Resonance states in the vibrational spectra of intermediate-valence semiconductors

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Resonance vibrational states of a new type that can be realized in intermediate-valence semiconductors (IVS) is proposed. Owing to the exceptional softness of local valence fluctuations in IVS, there arises a pseudo-Jahn–Teller exciton-photon interaction and exciton-polaron states of two types are formed: coherent exciton-polarons, manifested in the vibrational spectra as additional modes which interact strongly with LA phonons, and harder self-localized excitations, forming at sufficiently high temperatures defects of the force constants and creating dispersion-free local modes in the gap between the acoustic and optical branches of the spectrum. The model explains the origin of the "excess" modes in the inelastic neutron scattering spectra of $Sm_{0.75}Y_{0.25}S$ and SmB_6, and describes the experimentally observed sharp temperature dependence of these modes.

1. INTRODUCTION

It is well known that the strong electron-photon interaction in rare-earth semiconductors with intermediate valence (IV) is due mainly to the closeness of the characteristic lattice-vibration time ($\tau_{\rm ph}$) to the characteristic valence fluctuation time ($\tau_{\rm vf}$): 10^{-12} sec $<\tau_{\rm ph}$, $\tau_{\rm vf}<10^{-13}$ sec.[1,2] The effect of valence fluctuations on the phonon spectra of SmS, TmSe, and SmB_6 has been investigated well both experimentally and theoretically (see, for example, the review[3]). However, the unusual softness of collective electronic modes (valence fluctuations) in these compounds suggests not only that the normal vibrational modes are strongly renormalized but also that specific resonance effects appear in the lattice dynamics. Indeed, additional modes in the vibrational spectra of $Sm_{0.75}Y_{0.25}S$ (Refs. 4 and 5) and, apparently, TmS (Ref. 6) were already revealed by the first experiments on inelastic neutron scattering. Similar modes were later also found in SmB_6.[7] The existence of these excitations cannot be explained by the standard mechanisms of formation of local defect-induced lattice modes, and this circumstance together their unusual temperature dependence[8,9] make it necessary to search for a nontraditional mechanism, due precisely to the specific nature of intermediate-valence compounds, for the appearance of local modes in the vibrational spectra.

In the present paper we propose a new mechanism for the formation of local vibrational modes. This mechanism is associated with the softness of the local excitations of the electronic subsystem in the intermediate-valence semiconductor phase. We have previously constructed a theory of the electron-phonon interaction in these systems, based on taking into account the effect of soft exciton-like excitations in the intermediate-valence phase on the lattice vibrations.[10–12] This theory made it possible to explain the anomalies observed in the acoustic spectra of all semiconductors with an intermediate phase, but it did not give a satisfactory quantitative description of optical spectra and it did not explain the appearance of an additional mode in the vibrational spectrum, though it did indicate the source of this mode—soft fully symmetric fluctuations of the valence of Sm ions. The theory is insufficient because it is based on the adiabatic description of the electron-phonon interaction, using the model of charge-density distortions which adjust adiabatically to the motion of the ions.[13] According to optical data,[14] however, the exciton mode either falls into the gap between the acoustic and optical phonons or it is in resonance with the optical phonons, so that the adiabatic approximation, which is to some extent applicable to acoustic phonons, definitely breaks down for optical modes. This "nonequivalence" of the different modes of the vibrational spectrum with respect to one of the electronic modes is a distinguishing property of intermediate-valence semiconductors and requires a special analysis. Moreover, the characteristic electron energies in these systems are lower than room temperature, and this circumstance must be taken into consideration when describing an experiment.

Thus it is necessary to re-examine the standard theory of electron-phonon interaction as applied to intermediate-valence semiconductors, and this re-examination must start with a revision of the standard adiabatic approximation.

2. ADIABATIC APPROXIMATION FOR THE ELECTRON-VIBRATIONAL SYSTEM UNDER EXCITON-PHONON RESONANCE CONDITIONS

The object of our theoretical constructions are samarium sulfide $SmS_{(G)}$ in the gold phase under pressure or its cation-substituted analog $Sm_{0.75}Y_{0.25}S$ with a crystal lattice of NaCl-type, and also samarium hexaboride with a $CaCu_6$-type lattice. In studying the low-lying phonon branches on which the anomalies are observed the samarium hexaboride structure can be regarded, owing to the high rigidity of B_6 octahedra, as consisting of two structural elements, Sm ion and B_6 octahedron, which form a lattice of the CsCl type.[7]

It was noted already in the first theoretical papers describing[15–17] anomalies of the phonon spectra of these semiconductors that the fully symmetric displacement Γ_1^+

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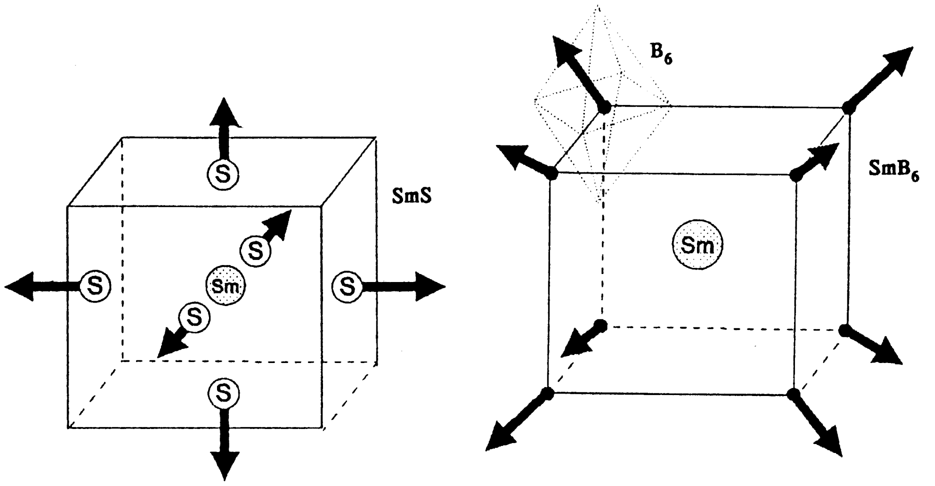

FIG. 1. Breather mode Γ_1^+ in the vibrational spectra of SmS and SmB$_6$.

of the nearest neighbors of Sm ions in the anionic sublattice (Fig. 1), which induces local Sm valence fluctuations of Sm of the same point symmetry Γ_1^+, makes the main contribution to the electron-lattice interaction. This interaction softens the longitudinal acoustic phonons, the softening being most pronounced along the [111] direction of the Brillouin zone in lattices of the NaCl type. On the other hand, it was shown in Refs. 18 and 19 that local fully symmetric valence fluctuations play a decisive role in the mechanism of the phase transition into the intermediate-valence state: according to the theory developed in these papers for excitonic instability, a new phase arises as a result of softening (for example, under pressure) of the fully symmetric exciton mode. The phase transition occurs when an almost degenerate situation arises—the energy of this mode differs from the ground-state energy by an amount comparable to the Coulomb and/or electron-lattice interaction energies. If the electron-electron interaction predominates, then we are dealing with an excitonic instability, which is removed by coulombic restructuring of the spectrum of low-lying electronic excitations. If, however, the interaction with the lattice predominates, then the phase transition can be interpreted as a cooperative pseudo-Jahn–Teller effect[20] in which the proximity of the electronic system to degeneracy is removed by an isostructural transition. In reality, both contributions are significant, and the new intermediate-valence phase inherits indications of both an exciton dielectric and a pseudo-Jahn–Teller crystal. This is manifested in the fact that soft excitons are also present in the intermediate-valence phase,[10,14] and the presence of soft excitations in the electronic subsystem induces a pseudo-Jahn–Teller interaction (see, for example, Ref. 21). As will be demonstrated below, it is this interaction that determines the mechanism responsible for the appearance of additional modes in the vibrational spectrum.

Thus our problem is to find the equations which describe the vibrational spectrum of the system in the case when the adiabaticity condition

$$\max[\hbar\omega] \ll E_{\mathrm{ex}} \tag{1}$$

is not satisfied for at least one electronic (excitonic) mode. The left-hand side of this inequality is the maximum characteristic frequency of lattice vibrations and the right-hand side is the excitation energy of the electronic subsystem (in our case—the energy of a local valence fluctuation). In order to solve the problem of lattice vibrations, the eigenfunctions of the Hamiltonian of the electron-ion system

$$H(r,Q) = H(r) + V(r,Q) + T(Q) \tag{2}$$

are usually sought in the form of the expansion

$$\Psi(r,Q) = \sum_n \chi_n(Q)\varphi_n(r,Q). \tag{3}$$

In the Hamiltonian (2) $H(r)$ describes the total energy of the electrons and all interelectronic interactions; $V(r,Q)$ is the ion-ion and electron-ion interaction operator, and $T(Q)$ is the kinetic energy operator of the nuclei. The eigenvalues $\varepsilon_n(Q)$ and the eigenfunctions $\varphi_n(r,Q)$ of the electronic subsystem depend on the coordinates Q of the nuclei as parameters.

If the electronic subsystem contains two almost degenerate low-lying electronic levels $\varepsilon_g(Q_0)=0$ and $\varepsilon_e(Q_0)=2\Delta$, corresponding to some equilibrium configuration of the lattice coordinates Q_0, then, according to the general theory of the pseudo-Jahn–Teller effect, the electron-ion potential must be represented in the form

$$V(r,Q) = V(r,Q_0) + \Delta V(r,Q) \tag{4}$$

and the adiabatic approximation must be reformulated for vibrations corresponding to these two levels, retaining in the expansion (3) only the electronic eigenfunctions of these states,

$$\Psi(r,Q) = \chi_g(Q)\varphi_g^{(0)}(r) + \chi_e(Q)\varphi_e^{(0)}(r). \tag{5}$$

Here $\varphi_{g,e}^{(0)}(r) = \varphi_{g,e}(r,Q_0)$ with the normalization condition

$$|\chi_g(Q)|^2 + |\chi_e(Q)|^2 = 1 \tag{6}$$

after which the problem of the adiabatic vibrational spectrum must be solved.

The eigenfunctions $\chi_n(Q)$ of the vibrational subsystem are now determined from the system of equations

$$\sum_n [T(Q)\delta_{mn}+U_{mn}(Q)]\chi_n(Q)=E\chi_m(Q), \qquad (7)$$

where $m,n=e,g$, and the matrix $U_{mn}(Q)$ contains both diagonal

$$U_n(Q)=\delta_{mn}[\varepsilon_n(Q_0)+\langle\varphi_n^{(0)}(r)\,|\,\Delta V(r,Q)\,|\,\varphi_n^{(0)}(r)\rangle] \qquad (8)$$

and off-diagonal

$$U_{mn}(Q)=\langle\varphi_m^{(0)}(r)\,|\,\Delta V(r,Q)\,|\,\varphi_n^{(0)}(r)\rangle \qquad (9)$$

elements, which admix the excited electronic state to the ground state. Thus, in contrast to the standard method of charge-density distortions (CDD)[13] employed in Refs. 10–12, when in the case of almost degenerate states of the electronic subsystem adiabaticity breaks down with respect to one of the electronic modes, this mode, instead of contributing to the dynamical matrix (through the polarizability of the electronic subsystem) in second-order perturbation theory, changes in a resonant manner the potential relief for ion vibrations. The problem of the vibrational spectrum of the system under conditions of resonance interaction of phonons with the continuum of valence fluctuations was studied in Refs. 22 and 23 on the basis of many-body perturbation theory. In our case there are grounds for assuming that valence fluctuations are described by a solitary mode, so that the nonadiabaticity of the electron-vibrational system is removed, to a significant degree, by the pseudo-Jahn–Teller restructuring of the lattice, and a modified form of the adiabatic CDD method can once again be employed.

In order to introduce fully symmetric CDD, corresponding to the pseudo-Jahn–Teller lattice distortions, into the dynamical matrix, we first determine their contribution to the interaction between ions in a neighborhood of a particular Sm atom, and consider next the problem of propagation of vibrations in a periodic sublattice. To this end, we select from the complete set of configurational coordinates the mode that is responsible for the pseudo-Jahn–Teller interaction in the cluster depicted in Fig. 1, namely, the above-mentioned "breathing" mode Γ_1^+. We separate in the effective potential of the excited state[8] the term that is linear in the configurational coordinate Q and characterizes the dependence of the energy of the excited state on the fully symmetric deformation

$$U_e(Q)=U_e^*(Q)+2\delta(Q-Q_0), \qquad (10)$$

where

$$\delta=\frac{1}{2}\left\langle\varphi_e^{(0)}(r)\left|\left(\frac{\partial V(r,Q)}{\partial Q}\right)_{Q=Q_0}\right|\varphi_e^{(0)}(r)\right\rangle. \qquad (11)$$

Then, diagonalizing the potential-energy matrix (assuming for convenience $Q_0=0$)

$$\begin{vmatrix} U_g(Q)-E & U_{eg}(Q) \\ U_{ge}(Q) & U_e(Q)+2\Delta+2\delta Q-E \end{vmatrix},$$

we obtain for the vibronic spectrum of the system the equations

$$E^{\pm}(Q)=\frac{U_e^*(Q)+U_g(Q)}{2}+\Delta+\delta Q \pm\sqrt{\left[\frac{U_e^*(Q)-U_g(Q)}{2}+\Delta+\delta Q\right]^2+|U_{eg}(Q)|^2}. \qquad (12)$$

These equations determine the potential relief, modified by the pseudo-Jahn–Teller contribution from the soft electronic mode, for vibrations of atoms in the vicinity of the distinguished Sm ion. After the resonance interaction with this slow mode is taken into account exactly, we can hope that in the new electronic-vibrational nomenclature the adiabaticity criterion (1) will hold, at least in the zeroth approximation, for the other excitations of the electronic subsystem, and the remaining deviations from adiabaticity can be taken into account with the help of perturbation theory.

3. LOCAL VALENCE FLUCTUATIONS AND THE PSEUDO-JAHN–TELLER MODES

As we have already mentioned, according to the theory proposed in Refs. 18 and 19 for excitonic instability, the mechanism of the normal semiconductor—intermediate-valence semiconductor phase transition and the anomalous properties of the intermediate-valence phase itself are associated with the fully symmetric local valence fluctuations, and the effect of the intermediate valence itself consists of the fact that a double-well potential is formed for the "last" electron in the f-shells of Sm ions in the cationic sublattice, so that the wave function of the ground state of the intermediate-valence semiconductor has the following structure:

$$\Phi_g^{(0)}(\mathbf{r})=\hat{A}\prod_{\mathbf{m}}\varphi_g^{(0)}(\mathbf{r}-\mathbf{R}_{\mathbf{m}}) =\hat{A}\prod_{\mathbf{m}}[\cos\theta|f_{\mathbf{m}}^6,{}^7F_0)+\sin\theta|f_{\mathbf{m}}^5B_{\mathbf{m}}^+,{}^7F_0)]. \qquad (13)$$

The parameter θ characterizes the value of the intermediate valence, $\hat{A}$ is the antisymmetrization operator, and $B_{\mathbf{m}}^+$ is a linear combination of electron-hole pairs with symmetry that makes it possible to construct a singlet fully symmetric state ${}^7F_0$, centered on the node $\mathbf{m}$, from the electrons of the $f_{\mathbf{m}}^5$ core and a weakly coupled electron, distributed between the central site and the nearest neighbors:

$$B_{\mathbf{m}}^+=\sum_{\mathbf{j}}F(\mathbf{j})a_{c,\mathbf{m}+\mathbf{j}}^+a_{f,\mathbf{m}}|f_{\mathbf{m}}^6,{}^7F_0). \qquad (14)$$

Here $a_f(a_c^+)$ is the operator annihilating (creating) an electron in the f-shell (conduction band) and $F(\mathbf{j})$ is the envelope, extending at least to the nearest neighbors of the cationic sublattice.

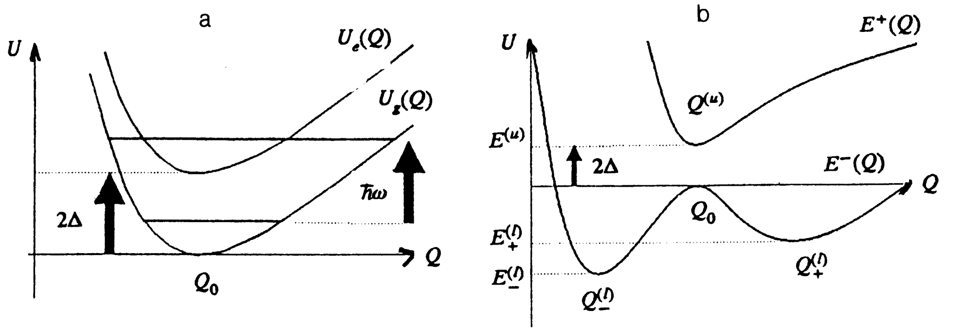

FIG. 2. Configurational diagrams for pseudo-Jahn–Teller vibrational modes determined by Eqs. (16)—(a) and (19)—(b).

For $\theta > \pi/4$ local valence fluctuations are exciton-like excitations with charge transfer "back" to the central Sm ion, and are described by antibonding linear combinations of the same type as the site functions appearing in Eq. (13):

$$\varphi_e^{(0)}(\mathbf{r}-\mathbf{R}_\mathbf{m}) = -\sin\theta|f_\mathbf{m}^6, {}^7F_0\rangle + \cos\theta|f_\mathbf{m}^5 B_\mathbf{m}^+, {}^7F_0\rangle. \tag{15}$$

The strong electron-phonon interaction in the intermediate-valence phase is associated with the response of the lattice to these charge fluctuations.[7,10,12] We shall show here that the same interaction leads to the appearance of additional modes in the vibrational spectrum. By virtue of their local nature, excitonic excitations interact primarily with the nearest-neighbor environment of the central ion, inducing pseudo-Jahn–Teller restructuring of this ion as defined by Eqs. (12). Correspondingly, the electronic wave function determining the adiabatic potential relief for vibrations of ions in this cluster is given by Eqs. (5) and (6).

The matrix elements in Eq. (12) have a quite complicated form, and expressions for them are unknown. However, the basic properties of the potential relief can be seen even in a simplified analysis, taking the seed potential energy of the ground and excited electronic states in the form of a quadratic potential with third- and fourth-order anharmonic corrections (Fig. 2a)

$$U_e^*(Q) \equiv U_g(Q) = \frac{K}{2}Q^2 + \frac{\gamma}{3}Q^3 + \frac{\varkappa}{4}Q^4; \quad \gamma < \langle 0,\kappa\rangle 0 \tag{16}$$

and the linear combination for the off-diagonal matrix element

$$U_{ge}(Q) = \lambda Q, \tag{17}$$

where

$$\lambda = \left\langle \varphi_g^{(0)}(r) \left| \left(\frac{\partial V(r,Q)}{\partial Q} \right)_{Q=0} \right| \varphi_e^{(0)}(r) \right\rangle. \tag{18}$$

In this case the vibrational potential energy has the form

$$E^\pm(Q) = \frac{K}{2}Q^2 + \frac{\gamma}{3}Q^3 + \frac{\kappa}{4}Q^4 + \Delta + \delta Q$$
$$\pm\sqrt{[\Delta+\delta Q]^2 + \lambda^2 Q^2}. \tag{19}$$

For sufficiently strong Jahn–Teller coupling (17) the adiabatic potential (19) acquires three minima, corresponding to the three possible vibrational modes for the configurational coordinate Q with different positions of equilibrium and frequencies (Fig. 2b). In the standard problem of the pseudo-Jahn-Teller effect the bottom sheet of the potential energy has two wells if

$$\alpha = \frac{\lambda^2}{K\Delta} > 1. \tag{20}$$

In the real case, when anharmonicity is present and the exciton energy depends on the coordinate Q ($\delta \neq 0$), a more stringent condition than (19) on the coefficient α may be required in order for two wells to appear in the bottom sheet of the potential (20). If, however, it is assumed that the main interaction in the system is pseudo-Jahn–Teller mixing, then the condition (20) does not change much. Taking into account anharmonicity and the correction δ (11), we obtain, to lowest order, the following parameters of the potential wells.

The minima of the top and the two bottom wells lie at the points (Fig. 2b)

$$Q^{(u)} = -\frac{\beta}{K^{1/2}}\left[\frac{2}{1+\alpha}\frac{\delta}{\lambda}\right],$$

$$Q_\pm^{(l)} = \frac{\beta}{K^{1/2}}\left[\pm\sqrt{1-\alpha^{-2}} - \alpha^{-1}\frac{\delta}{\lambda} + \beta\frac{|\gamma|}{K^{3/2}} \mp \beta^2\frac{\kappa}{K^2}\right] \tag{21}$$

with energies

$$E^{(u)} = 2\Delta,$$

$$E_\pm^{(l)} = \Delta\left\{\left[1 - \frac{1}{2}(\alpha+\alpha^{-1})\right] + \alpha\left[\pm(1-\alpha^{-1})\frac{\delta}{\lambda}\right.\right.$$
$$\left.\left.\mp\frac{1}{3}\beta\frac{|\gamma|}{K^{3/2}} + \frac{1}{4}\beta^2\frac{\varkappa}{K^2}\right]\right\} \tag{22}$$

and force constants

$$F^{(u)} = K[1+\alpha]$$

$$F_\pm^{(l)} = K\left[1 \mp 3\alpha^{-1}\frac{\delta}{\lambda} \mp 2\beta\frac{|\gamma|}{K^{3/2}} + 3\beta^2\frac{\varkappa}{K^2}\right]. \tag{23}$$

(Here $\beta = \lambda/K^{1/2}$).

The lowest state of a cluster corresponds to one of the minima of the bottom sheet of the adiabatic potential. We shall assume that the left-hand well has the lowest energy at the minimum $E_-^{(l)} < E_+^{(l)}$, which is equivalent to the condition

$$\frac{\delta}{\lambda} > \frac{1+\alpha^{-1}}{3} \beta \frac{|\gamma|}{K^{3/2}}. \tag{24}$$

It is this well that will determine the electronic ground state and the normal phonons after the cluster is embedded in an infinite lattice. As is evident from Eq. (23), the force constant in the right-hand bottom well is always less than in the left-hand well. The ratio of the force constants of the left-hand bottom and top wells depends on the values of the parameters. We assume that the system in the ground state has the highest force constant, i.e., in the bottom left-hand well

$$F_-^{(l)} > F_+^{(l)}, \quad F_-^{(l)} > F^{(u)}, \tag{25}$$

which is possible if

$$\alpha < 3\alpha^{-1} \frac{\delta}{\lambda} + 2\beta \frac{|\gamma|}{K^{3/2}} + 3\beta^2 \frac{\kappa}{K^2}, \tag{26}$$

which holds, together with the inequality (24), in the case of a sufficiently strong fourth-order anharmonicity.

The other two wells of the configurational curves displayed in Fig. 2b determine the excited states with transfer of the charge of the electronic subsystem; the additional vibrational modes correspond to these states. In order to clarify the character of the propagation of these modes, it is necessary to know the spatial distribution of the electron density determined by the expansion coefficients in the wave function (5). In the two bottom minima of the adiabatic potential these coefficients are given by the expressions

$$\chi_g(Q_\pm^{(l)}) = \mp \sqrt{\frac{1+\alpha^{-1}}{2}} \left[1 \pm \frac{1-\alpha^{-1}}{2} \frac{\delta}{\lambda} \mp \frac{\beta}{2\alpha} \frac{|\gamma|}{K^{3/2}} \right.$$
$$\left. + \frac{\beta^2}{2\alpha} \frac{\kappa}{K^2} \right],$$
$$\chi_e(Q_\pm^{(l)}) = \sqrt{\frac{1-\alpha^{-1}}{2}} \left[1 \mp \frac{1+\alpha^{-1}}{2} \frac{\delta}{\lambda} \pm \frac{\beta}{2\alpha} \frac{|\gamma|}{K^{3/2}} \right.$$
$$\left. - \frac{\beta^2}{2\alpha} \left(\frac{\kappa}{K^2} \right) \right]. \tag{27}$$

For states in the top well we have

$$\chi_g(Q^{(u)}) = -\frac{\alpha}{1+\alpha} \frac{\delta}{\lambda},$$
$$\chi_e(Q^{(u)}) = \sqrt{1 - \left(\frac{\alpha}{1+\alpha} \right)^2 \left(\frac{\delta}{\lambda} \right)^2} \approx 1. \tag{28}$$

Thus the electronic state in the top well is localized much more strongly than the states in the two bottom wells, and it is close to the seed exciton (15) in a rigid lattice. The ground state of the system, taking into account the pseudo-Jahn–Teller relaxation of the lattice, is characterized by a wave function of the type (13), in which the local orbitals in the positions of equilibrium have the form

$$\varphi_g^{(0)}(r) = \cos\theta' \, | f_{\mathbf{m}}^6, {}^7F_0) + \sin\theta' \, | f_{\mathbf{m}}^5 B_{\mathbf{m}}^+, {}^7F_0),$$
$$\cos\theta' = \chi_g(Q_-^{(l)}) \cos\theta - \chi_e(Q_-^{(l)}) \sin\theta, \tag{29}$$

where $\cos\theta'$ determines the true value of the intermediate valence taking into account Jahn–Teller restructuring.

Thus, the main effect of pseudo-Jahn–Teller relaxation is that instead of the renormalization of phonon frequencies ($\alpha < 1$) that occurs in the simple CDD method, the nomenclature of the vibronic states changes significantly ($\alpha > 1$). Assuming that the amplitudes of the vibrations in the ground and excited electronic states are small, we can describe in the zeroth approximation the corresponding vibronic states of the cluster by the wave functions

$$\Psi_n^{(u)}(r,Q) = \chi_n^{(u)}(Q - Q^{(u)}) \varphi^{(u)}(r),$$
$$\Psi_{(\pm)n}^{(l)}(r,Q) = \chi_{(\pm)n}^{(l)}(Q - Q_\pm^{(l)}) \varphi_{(\pm)}^{(l)}(r), \tag{30}$$

with energies $E_n^{(u)} = E^{(u)} + \hbar\omega^{(u)}[n+1/2]$ and $E_{(\pm)n}^{(l)} = E_\pm^{(l)} + \hbar\omega_\pm^{(l)}[n+1/2]$, where the frequencies of the vibrational quanta are determined by the force constants (23), and the electronic components have the form

$$\varphi^{(u)}(r) = [\chi_g(Q^{(u)}) \varphi_g^{(0)}(r) + \chi_e(Q^{(u)}) \varphi_e^{(0)}(r)],$$
$$\varphi_{(\pm)}^{(l)}(r) = [\chi_g(Q_\pm^{(l)}) \varphi_g^{(0)}(r) + \chi_e(Q_\pm^{(l)}) \varphi_e^{(0)}(r)]. \tag{31}$$

The approach proposed above preserves the advantages of the simple CDD method for calculating the phonon spectrum, though the change in the dynamical matrix does not reduce to a simple renormalization of its coefficients. The force constants $F_-^{(l)}$ (23) determining the normal phonons are calculated in the zeroth approximation by the standard method by differentiating expression (12) for the configurational energy $E^-(Q)$ with respect to the small displacements relative to the equilibrium position $Q_-^{(l)}$.

4. EXCITON-POLARON STATES IN THE LATTICE

Having determined the parameters of the cluster we must embed the cluster into a translationally invariant system and study the behavior of the excited states in the lattice. We now consider vibrations of the system in electronically excited states near the additional minima of the configurational curves (19) at the points $Q_+^{(l)}$ and $Q^{(u)}$. Near the excited ion the lattice is in a polarized state characterized by equilibrium positions which are shifted compared to the ground state $E_-^{(l)}(Q)$, and by altered force constants of the interatomic interaction. The exciton (exciton-polaron), together with the polarization field accompanying it, can either propagate coherently through the lattice or it can be localized near a particular node, depending on the conditions of excitation of the system and on the ratio of the kinetic and potential energies of this polaron.[24] In the latter case it is a local level in the electronic spectrum and a defect of the force constants for the vibrational spectrum.

To determine the propagation regime of the exciton-polaron it is necessary to know the resonance overlap integral for the excitonic wave functions. This integral, in turn, is determined by the hole $\varphi^{(l)}_{(-)}(r)$ and electronic wave functions $\varphi^{(l)}_{(+)}(r)$ and $\varphi^{(u)}(r)$ (31). Since both excitons are singlet, i.e., they do not have multipole moments, the corresponding overlap integrals $J^{(u)}(\mathbf{R})$ and $J^{(l)}_{(+)}(\mathbf{R})$ are of purely exchange origin:

$$\begin{aligned} J^{(u)}(\mathbf{R}) &= -\left\langle \varphi^{(u)}(\mathbf{r}_1-\mathbf{R})\varphi^{(l)}_{(-)}(\mathbf{r}_2)\left|\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right|\varphi^{(u)} \right. \\ &\qquad \left. \times(\mathbf{r}_1)\varphi^{(l)}_{(-)}(\mathbf{r}_2-\mathbf{R})\right\rangle, \\ J^{(l)}_{(+)}(\mathbf{R}) &= -\left\langle \varphi^{(l)}_{(+)}(\mathbf{r}_1-\mathbf{R})\varphi^{(l)}_{(-)}(\mathbf{r}_2)\left|\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right|\varphi^{(l)}_{(+)} \right. \\ &\qquad \left. \times(\mathbf{r}_1)\varphi^{(l)}_{(-)}(\mathbf{r}_2-\mathbf{R})\right\rangle. \end{aligned} \tag{32}$$

The exchange integrals are small, since they are determined only by the overlapping of localized electron wave functions. It can thus be expected that for both excitations the condition for the existence of a small-radius exciton-polaron can be satisfied:

$$J/E_b < s, \tag{33}$$

where s is a numerical factor that depends on the geometry of the lattice and is of order unity, and E_b is the exciton-polaron binding energy. For small-radius polarons above the temperature for which the exciton-energy uncertainty due to inelastic scattering is greater than the polaron-renormalized narrowing of the excitonic band $J\exp(-E_b/\hbar\omega)$, where ω is the frequency of the optical phonons), there arises an incoherent propagation regime in which displacement from one site to another is by hopping.[24]

The degree of overlapping of the hole wave functions $\varphi^{(l)}_{(-)}(r)$ is the same for both types of exciton, and the electronic states corresponding to the excitation into the right-hand lower well overlap significantly more strongly than in the upper pseudo-Jahn-Teller minimum, where the electronic component is practically localized in the f-shell and overlaps weakly the neighboring sites. For this reason we assume that

$$J^{(u)}(\mathbf{R}) \ll J^{(l)}_{(+)}(\mathbf{R}). \tag{34}$$

The binding energies for both types of exciton-polaron, which we designate as EPI and EPII respectively, are

$$\begin{aligned} E_b^{(I)} &= E^{+}(Q_-^{(l)}) - E^{(u)} \\ &= \hbar\omega\left(\frac{\Delta}{\hbar\omega}\right)\alpha\left\{\left[\frac{3}{2}-\alpha^{-1}\right]\right. \\ &\qquad \left. +\left[-(1-\alpha^{-1})\frac{\delta}{\lambda}+\frac{1}{3}\beta\frac{|\gamma|}{K^{3/2}}+\frac{1}{4}\beta^2\frac{\kappa}{K^2}\right]\right\}, \\ E_b^{(II)} &= E^{+}(Q_-^{(l)}) - E_+^{(l)} \\ &= \hbar\omega\left(\frac{\Delta}{\hbar\omega}\right)\alpha\left\{2-2\left(\frac{\delta}{\lambda}\right)+\frac{2}{3}\beta\left(\frac{|\gamma|}{K^{3/2}}\right)\right\}. \end{aligned} \tag{35}$$

These energies are virtually equal, so that on the basis of the inequality (34) a transition into the incoherent regime is most likely for excitation into the upper well (the EPI state). We now consider the condition under which this excitation is localized.

If the parameters J, E_b, ω, and $\Delta\omega$ ($\Delta\omega$ is a measure of the dispersion of optical phonons) characterizing the exciton-polaron satisfy the conditions

$$\left(\frac{J}{E_b}\right)\left(\frac{J}{\hbar\omega}\right)<1;\quad \left(\frac{J}{E_b}\right)\left(\frac{J}{\hbar\Delta\omega}\right)<1;\quad \left(\frac{2J}{E_b}\right)\left(\frac{\omega}{\Delta\omega}\right)<1 \tag{36}$$

for EPI, then the temperature of its transition into the incoherent regime is determined by the following relation:[24]

$$T_{\text{ncoh}} = \frac{\hbar\omega}{(E_b^{(I)}/2\hbar\omega)+\ln[(\Delta\omega/\omega)(E_b^{(I)}/2\hbar\omega)(E_b^{(I)}/2J^{(u)})^3]}. \tag{37}$$

We take as the upper limit of the overlap integral the exciton excitation energy, which, as we have already mentioned, is comparable to the energy $\hbar\omega$ of optical phonons. Then, setting $\alpha\sim 3$ and $\Delta/\hbar\omega\sim 3$ and taking into consideration the fact that $\Delta\omega/\omega\sim 1$ in $Sm_{0.75}Y_{0.25}S$ and SmB_6, we estimate the temperature of the transition into the incoherent regime as

$$T_{\text{ncoh}} \sim \hbar\omega/15 \approx 20\ \text{K}. \tag{38}$$

Thus at temperatures above 20 K the state EPI becomes incoherent, i.e., its stay near one site is significantly longer than the characteristic time of optical lattice vibrations. From the standpoint of lattice vibrations such a state of the exciton-polaron is the complete analog of a defect of the force constants. It is evident from the conditions (25) that the force constants in the vicinity of a localization site of an incoherent exciton are smaller than the force constants of an ideal lattice. An exciton in the lower right-hand well is an exciton-polaron which has an intermediate radius and propagates coherently through the lattice.

We have found thus that from the standpoint of the vibrational subsystem the local valence fluctuations are defects of the force constants. Vibrations which are a response to these fluctuations can be regarded as additional

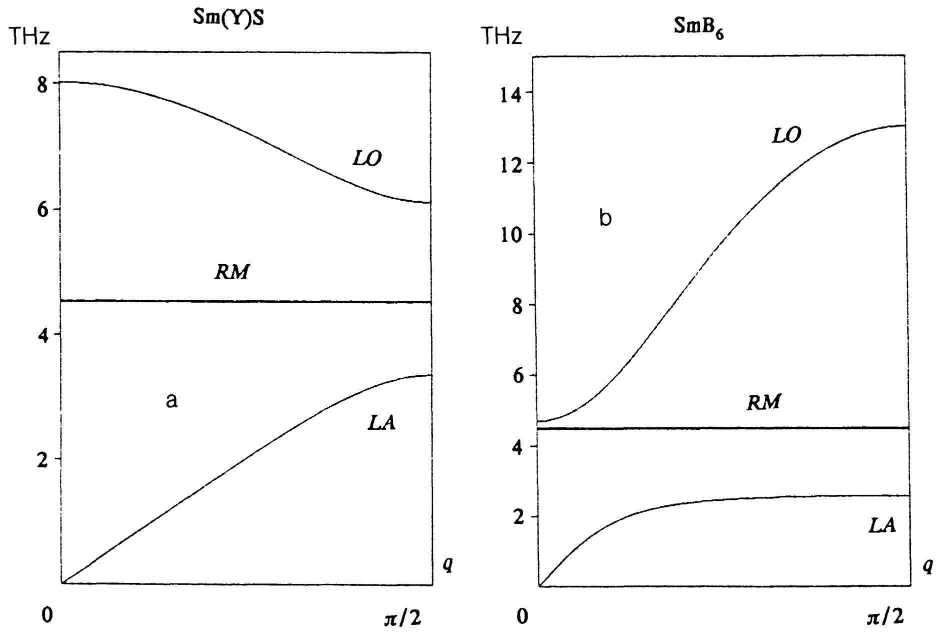

FIG. 3. Vibrational spectra of the SmS (a) and SmB$_6$ (b) types with local modes.

modes in the spectrum of lattice excitations, and the character of the propagation of these modes is different for different types of valence fluctuations: "weak" valence fluctuations with low excitation energy (EPII) correspond to the coherent regime of the polarization wave in the lattice and the harder "strong" EPI fluctuations correspond to incoherent excitations of the lattice which at not too low temperatures behave as local lattice modes.

The systematic analysis of the nonadiabatic (resonance) electron-phonon interaction in intermediate-valence semiconductors has led thus to the appearance of two types of additional states, such as defects of force constants in the vibrational spectrum, in contrast to preceding attempts in which the additional lattice mode was regarded as a two-phonon bound state, whose energy and symmetry depended significantly on the phenomenological parameters introduced,[25] or the valence fluctuations were assigned a fictitious mass, whose origin was not substantiated in any manner.[26] In the concluding sections of this paper we shall describe the properties of the additional local states.

5. LOCAL RESONANCE MODE

We now consider the problem of a defect of force constants that is associated with an EPI-type electronic excitation. We solve this problem by the standard method of lattice Green's functions.[27]

In this technique the equation of motion for a defect in an ideal lattice has the form

$$u_\alpha(\mathbf{l};t)=\sum_{\mathbf{l}_2 t_2 \gamma}\left[\sum_{\mathbf{l}_1 t_1 \beta} G^{\alpha\beta}_{tt_1}(\mathbf{l}-\mathbf{l}_1;\omega)\,\Delta^{\beta\gamma}(\mathbf{l}_1,\mathbf{l}_2;t_1,t_2)\right]u_\gamma(\mathbf{l}_2;t_2). \tag{39}$$

Here $u_\alpha(\mathbf{l};t)$ is the α component of the displacement of an ion of the $\mathbf{l}$th elementary cell of the sublattice t, G is the Green's function of the ideal crystal, and Δ is the matrix of perturbation of the ideal crystal by the defect.

$$G^{\alpha\beta}_{tt_1}(\mathbf{l}-\mathbf{l}_1;\omega)=\frac{1}{N}\frac{1}{\sqrt{M_t M_{t_1}}}\sum_{\mathbf{k}\gamma}\frac{e^{\alpha t}_{\mathbf{k}j}(e^{\beta t_1}_{\mathbf{k}j})^*}{\omega^2-\omega^2_{\mathbf{k}j}} \times\exp[2\pi i\mathbf{k}(\mathbf{l}-\mathbf{l}_1)], \tag{40}$$

where $\mathbf{l}$ is an elementary-translation vector, t is the index of the sublattice, M is the ion mass, and $e^{\alpha t}_{\mathbf{k}j}$ is the projection of the polarization vector of the tth ion of the jth phonon branch with wave vector $\mathbf{k}$ and frequency $\omega_{\mathbf{k}j}$ on the α axis.

$$\Delta^{\alpha\beta}(\mathbf{l},\mathbf{l}_1;t,t_1)=[M_t-M^{(0)}_{t_1}]\delta_{tt_1}\delta_{\mathbf{l}\mathbf{l}_1}\delta_{\alpha\beta} +[\Phi_{\alpha\beta}(\mathbf{l},\mathbf{l}_1;t,t_1)-\Phi^{(0)}_{\alpha\beta}(\mathbf{l},\mathbf{l}_1;t,t_1)], \tag{41}$$

where $\Phi^{(0)}$ and Φ are matrices of the force constants of the ideal and defective lattices, respectively.

The intermediate-valence systems of interest to us have effectively diatomic cubic lattices with a force-constant defect that is located at the position of an ion of the heavy sublattice. The crystal lattices have different structures, but these systems differ mainly by the fact that the ratios of the force constants of the intersublattice (Sm–S, Sm–B$_6$) and intrasublattice (Sm–Sm, S–S, B$_6$–B$_6$) interaction are different. In sulfides the Sm–S intersublattice interaction constants are significantly larger than all intrasublattice constants (Sm–Sm, S–S), and this leads to the usual (for the rock salt lattice) phonon spectrum (Fig. 3a), which we refer to below as a spectrum of the SmS type. The intersublattice force constants in hexaborides (Sm–B$_6$) are significantly smaller than the force constants of the interaction between the structural elements of the light sublattice B$_6$–B$_6$. For this reason, the phonon spectrum of

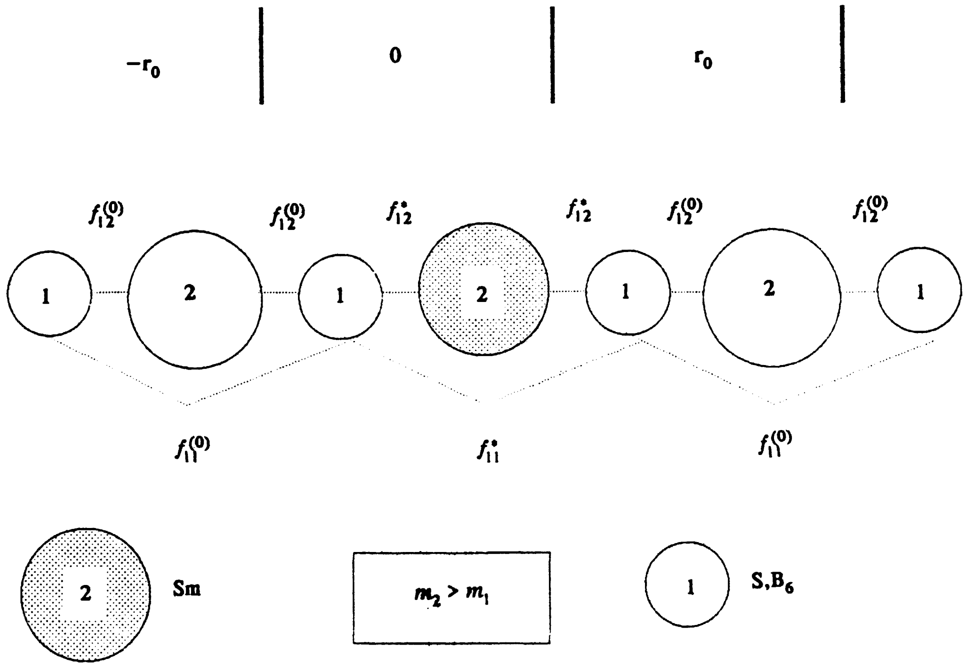

FIG. 4. One-dimensional model of the force interactions in two-sublattice rare-earth semiconductors.

hexaborides is characterized by strong dispersion of optical phonons and by acoustic branches with large flat sections (Fig. 3b). We shall call such a phonon spectrum a spectrum of the SmB$_6$ type.

If both compounds are modeled by a one-dimensional diatomic lattice (Fig. 4) with short-range force constants $f^{(0)}_{12}$ and $f^{(0)}_{11}$ of the interaction between the nearest neighbors of different sublattices and nearest ions of the light sublattice 1, respectively, then we obtain the SmS phonon spectrum (Fig. 3a) for $f^{(0)}_{12} \gg f^{(0)}_{11}$ and a SmB$_6$ spectrum (Fig. 3b) for $f^{(0)}_{12} \ll f^{(0)}_{11}$. In this model the defect under consideration can alter three force constants of the interaction with the nearest neighbor environment (Fig. 4), i.e., it can decrease the values of the two constants f^*_{12} and the constant f^*_{11} below the ideal-lattice values:

$$\delta f_{12}=f^*_{12}-f^{(0)}_{12}<0;\quad \delta f_{11}=f^*_{11}-f^{(0)}_{11}<0. \qquad (42)$$

In this model the defect space is bounded by the indices

$$(1t)=(01;02;\mathbf{r}_0 1) \qquad (43)$$

and Eq. (39) for the frequency and displacement vector of the additional local vibrations acquires the form

$$\begin{pmatrix} u(0,1)\\ u(0,2)\\ u(\mathbf{r}_0,1)\end{pmatrix}=\begin{pmatrix} G_{11}(0;\omega) & G_{12}(0;\omega) & G_{11}(\mathbf{r}_0;\omega)\\ G_{12}(0;\omega) & G_{22}(0;\omega) & G_{12}(0;\omega)\\ G_{11}(\mathbf{r}_0;\omega) & G_{12}(0;\omega) & G_{11}(0;\omega)\end{pmatrix}$$
$$\times\begin{pmatrix} \delta f_{12}+\delta f_{11} & -\delta f_{12} & -\delta f_{11}\\ -\delta f_{12} & 2\delta f_{12} & -\delta f_{12}\\ -\delta f_{11} & -\delta f_{12} & \delta f_{12}+\delta f_{11}\end{pmatrix}$$
$$\times\begin{pmatrix} u(0,1)\\ u(0,2)\\ u(\mathbf{r}_0,1)\end{pmatrix}. \qquad (44)$$

The system (44) can be significantly simplified on the basis of symmetry considerations, since for the defect under consideration only vibrations having the breather and dipole symmetry are possible with displacements in the defect space

$$[u(0,1),u(0,2),u(\mathbf{r}_0,1)]=(a,0,-a), \quad \text{(a)}$$

$$[u(0,1),u(0,2),u(\mathbf{r}_0,1)]=(b,c,b), \quad \text{(b)} \qquad (45)$$

respectively. Substituting these displacement vectors into the system of (44) we obtain the frequencies and displacements of local vibrations of both types.

The frequency of the local breather vibration is found from the equation

$$(\delta f_{12}+2\delta f_{11})[G_{11}(0;\omega)-G_{11}(\mathbf{r}_0;\omega)]=1. \qquad (46)$$

The displacements of ions have the form (45a) inside the defect space and are determined outside the defect space by the expression

$$u(\mathbf{1};t)=a(\delta f_{12}+2\delta f_{11})[G_{t1}(\mathbf{1};\omega)-G_{t1}(\mathbf{1}-\mathbf{r}_0;\omega)]. \tag{47}$$

To determine the frequency of the dipole mode we obtain the equation

$$\delta f_{12}[G_{11}(\mathbf{0};\omega)+G_{11}(\mathbf{r}_0;\omega)+2G_{22}(\mathbf{0};\omega)-4G_{12}(\mathbf{0};\omega)]=1. \tag{48}$$

The displacements in the defect space have the form (45b) with the ratio of the parameters b and c

$$\frac{b}{c}=\frac{\delta f_{12}[G_{11}(\mathbf{0};\omega)+G_{11}(\mathbf{r}_0;\omega)-2G_{12}(\mathbf{0};\omega)]}{\delta f_{12}[G_{11}(\mathbf{0};\omega)+G_{11}(\mathbf{r}_0;\omega)-2G_{12}(\mathbf{0};\omega)]-1}. \tag{49}$$

Displacements outside the defect space are given by the expression

$$u(\mathbf{1};t)=(b-c)\delta f_{12}[G_{t1}(\mathbf{1};\omega)+G_{t1}(\mathbf{1}-\mathbf{r}_0;\omega)$$
$$-2G_{t2}(\mathbf{1};\omega)]. \tag{50}$$

We find the SmS spectrum on the basis of the model of Fig. 4 with a single nonzero intersublattice constant $f_{12}^{(0)}$ and masses corresponding to the masses of samarium and sulfur ions. The frequencies of the local vibrations arising as the two force constants f_{12}^{*} are decreased (Fig. 4) by excitation of an exciton were found by solving Eqs. (46) and (48) numerically. A defect of this type leads to separation of a local fully symmetric vibration, whose frequency falls in the gap between the acoustic and optical phonons, from the phonon spectrum of the ideal lattice. The dipole vibration does not split from the spectrum. The position of the frequency of the local mode in the gap as a function of the ratio $f_{12}^{*}/f_{12}^{(0)}$ is presented in Fig. 5. Even for $f_{12}^{*}/f_{12}^{(0)}=0$, however, the frequency of the local mode cannot be (see Ref. 28) lower than the limiting value

$$\omega_{\mathrm{lim}}^2=\frac{\omega_{ac}^2(q=\pi/2)+\omega_{\mathrm{opt}}^2(q=\pi/2)}{2}, \tag{51}$$

while the experimentally obtained frequency of the resonance mode lies significantly lower. The reason is that the simple model with only one intersublattice constant $f_{12}^{(0)}$ does not completely reflect the characteristic features of the SmS spectrum, which is characterized by an appreciable contribution of the force constant $f_{11}^{(0)}$ of the interaction between the nearest-neighbor ions of the light sublattice and the force constant of the breather mode.[12] For certain values of the force constants $f_{12}^{(0)}$ and $f_{11}^{(0)}$ and the force constant of the breather mode $G^{\Gamma_1^+}$ we obtain dispersion curves (Fig. 3a) similar to the spectrum of $\mathrm{Sm_{0.75}Y_{0.25}S}$ in the direction [111]. Assuming that the lattice expansion due to excitation into the EPI state, in the neighborhood of a site breaks the bond between sulfur ions ($f_{11}^{*}=0$) and decreases by a factor of two the value of the intersublattice constant $f_{12}^{*}=f_{12}^{(0)}/2$, we obtain the resonance mode in the position corresponding to experiment (Fig. 3a). In the resonance mode the ion vibrations are localized in the neighborhood of an exciton within the limits of several elementary cells (Fig. 6a).

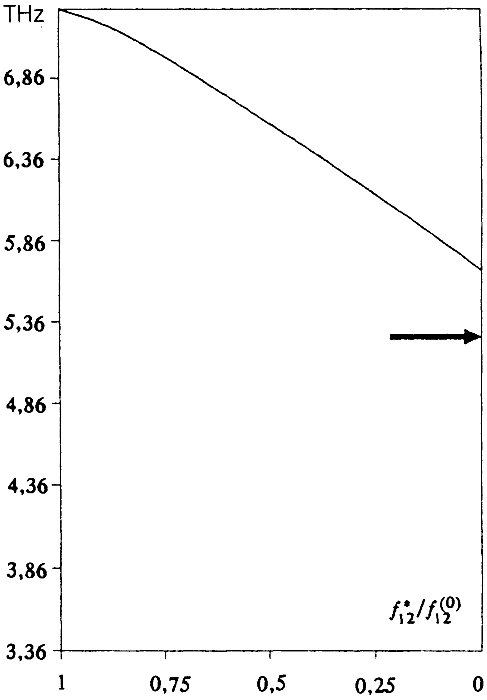

FIG. 5. Energy of the local mode determined by Eq. (46) versus the ratio of the force constants. The arrow indicates the experimental position of this mode in $\mathrm{Sm_{0.75}Y_{0.25}S}$.[4,5]

An entirely different situation is realized in the $\mathrm{SmB_6}$ spectrum which we modeled with the help of the interaction constants $f_{11}^{(0)}$ between ions of the light sublattice, which are much greater than the intersublattice force constants $f_{12}^{(0)}$. In a spectrum of this type only local dipole vibrations can be split off. As is evident from Eq. (48), the frequency of the split-off dipole vibration depends only on the changes in the intersublattice constant $f_{12}^{(0)}$, the frequency decreasing with the ratio $f_{12}^{*}/f_{12}^{(0)}$. Even if $f_{12}^{*}=0$ in the neighborhood of an incoherent excitation, however, the frequency of a local vibration lies near the top edge of the gap (Fig. 3b), in complete agreement with the experimental data.[7] The localization radius of ion vibrations in the resonance mode is quite large and amounts to several tens of unit cells (Fig. 6b).

Thus the "extra" mode observed in the inelastic neutron scattering spectra is due to transitions between levels of local vibrations of a defect of the force constants. For this reason, in accordance with experiment,[4,5,7] this mode is dispersion-free and is seen in both the longitudinal and transverse neutron-scattering geometries.

According to our calculations the lattice modes induced by valence fluctuations are even in NaCl-type lattices and odd in $\mathrm{SmB_6}$-type lattices. The symmetry of the dispersion-free mode cannot be determined from neutron experiments, but it can be determined by analyzing the selection rules for defect-induced phonon Raman scattering,[29] which allow first-order processes only for even local vibrations. In the compounds $\mathrm{Sm_{1-x}Y_xS}$ with an NaCl-type lattice first-order Raman scattering of the fully

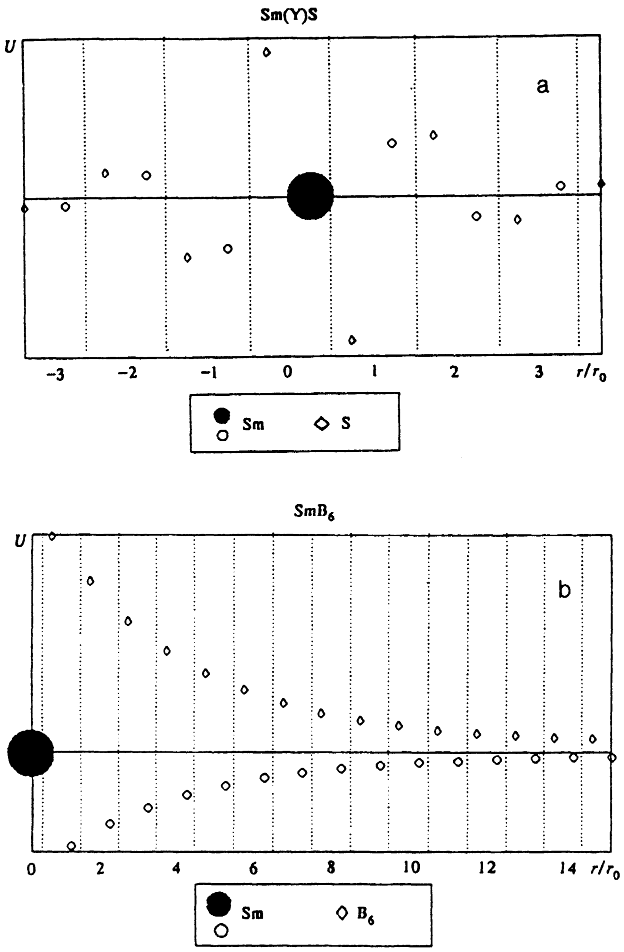

FIG. 6. Displacement of ions in local modes in compounds with SmS (a) and SmB$_6$ (b) type spectra.

symmetric character Γ_1^+ is observed at energies near the resonance mode.[6] We can therefore conclude that, irrespective of whether light scattering occurs on the coherent or incoherent local mode, local vibrations in such lattices are even. On the other hand, the Raman scattering experiment performed in samarium hexaboride[30] completely excludes first-order scattering of even symmetry in the energy range of the resonance mode.

6. RESONANCE COHERENT MODE

Vibronic states corresponding to the right-hand well of the pseudo-Jahn–Teller configurational diagram (EPII) are intermediate-radius exciton-polarons propagating with wave vector **q** through the lattice. The EPII wave function can be written in the form

$$T_{\mathbf{q}}^{+}=\frac{1}{\sqrt{N}}\sum_{\mathbf{m}}\exp(i\mathbf{q}\mathbf{R}_{\mathbf{m}})B_{\mathbf{m}}^{+}D_{\mathbf{q}}(\mathbf{m})\,|0\rangle, \qquad (52)$$

where $|0\rangle$ is the vacuum state, $B_{\mathbf{m}}^{+}$ is a linear combination of electron-hole pairs of the type (14), and $D_{\mathbf{q}}(\mathbf{m})$ characterizes the lattice vibrational spectrum deformed in a neighborhood of the site m:

$$D_{\mathbf{q}}(\mathbf{m})=\exp\left[\sum_{\mathbf{k}j}\left(f_{\mathbf{q}j}(\mathbf{k})e^{-i\mathbf{k}\mathbf{R}_{\mathbf{m}}}b_{\mathbf{k}j}-\text{h.c.}\right)\right], \qquad (53)$$

where $b_{\mathbf{k}j}$ is the operator annihilating a j-branch phonon with wave vector **k**.

In reality, however, the lower branch of the configurational diagram in Fig. 1 is a two-well potential for coherent excitations in the system, and excitations in each valley of this potential are independent only to the extent that the states in each valley are adiabatic. Since in constructing the complete three-well configurational diagram we took into account exactly only the fully symmetric adiabatic interaction of the electronic subsystem with the optical phonons, all other contributions to the vibronic interaction, as well as the nonadiabatic part of the fully symmetric interaction with optical vibrations, lead generally speaking to the fact that excitation of EPII-type states influences the spectrum of normal phonons and vice versa, the nonadiabatic interaction with phonons must be taken into account for excitation of EPII. In particular, the EPII excitation energy in SmB$_6$ is close to the energy of acoustic phonons at the boundary of the Brillouin zone, and the corresponding nonadiabatic renormalization of the vibronic states must be taken into account first.

Using the standard formalism of the theory of electron-vibrational interaction (see, for example, Ref. 31), we expand the EPII wave function in a complete set of adiabatic wave functions of the ground g and excited $\Psi_{\beta}^{\mathbf{q}}(\mathbf{r},Q)$ states:

$$\Psi(\mathbf{r},Q)=\sum_{\beta}\left\{\xi_{g\beta}\chi_{g\beta}(Q)\varphi_g(\mathbf{r},Q)+\sum_{\mathbf{q}}\left[\xi_{\mathbf{q}\beta}\chi_{\mathbf{q}\beta}(Q)\varphi^{\mathbf{q}}(\mathbf{r},Q)\right]\right\}, \qquad (54)$$

where g, **q** is the electronic state, β is the phonon quantum number, and the coefficients $\xi_{g\beta}$ and $\xi_{\mathbf{q}\beta}$ are determined by solving the system of equations

$$\begin{aligned}(E-E_{g\beta})\xi_{g\beta}&=\sum_{\mathbf{q}\beta'}\left(\mathscr{A}_{g\mathbf{q}}^{\beta\beta'}+\mathscr{B}_{g\mathbf{q}}^{\beta\beta'}\right)\xi_{\mathbf{q}\beta'},\\(E-E_{\mathbf{q}\beta})\xi_{\mathbf{q}\beta}&=\sum_{\beta'}\left([\mathscr{A}_{g\mathbf{q}}^{\beta\beta'}]^{*}+[\mathscr{B}_{g\mathbf{q}}^{\beta\beta'}]^{*}\right)\xi_{g\beta'},\end{aligned} \qquad (55)$$

$$\begin{aligned}\mathscr{A}_{g\mathbf{q}}^{\beta\beta'}&=-\sum_{st}\frac{1}{M_t}\int\left\{dQ\chi_{g\beta}^{*}(Q)\right.\\&\quad\left.\times\left[\int d\mathbf{r}\varphi_g^{*}(\mathbf{r},Q)\nabla_{\mathbf{R}_{st}}\varphi^{\mathbf{q}}(\mathbf{r},Q)\right]\nabla_{\mathbf{R}_{st}}\chi_{\mathbf{q}\beta'}(Q)\right\},\\\mathscr{B}_{g\mathbf{q}}^{\beta\beta'}&=-\sum_{st}\frac{1}{2M_t}\int\left\{dQ\chi_{g\beta}^{*}(Q)\right.\\&\quad\left.\times\left[\int d\mathbf{r}\varphi_g^{*}(\mathbf{r},Q)\nabla_{\mathbf{R}_{st}}^{2}\varphi^{\mathbf{q}}(\mathbf{r},Q)\right]\chi_{\mathbf{q}\beta'}(Q)\right\}.\end{aligned} \qquad (56)$$

The matrix element $\mathscr{B}_{g\mathbf{q}}^{\beta\beta'}=\mathscr{B}_{g\mathbf{q}}^{\beta}\delta_{\beta\beta'}$ is diagonal in the phonon quantum numbers β. For this reason, in accordance with the law of conservation of momentum, it is zero for $\mathbf{q}\neq 0$ and it cannot mix the ground electronic state with a coherent vibron having a nonzero wave vector. The only matrix element of the nonadiabatic interaction mixing different electronic states is the matrix element of the operator $\mathscr{A}_{g\mathbf{q}}^{\beta\beta'}$, where the state β differs from the state β' by the occupation number of one of the phonons:

$$\mathscr{A}_{g\mathbf{q}}^{n_{\mathbf{q}\gamma},n_{\mathbf{q}\gamma}\pm 1}=\frac{\hbar\omega_{\mathbf{q}\gamma}}{E_{\mathbf{q}\beta}-E_{g\beta}}\,T_{\mathbf{q}}^{n_{\mathbf{q}\gamma},n_{\mathbf{q}\gamma}\pm 1}. \tag{57}$$

Here $T_{\mathbf{q}}^{n_{\mathbf{q}\gamma},n_{\mathbf{q}\gamma}\pm 1}$ is the matrix element of transitions from the electronic ground state into the state $\Psi^{\mathbf{q}}_{n_{\mathbf{q}\gamma}\pm 1}(\mathbf{r},Q)$.

When calculating the vibronic wave function it is necessary to take into consideration the fact that the excitation into EPII (52) is not only a change in the electronic state of the system but it is also a restructuring of the vibrational state (53) of the system. The vibrational component of this vibron (53) is a local mode $\tilde{Q}_e^{\mathbf{m}}$ at the site m with possible polarizations $e=1,\dots,W$, which accompanies propagation of an electron density wave produced by the fully symmetric exciton $B_{\mathbf{m}}^{+}$ (14). The displacement of ions near a center have a back effect on the electronic component of the coherent vibron. This effect is especially pronounced in the form of CDD in SmB$_6$, since in this system the Γ_{15}^{-} symmetry of the local vibration is different from the symmetry Γ_1^{+} of the seed exciton. For this reason, the dipole component $\Delta^{e\Gamma_{15}^{-}}\varphi_{(+)}^{(l)}(\mathbf{r}-\mathbf{R}_{\mathbf{m}}^{(0)};\tilde{Q}_e^{\mathbf{m}})$ is added to its fully symmetric wave function $\varphi_{(+)}^{(l)}(\mathbf{r}-\mathbf{R}_{m}^{(0)})$ (31).

Thus the wave function of the coherent vibron can be written as a Bloch superposition of local vibronic states

$$\varphi^{\mathbf{q}}(\mathbf{r},Q)=\frac{1}{\sqrt{N}}\sum_{\mathbf{m}}\exp(i\mathbf{q}\mathbf{R}_{\mathbf{m}})\Phi(\mathbf{r}-\mathbf{R}_{\mathbf{m}}^{(0)};\tilde{Q}_1^{\mathbf{m}},\dots,\tilde{Q}_W^{\mathbf{m}}), \tag{58}$$

where the electron-vibrational function of the node **m** has the form

$$\begin{aligned}\Phi(\mathbf{r}-\mathbf{R}_{\mathbf{m}}^{(0)};\tilde{Q}_1^{\mathbf{m}},\dots,\tilde{Q}_W^{\mathbf{m}}) &= \sum_{e=1}^{W}[\varphi_{(+)}^{(l)}(\mathbf{r}-\mathbf{R}_{\mathbf{m}}^{(0)}) \\ &\quad +\Delta^{e\Gamma_{15}^{-}}\varphi_{(+)}^{(l)}(\mathbf{r}-\mathbf{R}_{\mathbf{m}}^{(0)};\tilde{Q}_e^{\mathbf{m}})]\chi_e^{(0)}(\tilde{Q}_e^{\mathbf{m}}).\end{aligned} \tag{59}$$

The matrix elements of the transition from the ground electronic state into the coherent-vibron state (58) is obtained by the standard procedure of expanding the electron-ion potential in the displacements. In the linear approximation only transitions with a change in the occupation number of one phonon $n_{\mathbf{q}\gamma}$ by 1 are possible. In the case of a transition from the ground state into the coherent-vibron state the phonon-produced distortion of the electron-ion potential should not only excite an exciton, but should also produce a wave packet consisting of vibrational functions of the phonons and describing a local vibration. In calculating the matrix elements of the nonadiabaticity operator it is convenient to project the coherent phonons of the ground state on the local basis $\tilde{Q}_e^{m}$ with the help of van Vleck coefficients, thereby forming the wave packet $\tilde{\chi}(\tilde{Q}_e^{m})$. The standard procedure for calculating the matrix element of the nonadiabaticity operator must also be modified accordingly for the case of a transition with a change in the nomenclature of the vibrational states.

We present here only the computation results for the particular case of electron-polaron excitation in SmB$_6$. The matrix element of the transition from the electronic ground state into the EPII state, whose local vibrational state is described by the wave function $\chi_e^{(0)}(\tilde{Q}_e^{m})$, with a unity change in the occupation number of one phonon, has the form

$$\begin{aligned}T_{\mathbf{q}}^{n_{\mathbf{q}\gamma},n_{\mathbf{q}\gamma}\pm 1} &= [(\hbar/2\omega_{\mathbf{q}\gamma})(n_{\mathbf{q}\gamma}\pm 1/2+1/2)]^{1/2} \\ &\quad\times\sum_{e=1}^{W}\{\mathscr{F}_{\mathbf{q}\gamma}^{e\Gamma_1^{+}}+\mathscr{F}_{\mathbf{q}\gamma}^{e\Gamma_{15}^{-}}\},\end{aligned} \tag{60}$$

where

$$\mathscr{F}_{\mathbf{q}\gamma}^{e\Gamma}=\int d\tilde{Q}_e^{\mathbf{m}}\tilde{\chi}(\tilde{Q}_e^{\mathbf{m}})\Theta_{\mathbf{q}\gamma}^{e\Gamma}(\tilde{Q}_e^{\mathbf{m}})\chi_e^{(0)}(\tilde{Q}_e^{\mathbf{m}}), \tag{61}$$

$$\begin{aligned}\Theta_{\mathbf{q}\gamma}^{e\Gamma}(\tilde{Q}_e^{\mathbf{m}}) &= \int d\mathbf{r}\{\varphi_{(-)}^{(l)}(\mathbf{r})\}P_{\mathbf{q}\gamma}^{\Gamma}(\mathbf{r}) \\ &\quad\times\{\varphi_{(+)}^{(l)}(\mathbf{r})+\Delta^{e\Gamma_{15}^{-}}\varphi_{(+)}^{(l)}(\mathbf{r};\tilde{Q}_e^{\mathbf{m}})\},\end{aligned} \tag{62}$$

and the $P_{\mathbf{q}\gamma}^{\Gamma}(\mathbf{r})$ component of the operator of the distortion of the electron-ion potential is

$$P_{\mathbf{q}\gamma}^{\Gamma}(\mathbf{r})=\sum_{\mathbf{m}t}\mathrm{M}_t^{-1/2}\mathrm{e}_{\mathbf{q}\gamma}^{t}\exp(i\mathbf{q}\mathbf{R}_{\mathbf{m}})\nabla_{\mathbf{r}}^{\Gamma}V(\mathbf{r}-\mathbf{R}_{\mathbf{m}t}), \tag{63}$$

where t is the sublattice index.

Thus, compared to the standard expression for the matrix element of the operator $\nabla_{\mathbf{r}}^{\Gamma}V(\mathbf{r})$, in our case there arises an additional integral over the coordinate of the local mode $\tilde{Q}_e^{\mathbf{m}}$ and a dipole correction to the electronic wavefunction $\Delta^{e\Gamma_{15}^{-}}\varphi_{(+)}^{(l)}(\mathbf{r};\tilde{Q}_e^{\mathbf{m}})$. These peculiarities influence significantly the dependence of the matrix element (60) on the wave vector. The dipole symmetry of the local vibration $\chi_e^{(0)}(\tilde{Q}_e^{\mathbf{m}})$ causes the fully symmetric contribution $\mathscr{F}_{\mathbf{q}\gamma}^{e\Gamma_1^{+}}$ to vanish, and the dipole component $\mathscr{F}_{\mathbf{q}\gamma}^{e\Gamma_{15}^{-}}$ contributes only to the extent of the dipole correction to the wave function $\Delta^{e\Gamma_{15}^{-}}\varphi_{(+)}^{(l)}(\mathbf{r};\tilde{Q}_e^{\mathbf{m}})$.

The additional interaction arising in the double-well system due to the matrix elements of the type (57) leads to renormalization of the wave functions and energies of the seed states. One of the most pronounced manifestations of nonadiabaticity is the appearance of additional (compared to the usual adiabatic situation) signals in nuclear inelastic neutron scattering. Consider the process in which a vibron with wave vector **q** is excited in the case of inelastic scattering by the same wave vector. It is obvious from the law of conservation of momentum that the phonon occupation numbers do not change in this process and we can thus represent the inelastic neutron scattering as a process coupled with a transition between exact states of the type (54), corresponding to a change in the quantum numbers

$$g\beta\rightarrow\mathbf{q}\beta$$

We consider now the important, for comparison with experiment, case when the phonon state β' in the matrix element (57) is different from β in that one occupation number $n_{\mathbf{q}\gamma}$ is reduced by 1 and

$$E_{g,n_{\mathbf{q}\gamma}} \approx E_{\mathbf{q},n_{\mathbf{q}\gamma}-1}. \tag{64}$$

In this case the principal interaction can be singled out of the infinite system of equations (55), and the system for determining the coefficients ξ assumes the simple form

$$\begin{aligned}(E-E_{g,n_{\mathbf{q}\gamma}})\xi_{g,n_{\mathbf{q}\gamma}} &= \mathscr{A}_{g\mathbf{q}}^{n_{\mathbf{q}\gamma},n_{\mathbf{q}\gamma}-1}\xi_{\mathbf{q},n_{\mathbf{q}\gamma}-1},\\ (E-E_{\mathbf{q},n_{\mathbf{q}\gamma}-1})\xi_{\mathbf{q},n_{\mathbf{q}\gamma}-1} &= (\mathscr{A}_{g\mathbf{q}}^{n_{\mathbf{q}\gamma},n_{\mathbf{q}\gamma}-1})^{*}\xi_{g,n_{\mathbf{q}\gamma}}.\end{aligned} \tag{65}$$

Correspondingly, we find the following expression for the electron-vibrational wave functions between which the transition occurs:

$$\begin{aligned}\Psi_{g,n_{\mathbf{q}\gamma}}(\mathbf{r},Q) &= \xi_{1,n_{\mathbf{q}\gamma}}\chi_{g,n_{\mathbf{q}\gamma}}(Q)\varphi_g(\mathbf{r},Q)\\ &\quad -\xi_{2,n_{\mathbf{q}\gamma}}\chi_{g,n_{\mathbf{q}\gamma}-1}(Q)\varphi^{\mathbf{q}}(\mathbf{r},Q),\\ \Psi^{\mathbf{q}}_{n_{\mathbf{q}\gamma}}(\mathbf{r},Q) &= \xi_{1,n_{\mathbf{q}\gamma}+1}\chi_{g,n_{\mathbf{q}\gamma}}(Q)\varphi^{\mathbf{q}}(\mathbf{r},Q)\\ &\quad +\xi_{2,n_{\mathbf{q}\gamma}+1}\chi_{g,n_{\mathbf{q}\gamma}+1}(Q)\varphi_g(\mathbf{r},Q),\end{aligned} \tag{66}$$

where the mixing coefficients

$$\xi_{1,n_{\mathbf{q}\gamma}} = \sqrt{\frac{1}{2}+\frac{1}{2}\,|\Delta E_{\mathbf{q}\gamma}|\{(\Delta E_{\mathbf{q}\gamma})^2+4|\Xi^{e\Gamma}_{\mathbf{q}\gamma}|^2 n_{\mathbf{q}\gamma}\}^{-1/2}};$$

$$\xi_{2,n_{\mathbf{q}\gamma}} = \mathrm{sgn}(\Delta E_{\mathbf{q}\gamma})\,\sqrt{1-(\xi^{(g)}_{1,n_{\mathbf{q}\gamma}})^2}$$

depend on the resonance energy difference

$$\Delta E_{\mathbf{q}\gamma} = E_{\mathbf{q}\beta}-E_{g\beta}-\hbar\omega_{\mathbf{q}\gamma} \tag{67}$$

and the matrix element (57), in which, for simplicity, we consider the case, important for analysis of an experiment, when only one term with definite Γ and e makes a significant contribution to the sum (60):

$$\Xi^{e\Gamma_{15}^{-}}_{\mathbf{q}\gamma} = \sqrt{\frac{\hbar^{3/2}\omega_{\mathbf{q}\gamma}}{2}}\,\frac{\mathscr{F}^{e\Gamma_{15}^{-}}_{\mathbf{q}\gamma}}{E_{\mathbf{q}\beta}-E_{g\beta}}. \tag{68}$$

Since the electronic adiabatic functions with given Q are orthogonal to one another, we find that in a nonadiabatic system there appears an inelastic scattering peak with energy $E_{\mathbf{q}\beta} - E_{g\beta}$ in a polarization identical to that in the case of scattering by the phonon the exchange of which produces nonadiabatic mixing (68). It is this mechanism that explains why the inelastic neutron scattering spectrum in SmB_6 contains an additional peak of longitudinal polarization with energy close to the energy of LA phonons.[9] Owing to the change in local symmetry of the exciton-phonon interaction from fully symmetric to dipole the resonance mode, in contrast to the breather mode Γ_1^{+}, the maximum interaction of which with the acoustic phonons occurs midway between the directions [110] and [111] (see Ref. 7), interacts mainly with phonons at the boundary of the Brillouin zone.

No such an extra neutron scattering peak with longitudinal polarization is observed in intermediate-valence systems with NaCl-type crystal lattices. The reason is the strong damping of the coherent vibron occurring in these systems and leading to strong broadening, absent in samarium hexaboride, of longitudinal phonon branches.

Detailed analysis of the matrix element of inelastic neutron scattering corresponding to this transition explains also the dependence of the relative intensity of this additional peak on the wave vector. We consider here the reasons for the unusually strong temperature dependence of the position and intensity of the additional peaks in the neutron spectra.

7. TEMPERATURE DEPENDENCE OF THE RESONANCE VIBRATIONAL MODES OF SmB_6

Strong temperature dependence is typical of the vibrational spectra of SmB_6 and especially of the additional modes.[9] Thus the local resonance EPI mode with energy $\hbar\omega = 4.5$ THz is clearly seen at room temperature, but it virtually disappears at 1.8 K. At the same time the additional neutron-scattering peak associated with excitation of a coherent EPII vibron softens sharply with increasing temperature, from 3.8 THz at 1.8 K to ≈ 1.5 THz at 100 K, and the energy of this peak changes most rapidly at temperatures ranging from 0 to 40–60 K. The dispersion of the longitudinal acoustic phonons undergoes sharp changes in the same temperature range. The proposed theory can explain all of these features.

The existence of a local dispersion-free mode only at sufficiently high temperatures is explained by the fact that the formation of a defect of the force constants requires the presence of a real local exciton responsible for the appearance of this effect. Thus, a local mode exists only to the extent of temperature excitation of EPI states, and the intensity of the corresponding inelastic neutron scattering peak should drop continuously with no change in the excitation energy. It is this temperature dependence of the resonance mode that was recorded in samarium hexaboride.[9]

The temperature dependence of the energy of a coherent vibron is due to the sharp change in the electronic properties of SmB_6 heated to 40–60 K. In this temperature interval the free-carrier density increases sharply, as a result of which the semiconductor behavior of the conductivity and the Hall effect changes to a behavior characteristic of a quasimetal.[32] The appearance of free carriers results, in particular, in screening of the fully symmetric deformation potential, characterized by the constant δ (11). It can be concluded from the experimentally recorded decrease of the energy gap in SmB_6 under pressure that $\delta > 0$.[33] It is this sign of the parameter δ that ensures a positive energy difference between the coherent vibron state in the right-hand lower well and the ground state of the left-hand lower well (24). When the constant δ decreases the lower wells of the adiabatic potentials become symmetrized (Fig. 2) and, as a consequence, the energy of the coherent vibron decreases sharply precisely in the temperature range from 0 to 40–60 K.

8. CONCLUSIONS

We have thus shown that the additional modes in the vibrational spectrum of intermediate-valence semiconductors appear as a result of pseudo-Jahn–Teller instability of the electron-vibrational system with respect to the fully symmetric lattice mode associated with optical phonons. The instability-induced restructuring of the adiabatic potential results in a double-sheet configurational diagram for local vibrations near the intermediate-valence rare-earth ion. Vibronic states associated with the top sheet of this diagram are self-localized. They exist only at sufficiently high temperatures and can be regarded as local defects induced in the force constants in the vibrational system by local valence fluctuations. It is these states that are responsible for the "extra" dispersion-free modes, whose existence in the inelastic neutron scattering spectra of crystals of intermediate-valence semiconductors could not be explained theoretically for 15 years. The lower sheet of the configurational diagram is an asymmetric potential with two valleys, and the vibrations corresponding to these valleys are coherent. The exciton-polaron states corresponding to vibrations in the upper valley interact nonadiabatically with acoustic phonons in the valley corresponding to the ground state of the system, and this interaction in a semiconductor with a microgap is strongly temperature dependent owing to the fact that at temperatures comparable to the width of the bandgap the screening of charge fluctuations changes from semiconducting to metallic. The proposed picture explains completely the complicated pattern of "extra" states in the inelastic neutron-scattering spectra of samarium sulfide and hexaboride single crystals.

In conclusion we note that the existence of valence fluctuations with energies comparable to the Debye temperature results in another completely unusual (for the theory of lattice vibrations) consequence: These fluctuations interact differently with the low- and high-frequency branches of the spectrum, and as a result it is found that even in the adiabatic approximation the optical and acoustic vibrations are determined by different force constants. The fact that the phonon branches exhibit *different* degrees of nonadiabiticity with respect to valence fluctuations in the electronic subsystem makes the picture of phonon spectra even more nonstandard. Anomalies which occur in the phonon spectra and are connected with such a nontraditional exciton-phonon interaction must be studied separately.

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