction of the phonons with the Γ_{15}^- mode becomes adiabatic in the "gold" phase. While some softening of the dipole exciton mode $\Delta_{ex}^{\Gamma_{15}^-}$ compared with $\text{SmS}_{(B)}$ can be expected, as well as its smearing by the increased exciton dispersion, no anomalously soft dipole excitation seems to occur in $\text{SmS}_{(G)}$. Judging from optical reflection data,²² the main fd transitions occur in the 0.1–1 eV range.

It is difficult to calculate the contribution of the interband transitions to the "gold" phase $\text{SmS}_{(G)}$, since the structure of the one-electron elementary excitations in the IV state has hardly been investigated. It is clear, however, from general symmetry considerations that the most "dangerous" $f-f$ transitions through a spectrum microgap of width $\Delta \approx 70$ meV (Ref. 24) make no contribution to the phonon spectra, since they correspond to $\mathbf{q} = (2\pi/a)[1,0,0]$, and the form factor $\Phi^{\Gamma_1^+}(\mathbf{q})$ is zero at the X point of the Brillouin band (Fig. 4a). We see that for a classical explanation of the dispersion of the $\text{SmS}_{(G)}$ phonon spectrum it suffices to take only the exciton contribution into account. It is easy to verify [see (2.34)] that the form factors for the contribution from the interband transitions differ little from the exciton form factors, so that their separation in experiment is problematic, and a theoretical calculation calls for an improvement of the very theory of the "gold" phase of a semiconductor with IV.

We have thus shown that the contribution of the electrons to the softening of the phonon spectra of RE semiconductors can be explained within the framework of the adiabatic model of deformed clusters, the microscopic justification of which leads to the Anderson lattice Hamiltonian.^{18,19} In a semiconductor phase with IV, the main contribution to the charge deformation modes is made by monopole excitation of exciton type, which are specific for IV, although one cannot exclude also an interband contribution to the phonon renormalization. The close values of the characteristic times of valence fluctuations and lattice vibrations suggests a strong interaction between these excitations. However, notwithstanding the lack of formal smallness of the parameter $\hbar\omega_{ph}/\Delta_{vf}$, where Δ_{vf} is the characteristic energy of the valence fluctuations, the nonadiabatic coupling constant may turn out to be small enough, since fast local electron-density deformations of like symmetry screen the ion displacement to a considerable degree. We have in mind

the screening of the band Γ_{15} corrections by dipole localized adiabatic electrons. Nonetheless, there are apparently grounds for ascribing a nondispersive mode to the phonon spectrum of $\text{Sm}_{1-x}\text{R}_x\text{S}$, where R are trivalent RE ions that replace Sm, to a resonance between the valence fluctuations and the lattice vibrations.²⁵

APPENDIX

Calculation of renormalization form factors and of phonon damping

Let us calculate the formfactors for the adiabatic model of deformable shells^{26,2} in a NaCl lattice. The equations of motion of this model are, in matrix form,

$$M\omega^2 u = D^R u + \sum_j D^{F_j} u, \quad D^{F_j} = F^{F_j} S^{F_j}(\mathbf{q}). \quad (A.1)$$

Here D^R is the contribution to the dynamic matrix from the hard ions, D^{F_j} is the contribution from the deformation of the charge density of point symmetry Γ_j , in which the dependence on \mathbf{q} is incorporated in the factor $S^{F_j}(\mathbf{q})$. Let us consider the renormalizations connected with the CDD by modes of symmetry Γ_1^+ and Γ_{15}^- in the nearest-neighbor approximation. For longitudinal modes in symmetric directions, the dynamic matrix reduces to the form^{26,27}

$$\bar{D} = \begin{vmatrix} D_1 & D \\ D & D_2 \end{vmatrix} = \begin{vmatrix} D_1^R & D^R \\ D^R & D_2^R \end{vmatrix} - F^{\Gamma_1^+} \begin{vmatrix} 0 & 0 \\ 0 & n \sin^2 q \end{vmatrix} - F^{\Gamma_{15}^-} S^{\Gamma_{15}^-}, \quad (A.2)$$

where 1 and 2 are the indices of the cation and anion sublattices,

$$\begin{aligned} S^{\Gamma_{15}^-}[111] &= \begin{vmatrix} 3 & -3 \cos q \\ -3 \cos q & 3 \cos^2 q \end{vmatrix}, \quad S^{\Gamma_{15}^-}[110] \\ &= \begin{vmatrix} 3 & -1-2 \cos q \\ -1-2 \cos q & \cos^2 q + 1/2(1+\cos q)^2 \end{vmatrix}, \\ S^{\Gamma_{15}^-}[100] &= \begin{vmatrix} 3 & -2-\cos q \\ -2-\cos q & 2+\cos^2 q \end{vmatrix}. \end{aligned} \quad (A.3)$$

In the matrix (A.3) the vector q is made nondimensional by the Brillouin-zone vector, so that $0 < q < \pi/2$ in the $[111]$ direction and $0 < q < \pi$ in the $[110]$ and $[100]$ directions; for these directions $n = 3, 2$, and 1 , respectively. Substituting (A.2) in (A.1) we obtain the solutions of the secular equation

$$\omega_{q\alpha}^2 = 1/2[\omega_+^2 \pm (\omega_-^4 + 4|D|^2/(M_1 M_2))^{1/2}], \quad (A.4)$$

where

$$\omega_{\pm}^2 = D_2/M_2 \pm D_1/M_1, \quad \alpha = LO, LA, TO, TA, \dots \quad (A.5)$$

In first order in $F^{\Gamma_1^+}$ we obtain for the renormalization of the phonons from the totally symmetric mode

$$\begin{aligned} \Delta_{\Gamma_1^+ \omega_{q\alpha}^2} &= -\frac{nF^{\Gamma_1^+}}{M_2} \sin^2 q \frac{\omega_{0,q\alpha}^2 - 1/2(\omega_+^2 - \omega_-^2)}{2\omega_{0,q\alpha}^2 - \omega_+^2}, \\ \alpha &= LO, LA, \end{aligned} \quad (A.6)$$

where $\omega_{0,q\alpha}$ are the frequencies calculated in the hard-ions approximation.

Since vibrations at the L points of the Brillouin zone for an $LA(LO)$ mode corresponds to S (Sm) atoms at rest in an

NaCl lattice, the dynamic matrix off-diagonal elements are $D^R = 0$ for the [111] direction, so that the limiting acoustic and optical frequencies on these faces of the Brillouin zone are determined only by the diagonal elements of the dynamic matrix of the hard-ion model

$$\omega_{LA}^2[111] = \frac{1}{2}(\omega_+^2 - \omega_-^2), \quad \omega_{LO}^2[111] = \frac{1}{2}(\omega_+^2 + \omega_-^2). \quad (\text{A.7})$$

From this we get for the polarization contribution of the CDD breathing mode (A.6)

$$\Delta_{\Gamma_1^+}(\omega_{q\alpha})^2 = -\frac{nF^{\Gamma_1^+} \omega_{0,q\alpha}^2 - \omega_{LA}^2[111]}{M_2} \frac{2\omega_{0,q\alpha}^2 - \omega_+^2}{2\omega_{0,q\alpha}^2 - \omega_+^2} \sin^2 q, \quad \alpha = LO, LA. \quad (\text{A.8})$$

A similar calculation for the CDD dipole mode yields for opposite renormalization directions the following result: for [111]

$$\Delta_{\Gamma_{15}^-}(\omega_{q\alpha})^2 = -\frac{F^{\Gamma_{15}^-}}{2\omega_{0,q\alpha}^2 - \omega_+^2} \left\{ \frac{3 \cos^2 q}{M_2} [\omega_{0,q\alpha}^2 - \omega_{LA}^2[111]] + \frac{3}{M_1} [\omega_{0,q\alpha}^2 - \omega_{LO}^2[111]] + \frac{6|D| \cos q}{M_1 M_2} \right\}, \quad (\text{A.9a})$$

for [110]

$$\Delta_{\Gamma_{15}^-}(\omega_{q\alpha})^2 = -\frac{F^{\Gamma_{15}^-}}{2\omega_{0,q\alpha}^2 - \omega_+^2} \times \left\{ \frac{\cos^2 q + \frac{1}{2}(1 + \cos q)^2}{M_2} [\omega_{0,q\alpha}^2 - \omega_{LA}^2[111]] + \frac{3}{M_1} [\omega_{0,q\alpha}^2 - \omega_{LO}^2[111]] - \frac{2D(1 + 2 \cos q)}{M_1 M_2} \right\}. \quad (\text{A.9b})$$

and for [100]

$$\Delta_{\Gamma_{15}^-}(\omega_{q\alpha})^2 = -\frac{F^{\Gamma_{15}^-}}{2\omega_{0,q\alpha}^2 - \omega_+^2} \left\{ \frac{2 + \cos^2 q}{M_2} [\omega_{0,q\alpha}^2 - \omega_{LA}^2[111]] + \frac{3}{M_1} [\omega_{0,q\alpha}^2 - \omega_{LO}^2[111]] - \frac{2D(2 + \cos q)}{M_1 M_2} \right\}. \quad (\text{A.9c})$$

Note that on the Brillouin-zone face at the L point we have

$$\Delta_{\Gamma_{15}^-}(\omega_{LA})^2 = -\frac{3F^{\Gamma_{15}^-} \omega_{0,LO}^2[111] - \omega_{0,LA}^2[111]}{M_1 \omega_-^2} \neq 0. \quad (\text{A.10})$$

It is seen from (A.8) that for a totally symmetric mode the dependence of the renormalization on the wave vector (the form factor) of the LA mode is determined mainly by the function $\sin^2 q$ and by the numerator in the fraction, since the latter vanishes at the points L and at points close to $q = \pi/2$ in the [110] and [100] directions. For the LO mode it is determined by the function $\sin^2 q$, since the dispersion of the LO mode is small. Calculation in the neutral nearest-neighbor approximation yields for the contribution from the totally symmetric (Γ_1^+) and the dipole (Γ_{15}^-) CDD modes the form factors shown in Figs. 4a and 3a, respectively.

We calculate now the contribution made to the form factor by the covalent additions to the dynamic matrix and due to fd mixing. In the renormalization (3.13) from the CDD Γ_{15}^- mode, the corresponding dependence is contained in the factor $|R_q^{\Gamma_{15}^-}|^2$ (2.26b), while in the renormalization from the CDD Γ_1^+ mode this dependence is determined by the factor $|R_q^{\Gamma_1^+}|^2$ (2.32). From this we get for the CDD dipole mode in symmetric directions the form factors

$$\begin{aligned} R_{\Gamma_{15}^-}(qqq) &= A^2 + 6(VG)^2(1 + \cos 2q), & R_{\Gamma_{15}^-}(qq0) &= A^2 + 2(VG)^2(1 + \cos 2q + 4 \cos q), \\ R_{\Gamma_{15}^-}(q00) &= A^2 + 4(VG)^2(1 + 2 \cos q), \end{aligned} \quad (\text{A.11})$$

and for the totally symmetric CDD mode

$$\begin{aligned} R_{\Gamma_1^+}(qqq) &= 6(1 - \cos 2q), & R_{\Gamma_1^+}(qq0) &= 10 - 2 \cos 2q - 8 \cos q, \\ R_{\Gamma_1^+}(q00) &= 8(1 - \cos q). \end{aligned} \quad (\text{A.12})$$

The covariant increments to the form factor are shown in Figs. 3b and 4b, respectively.

¹¹Since only the acoustic modes have been measured for the "gold" phase under pressure,¹⁴ Fig. 2 shows the spectra for the cation-replaced $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ in the IV phase.¹⁵

¹²The intercenter hybridization integrals without such operators, introduced in Ref. 23, lead to a mixing, forbidden in cubic crystals, at the points Γ and X .

¹³H. Bilz and W. Kress, *Phonon Dispersion Relations in Insulators*, Springer, 1979.

¹⁴W. Cochran, *Crit. Rev. Sol. St. Sci.* **2**, 1 (1971).

¹⁵H. Bilz, *Comput. Solid State Physics*, F. Herman, N. V. Dalton and T. R. Kohler, eds., Plenum, 1972, p. 309.

¹⁶P. Allen, *Phys. Rev. B* **16**, 5139 (1977).

¹⁷S. K. Sinha and B. Harman, *Phys. Rev. Lett.* **35**, 1515 (1975).

¹⁸C. M. Varma, W. Weber, E. I. Blount, and P. Vashishta, *Phys. Rev. B* **19**, 6130 (1979).

¹⁹E. G. Brovman and Yu. M. Kagan, *Zh. Eksp. Teor. Fiz.* **52**, 557 (1967) [*Sov. Phys. JETP* **25**, 365 (1968)].

²⁰E. G. Maksimov, *ibid.* **69**, 2236 (1975) [**42**, 1138 (1975)].

²¹D. I. Khomskii, *Quantum Theory of Solids*, I. M. Lifshitz, ed., Mir, Moscow, 1982, p. 70.

²²N. Wakabayashi, *Phys. Rev. B* **22**, 5833 (1980).

²³H. Bilz, G. Güntherodt, W. Kleppmann, and W. Kress, *Phys. Rev. Lett.* **43**, 1998 (1979).

²⁴P. Entel, N. Grewe, M. Seitz, and K. Kovalski, *ibid.* **43**, 2002 (1979).

²⁵S. K. Ghatak and K. H. Benneman, *J. Phys.* **F8**, 571 (1978).

²⁶H. A. Mook, D. B. McWhan, and F. Holtzberg, *Phys. Rev. B* **25**, 4321 (1982).

²⁷H. A. Mook, R. M. Nicklow, T. Penney, *et al.*, *ibid.* **B28**, 2925 (1978).

²⁸G. Güntherodt, *Phys. Kond. Mat.* **18**, 37 (1974).

²⁹G. Güntherodt, J. L. Freeouf, and H. Holtzberg, *Sol. St. Comm.* **47**, 677 (1983).

³⁰K. A. Kikoin, *ibid.* **33**, 323 (1980).

³¹K. A. Kikoin, a) *Zh. Eksp. Teor. Fiz.* **85**, 1000 (1983) [*Sov. Phys. JETP* **58**, 582 (1983)]; b) *J. Phys.* **C17**, 6676 (1984).

³²K. W. H. Stevens, *J. Phys.* **C9**, 1417 (1976).

³³T. Matsuura, R. Kittler, and K. H. Bennemann, *Phys. Rev. B* **21**, 3467 (1980).

³⁴G. Trawaglini and P. Wachter, *ibid.* **B30**, 5877 (1984).

³⁵P. Entel, H. L. Leder, and N. Grewe, *Z. Phys.* **B30**, 277 (1986).

³⁶F. Lopez-Aguilar and J. Costa-Quintana, *J. Phys.* **C19**, 2485 (1986).

³⁷G. Solt and H. Besk, *Helv. Phys. Acta* **60**, 560 (1987).

³⁸A. D. B. Woods, W. Cochran, and B. N. Brockhouse, *Phys. Rev.* **119**, 980 (1960).

³⁹K. Fischer, H. Bilz, R. Haberkorn, and W. Weber, *Phys. Stat. Sol. (b)* **54**, 285 (1972).

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