Deformable shell description for the phonon spectra of semiconductors with unstable valency

K A Kikoin and A S Mishchenko

I V Kurchatov Institute of Atomic Energy, 123182 Moscow, USSR

Abstract. The theory of interaction between charge-density distortions (CDD) and phonons is proposed for insulating crystals with soft intra-atomic modes. A general classification of the possible types of phonon renormalisation is given for cubic crystals with NaCl and CsCl structures. A novel excitonic mechanism of CDD is offered and additional dispersion of the phonon renormalisation due to non-locality of such excitons is discussed in comparison with the standard theory of CDD. The theory is applied to the special case of rare-earth semiconductors with unstable valency. In these systems the sources of such CDD modes are the dipole excitations of the f shells and the very soft monopole excitons corresponding to valency fluctuations. The theory is compared with the experimental phonon spectra of SmS.

1. Introduction

Two approaches coexist in the contemporary theory of electron–phonon renormalisation of the phonon spectra in metals and insulators. The first one, phenomenological *par excellence*, adds to the rigid-ion dynamical matrix of Born–von Karman–Kellerman the contributions due to the electronic density deformations accompanying adiabatically the ion motion and polarising the cores (see e.g. Allen 1977). Different versions of this phenomenological approach are known as the local charge-density deformation (CDD) model, deformable cluster model, etc. These models have been used to describe the phonon spectra in various metallic and insulating compounds, and the results of such calculations are listed, for example, in the book of Bilz and Kress (1979). On the other hand, the 'microscopic' methods based on the Fröhlich Hamiltonian for the electron–phonon interaction have been widely applied to a great variety of pure metals, metallic compounds and semiconductors (see e.g. Sinha 1977). These methods start from the band description of the electronic subsystem and consider the virtual intraband and interband transitions induced by lattice distortions as the main contribution to the electronic response function. Certainly, numerous attempts have been undertaken to use this microscopic description to substantiate the CDD approach (see e.g. Weber 1973). But the Fröhlich Hamiltonian by itself demands microscopic derivation because of the ambiguity in defining the 'adiabatic' phonons (Brovman and Kagan 1974); hence such substantiation seems to be rather dubious.

The starting point of this paper is the intention to include in the microscopic grounds of CDD theory not only the virtual excitations of the free electron–hole pairs but also the contribution of the virtual bound pairs, i.e. the excitonic states. Such extension of the

theory can introduce new features in the description of the electron–ion interaction in the case of local or intermediate-radius excitons, which can be naturally treated as the source of local charge deformations. The task seems to be particularly relevant for crystals containing transition-metal and rare-earth elements with unfilled d and f shells. There are at least three reasons for such expectations. First, the local character of the valence d(f)-electron wavefunctions imply in principle the predominantly local character of the interaction between the electron motion and lattice displacements. Secondly, the intra-atomic degrees of freedom of the cores with unfilled shells allow additional possibilities for generation of Frenkel-type excitonic states in a crystal that are absent in ordinary sp semiconductors and metals. Thirdly, the poorly overlapped d and f shells of those elements form narrow bands in a crystal; hence the validity of the adiabatic approximation for band motion becomes dubious in this limit. Thus one may expect that the excitations of the fast intrashell degrees of freedom will be the preferred way of adjusting the electronic subsystem to the lattice displacements. In this paper we focus mainly on the first two points.

2. General approach

The deformable shell model (DSM) is based first on the adiabatic approach to the electron–ion system, and secondly on the local description of the electronic degrees of freedom (Allen 1977). Introducing the localised basis for the electron charge deformation $\delta\rho(r)$,

$$\delta\rho(r) = \sum_\Gamma \rho_{\Gamma i}(l) f_{\Gamma i}(r - R_l) \tag{2.1}$$

where R_l is the lattice site coordinate and i stands for the Cartesian components of distortions obeying the point group symmetry representation Γ, this approach eliminates the electronic variables from the system of coupled equations for the atomic distortions u and charge deformation $\delta\rho$. As a result, the electronic contribution to the force matrix has the form

$$K_{ll'} = \left(0 \left| \frac{\partial H_{ei}(r, R)}{\partial R_l} \chi(r, r') \frac{\partial H_{ei}(r', R)}{\partial R_{l'}} \right| 0 \right) \tag{2.2}$$

where $(0|\ldots|0)$ means integration over electronic coordinates in the ground state of the electronic subsystem, $\chi(r, r')$ is the charge density response function, which generally has the form

$$\chi(r, r') = \sum_p \frac{|P)(P|}{E - E_p} \tag{2.3}$$

H_{ei} is the electron–ion interaction Hamiltonian admixing the excited states $|P)$ of the electron subsystem to the ground state $|0)$. Transitions $(0–P)$ describe consistently the dielectric response of the electronic subsystem to the lattice site displacements, provided we know exactly the set of excited states that describe the adiabatic adjustment of the electron density $\delta\rho(r)$ to those displacements.

Ensuring that the electron–hole pairs of free carrier excitations above the ground state of the occupied Fermi sphere

$$|k, q) = N^{-1} \sum_{jl} b^+_{j+l,a} b_{j,a'} |0) \exp[-iqR_j + i(k + q)R_l] \tag{2.4}$$

exhaust the set of relevant excited states of the electron subsystem (a is the band index), we come to the well known dielectric formalism (Sham and Ziman 1963), and the main difficulty we meet is the problem of calculating the band structure and inverting the dielectric function of the crystal (Sinha 1969). However, the intra- and interband electronic transitions are not the only excitations that can contribute to the dielectric function. There are at least two extra contributions to the electronic response, i.e. collective excitations (excitons, plasmons, . . .) and intershell atomic transitions describing the deformation of atomic cores of the lattice ions, which can be inserted in the P sum in (2.3). To be more exact, the latter branch can also be treated as coherent Frenkel-type excitations, and the bound electron–hole pairs can be included into the set $\{P\}$, being written in the Wannier–Mott representation

$$|B_q\rangle = N^{-1/2} \sum_{jl} F(l) b^+_{j+l,a} b_{j,a'} \exp(i q \cdot R_l) \tag{2.5}$$

where a, a' stand for the empty conduction and occupied valence states of non-metallic crystal, for which the excitonic language is adequate, $F(l)$ is the envelope function, which characterises the radius of the exciton, and can be small ($l = 0$, Frenkel-type), large ($l \gg a$, Mott-type) or intermediate ($l = 0$, NN, NNN).

Our aim is to give the microscopic definition of the 'entities' (Allen 1977) whose motion is responsible for the charge-density distortions, to understand some general properties of the deformable shell model and to exploit this understanding in a special case of the rare-earth semiconductors with unstable f shells. For this sake we begin with the general investigation of the electronic contribution to the lattice dynamics of a two-sublattice crystal. We consider the equations of motion for the lattice displacements (polarisation vectors) and propose the procedure of separating the contribution of the rigid ion (RI) part of the dynamical matrix from the CDD contribution to the dispersion curves of the acoustic and optic phonons in high-symmetry directions of the Brillouin zone in NaCl and CsCl lattices.

Hence we introduce the dynamical matrix $D(q)$ in the form

$$\hat{D}(q) = \hat{D}^{(RI)}(q) + \hat{D}^{(CDD)}(q) \tag{2.6}$$

where $\hat{D}^{(RI)}(q)$ is the Kellerman-type dynamical matrix for the purely ionic crystal and $\hat{D}^{(CDD)}(q)$ is the adiabatic electronic contribution, which is obtained by Fourier transforming the force matrix (2.2),

$$M\omega^2_{q\alpha} u_q = D^{(RI)}(q) u_q + \sum_\Gamma D^{(\Gamma)}(q) u_q \tag{2.7}$$

where the expansion

$$D^{(CDD)}(q) = \sum_\Gamma D^{(\Gamma)}(q)$$

reflects the possibility of classifying CDD by the irreducible representations of the crystal point group (2.1). Generally speaking, the expression (2.1) also results in non-diagonal contributions $D^{(\Gamma\Gamma')}$ to the dynamical matrix, but these non-diagonal elements are small as a rule (see e.g. Allen 1977) and are often symmetry-forbidden (e.g. in the case of excitonic contributions), so we will omit these terms for the sake of simplicity. The diagonal CDD–CDD intersite self-energy $\Phi^{(\Gamma\Gamma)}(q)$ is neglected, and its influence is discussed in section 3.

Each CDD contribution to the frequency renormalisation can be factorised as

$$\Delta^{(\Gamma)}\omega^2_{q\alpha} = \lambda^{(\Gamma)}_\alpha \Phi^{(\Gamma)}(\boldsymbol{q}, \omega_{q\alpha}) \tag{2.8}$$

where the net $\boldsymbol{q}$ dependence entering the form factor $\Phi^{(\Gamma)}(\boldsymbol{q}, \omega_{q\alpha})$ is determined by the lattice and CDD symmetry, by the spatial extent of the electronic states and by the dispersion of the electron excitation spectra. Here λ is the coupling strength parameters characterising the physical mechanism switching on the contribution of the CDD of given symmetry Γ. Factorisation (2.8) allows one to analyse the dispersion of lowest-order CDD contribution to the renormalisation of a given phonon branch in a crystal of a given structure before considering its microscopic nature and irrespective of its strength. The factor $\Phi^{(\Gamma)}(\boldsymbol{q}, \omega_{q\alpha})$ can in turn be factorised in many cases

$$\Phi^{(\Gamma)}(\boldsymbol{q}, \omega_{q\alpha}) = \Phi^{(\Gamma)}_0(\boldsymbol{q}, \omega_{q\alpha})\Phi^{(\Gamma)}_1(\boldsymbol{q}, \omega_{q\alpha}) \tag{2.9}$$

thus separating the standard contribution $\Phi^{(\Gamma)}_0(\boldsymbol{q}, \omega_{q\alpha})$ of the localised CDD model (see e.g. Allen 1977, Miura *et al* 1984) from all other contributions $\Phi^{(\Gamma)}_1(\boldsymbol{q}, \omega_{q\alpha})$ to the dispersion of phonon renormalisation.

Moreover the inverse problem of restoring the symmetry of essential CDD, which dominates in the electronic contribution to the phonon spectrum from the experimentally measured phonon dispersion, can also be formulated and solved in some cases. To make the problem solvable we begin with an analytical consideration of the system (2.7) for the NaCl lattice in the high-symmetry direction with

$$\hat{M} = \begin{pmatrix} M_1 & \\ & M_2 \end{pmatrix} \qquad \hat{D} = \begin{pmatrix} D_1 & D \\ D & D_2 \end{pmatrix} \qquad \hat{D}^{(\Gamma)} = \begin{pmatrix} D^{(\Gamma)}_1 & D^{(\Gamma)} \\ D^{(\Gamma)} & D^{(\Gamma)}_2 \end{pmatrix} \tag{2.10}$$

for the matrices entering the system (2.7), where indices 1 and 2 stand for the cationic and anionic sublattices, respectively.

Starting from the standard Kellerman-type rigid ion description of the phonon spectrum, we are interested in calculating the frequency renormalisation $\Delta\omega^2_{q\alpha}$ due to the CDD contribution (α is the branch index). The first-order frequency shift is given by

$$\Delta\omega^2_{q\alpha} = \sum_\Gamma \left(\frac{\partial\omega^2_{q\alpha,0}}{\partial D^{(\Gamma)}_1} D^{(\Gamma)}_1(\boldsymbol{q}) + \frac{\partial\omega^2_{q\alpha,0}}{\partial D^{(\Gamma)}_2} D^{(\Gamma)}_2(\boldsymbol{q}) + \frac{\partial\omega^2_{q\alpha,0}}{\partial D^{(\Gamma)}} D^{(\Gamma)}(\boldsymbol{q}) \right) \tag{2.11}$$

where $\omega_{q\alpha,0}$ are the phonon frequencies in an RI model, for which one has the analytical expression for the high-symmetry directions [100], [110] and [111] (Woods *et al* 1960):

$$\omega^2_{q\alpha,0} = \tfrac{1}{2}[\omega^2_+ \pm (\omega^4_- + 4|D|^2/M_1M_2)^{1/2}] \tag{2.12}$$

where

$$\omega^2_\pm = |(D_1/M_1) \pm (D_2/M_2)|. \tag{2.13}$$

For the contributions of the CDD of different sublattices to the renormalisation (2.11) in the high-symmetry directions simple calculations give the following equation:

$$\Delta\omega^2_{q\alpha} = \frac{1}{2\omega^2_{q\alpha,0} - \omega^2_+} \sum_\Gamma \left(\frac{D^{(\Gamma)}_1}{M_1} \{\omega^2_{q\alpha,0} - \tfrac{1}{2}[\omega^2_+ + \mathrm{sgn}(M_1 - M_2)\omega^2_-]\} \right.$$

$$\left. + \frac{D^{(\Gamma)}_2}{M_2} \{\omega^2_{q\alpha,0} - \tfrac{1}{2}[\omega^2_+ + \mathrm{sgn}(M_2 - M_1)\omega^2_-]\} + \frac{2DD^{(\Gamma)}}{M_1M_2} \right). \tag{2.14}$$

In the nearest-neighbour approximation for the RI dynamical matrix

$$\tfrac{1}{2}(\omega_+^2 \pm \omega_-^2) = \omega_{q=L,\alpha=LO,LA}^2 \tag{2.15}$$

Now we turn to the analysis of the formfactors (2.8) for the different symmetries of CDD modes. Such analysis can be carried out independently of the model chosen for calculating the RI phonon spectra.

To demonstrate the method of extracting the deformable shell contribution, we begin by calculating the standard formfactor $\Phi_0^{(\Gamma)}(q, \omega_{q\alpha})$ of the localised CDD model (Allen 1977) and restrict ourselves to the interaction of the polarisable ion shell with ions of other sublattice in the NN approximation. In this approximation the shell deformation in a given sublattice induces the effective interaction between the ions of another sublattice and hence contributes only to the diagonal matrix elements $D_i^{(\Gamma)}$ ($i = 1, 2$) of this second sublattice (except $\Gamma = \Gamma_{15}^-$). The dipole CDD mode will be considered separately, and now we turn to the even modes, the only possible ones of which in the NN approximation are Γ_1^+, Γ_{12}^+, Γ_{15}^+ and Γ_{25}^+.

The standard procedure for calculating the matrix elements of $D^{(\Gamma)}$ (see e.g. Allen 1977) gives the following compact representation for the contribution of CDD on the sublattice 1 to the frequency renormalisation:

$$\Delta\omega_{q\alpha,1}^2[\xi_1\xi_2\xi_3] = -A_{\alpha M_1}\sin^t\left(\frac{q}{p}\right)\sum_\Gamma F_1^{(\Gamma)}n_\alpha^{(\Gamma)}[\xi_1\xi_2\xi_3] \tag{2.16}$$

with

$$A_{\alpha M_1}(q) = \frac{1}{M_2}\frac{\omega_{q\alpha,0}^2 - \tfrac{1}{2}[\omega_+^2 + \mathrm{sgn}(M_1 - M_2)\omega_-^2]}{2\omega_{q\alpha,0}^2 - \omega_+^2}$$

$$F_1^{(\Gamma)} = \frac{4C^{2(\Gamma)}}{k^{(\Gamma)} + 2C^{(\Gamma)}}. \tag{2.17}$$

Here $0 < q < \pi$, for [100] and [110] directions, $0 < q < \pi/2$ for [111] direction; $p = 1$, $t = 2$; factors $n_\alpha^{(\Gamma)}[\xi_1\xi_2\xi_3]$ are listed in table 1(a); the constant $F_1^{(\Gamma)}$ is combined from the parameters of shell–shell overlap ($C^{(\Gamma)}$) and core–shell spring ($k^{(\Gamma)}$) forces. Equation (2.16) is consistent with table 1 for the dynamical matrix in the article of Fischer *et al* (1972)†. Our renormalisation can be obtained using the matrix elements $D_{xx}^{(\Gamma)}$ and $D_{xy}^{(\Gamma)}$ listed in that table after reducing these elements to the symmetry directions of the cubic lattice (see e.g. table 1 in Woods *et al* 1960).

Hence the procedure of selecting the symmetry-dependent factors $\Phi_0^{(\Gamma)}(q, \omega_{q\alpha})$ in the cases of Δ, Σ and Λ directions of the Brillouin zone gives the simple form of standard dispersion of renormalisation (2.9):

$$\lambda_\alpha^{(\Gamma)} = F_1^{(\Gamma)} \qquad \Phi_0^{(\Gamma)}(q, \omega_{q\alpha}) = A_{\alpha M_1}(q)n_\alpha^{(\Gamma)}[\xi_1\xi_2\xi_3]\sin^t(q/p). \tag{2.18}$$

Owing to the absence of the last term in (2.14) for the even modes (see above), all possible types of CDD softening can be simply classified in accordance with figure 1 and table 1(b).

Now turning to the odd modes we consider first the Γ_{25}^- deformation. The same procedure results in the phonon renormalisation given by equation (2.16) with $p = 2$,

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† One should note a misprint in table 1 of Fischer *et al* (1972): the matrix element $D_{xx}^\Gamma(kk|q)$ for $\Gamma = \Gamma_{25}^-$ has the form $(\cos q_y - \cos q_z)^2$.

Table 1. Even modes.

(*a*) Factors $n_\alpha^{(\Gamma)}[\xi_1, \xi_2, \xi_3]$ entering equations (2.16) and (2.18) for even CDD modes.

Direction		[100]		[110]			[111]	
Polarisation[a]		L	T	L	T_1	T_2	L	T
Longitudinal	Γ_1^+	1	0	2	0	0	3	0
coupling	Γ_{12}^+	2	0	1	0	3	0	3
Transverse	Γ_{15}^+	0	1	0	2	2	0	3
coupling	Γ_{25}^+	0	1	2	2	0	4	3

(*b*) Types of formfactors for phonon renormalisations due to CDD distortions of the heavy and light ions in the NaCl structure (see figure 1).

Direction	[100], [110]		[111]	
Branch	Acoustic	Optic	Acoustic	Optic
Heavy	3 (2)	2	2	1
Light	2	3 (2)	1	2

[a]Polarisations: T_1, $q \| [001]$, $q \perp$ to $[100]$ plane; T_2, $q \| [1\bar{1}0]$, $q \|$ to $[100]$ plane.
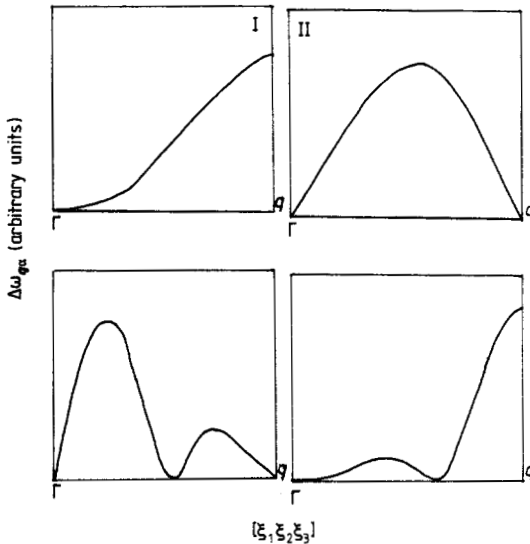

Figure 1. Types of phonon frequency renormalisation in crystals with NaCl structure, $\Delta^{(\Gamma)}\omega_{q\alpha} \simeq \Phi_0^{(\Gamma)}/2\omega_{q\alpha}^0$ (see equations (2.16) and (2.17)).
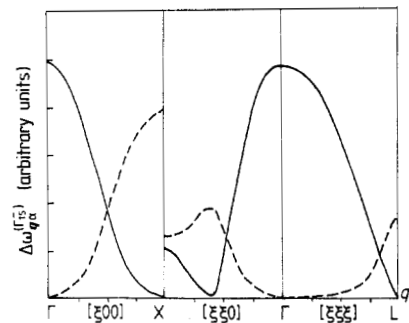

Figure 2. Typical dipolar renormalisation of phonon branches in the NaCl structure (see equation (2.19)) for polarisable heavy ions. Full (broken) curves stand for optic (acoustic) branches.

Table 2. Odd modes. (See notations to table 1.)

(a)

Direction	[100]		[110]			[111]	
Polarisation	L	T	L	T$_1$	T$_2$	L	T
Γ_{25}^{-}	0	4	4	0	4	0	0

(b)

Direction	[100], [110]		[111]	
Branch	Acoustic	Optic	Acoustic	Optic
Heavy	4 (1)	1	Absent	Absent
Light	1	4 (1)	Absent	Absent

$t = 4$. The types of formfactors and the meanings of $n_\alpha^{(\Gamma)}[\xi_1\xi_2\xi_3]$ are listed in table 2 and figure 1.

Zeros of types 3 and 4 arise at such wavevectors for which the nearest neighbours of the polarisable ion in the given branch are at rest (see below (2.20)). This is the case of the points in the Brillouin zone where intersublattice RI matrix elements of $D(q)$ are zero. Such situations are found for L[ξ00], L[$\xi\xi$0] and T$_2$[$\xi\xi$0] branches, but as a rule $D(q) \neq 0$ for all q for T[ξ00] and T$_1$[$\xi\xi$0] branches. In these cases zeros vanish and types 3 and 4 transform to types 2 and 1 respectively (the types for the latter case in table 1 are given in parentheses).

The last mode is the dipole deformation Γ_{15}^{-}, which was considered in the original shell model (see e.g. Woods *et al* 1960) and in the first attempts to interconnect the dielectric formalism and the local description of CDD (Sinha 1969). In the absence of long-range Coulomb forces, dipolar contribution to the phonon renormalisation is given by the equation

$$\Delta^{\Gamma_{15}}\omega_{q\alpha,1}^2 = -\frac{1}{\omega_{q\alpha,0}^2 - \omega_+^2/2}\frac{1}{2}\left[\frac{1}{M_1}\left(\frac{S^2}{k_2 + S_0} + \frac{S_0^2}{k_1 + S_0}\right)\right.$$

$$\times\left(\omega_{q\alpha,0}^2 - \frac{\omega_+^2 - \mathrm{sgn}(M_2 - M_1)\omega_-^2}{2}\right)$$

$$+\frac{1}{M_2}\left(\frac{S^2}{k_1 + S_0} + \frac{S_0^2}{k_2 + S_0}\right)\left(\omega_{q\alpha,0}^2 - \frac{\omega_+^2 + \mathrm{sgn}(M_2 - M_1)\omega_-^2}{2}\right)$$

$$\left.+\frac{4}{M_1M_2}D(q)SS_0\left(\frac{1}{k_1 + S_0} + \frac{1}{k_2 + S_0}\right)\right] \tag{2.19}$$

where S_0 and $S(q)$ are the usual diagonal and intersublattice overlap matrices, which are similar to the corresponding ones of the NN rigid ion model (see e.g. Woods *et al* 1960). Figure 2 represents the phonon renormalisations $\Delta\omega_{q\alpha}$ in this case.

A similar procedure can be realised for the CsCl structure. Here we present the phonon renormalisation $\Delta\omega_{q\alpha}$ described by the formfactor $\Phi_0^{\Gamma}(q, \omega_{q\alpha})$ calculated by means of equation (2.14) for the two most important cases of monopole and dipole CDD modes (figure 3).
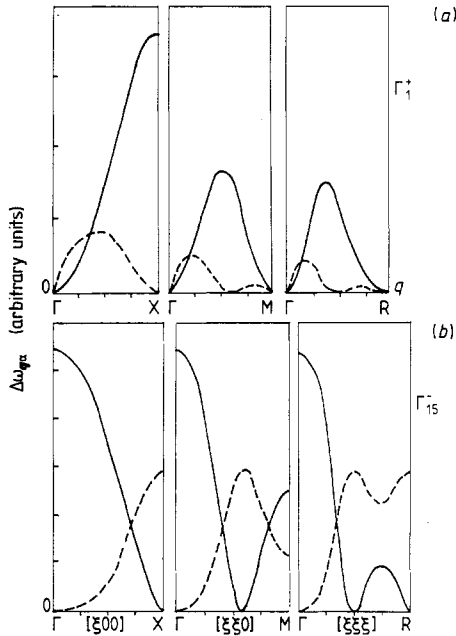
Figure 3. Typical frequency renormalisation for the CsCl structure in the case of polarisable heavy ions. Full (broken) curves stand for optic (acoustic) branches. (*a*) Γ_1^+ mode; (*b*) Γ_{15}^- mode.

It is worth noting that the analytical expressions (2.14), (2.17) and (2.19), which are equivalent to the second-order perturbation theory for the CDD contribution to the phonon frequency shift (see below), are valid only for small enough CDD renormalisation, but the specific form of the formfactor is defined mainly by symmetry considerations; thus the characteristic dispersion of this renormalisation (figures 1–3) remains the same as in the exact solution of the system of dynamical equations (2.7).

At the end of this section we present the analytical expression for the relative displacement of the ions in both sublattices of a diatomic crystal for the high-symmetry directions via the same quantities $A_{\alpha M_i}(q)$ that enter the equation (2.16) for the phonon shift. The routine procedure of solving the system of two linear equations gives for u_q

$$u_{q\alpha} = \begin{pmatrix} u_{1\alpha}(q) \\ u_{2\alpha}(q) \end{pmatrix} = \begin{bmatrix} [A_{\alpha M_2}(q)]^{1/2} \\ [A_{\alpha M_1}(q)]^{1/2}(-1)^s \, \mathrm{sgn}[D(q)] \end{bmatrix} \tag{2.20}$$

where $s = 1$ (2) for acoustic (optic) branches.

Substituting these u_q into the standard formula for the electron–phonon coupling constant, and calculating the second-order contribution to the phonon frequency, we obtain the above equation (2.16) for $\Delta\omega_{q\alpha}^2$ when neglecting all contributions to the phonon dispersion beyond the RI and point CDD approximation, which are accumulated in factor $\Phi_1^{(\Gamma)}(q, \omega_{q\alpha})$ in equation (2.9).

Thus we see that the phenomenological model of CDD specifying only the symmetry of this distortion is capable of describing the characteristic features of the electronic contribution to the phonon renormalisation *without* appealing to the microscopic nature of CDD excitations. For example, the calculations of Ichinose and Tamura (1983) for mixed-valent TmSe and of Matsuura *et al* (1980) for mixed-valent $Sm_{1-x}Y_xS$, starting

with 'microscopic' considerations of band contribution to the self-energy part of the phonon Green function, end with the simplest expressions for the electron–phonon coupling constant in which we recognise the RI and point CDD phenomenological contribution for the breathing mode Γ_1 (2.16).

Now we turn to considering the more refined details of CDD contributions, which in principle cannot be described in the framework of the general approach and demand microscopic analysis of the elementary excitations in specific systems.

3. Electronic and excitonic contributions to CDD mode in narrow-gap semiconductors

One of the most advanced attempts to understand the microscopic grounds of the CDD approach was undertaken by Weber, who introduced the 'double-shell model' to describe the phonon softening in transition-metal carbides (Weber 1973). He realised and utilised the ambivalent nature of d electrons: these electrons quit the core region in the condensed state, but remain localised enough, and their interaction with the lattice vibrations can be treated in terms of local charge redistribution in real space. He introduced the loosely bound outer shell at the transition–metal site and considered its additional contribution to the ion–ion interaction. This interaction has the features of the resonance 'screening' of RI interaction and compensates the latter for a definite region of the Brillouin zone. In fact the specific electron contribution to the phonon renormalisation in the double-shell model is determined by the singularities of the density response function (2.3). This model in turn parametrises the singular behaviour of the band contribution to the self-energy part of the phonon Green function (Varma and Weber 1979).

Another attempt at microscopic substantiation of the CDD model was undertaken by Wakabayashi (1977). In his 'charge-fluctuation model' CDD are treated as the charge transfer induced by the lattice distortions in the spirit of the general CDD model of Allen (1977) with the Γ_1^+ contribution only. The comparative success of the description of the phonon anomalies by the general Allen model (e.g. Wakabayashi 1980, Miura *et al* 1984) lies in the strong q dependence of the intersite CDD–CDD self-energy matrix $\Phi^{(\Gamma\Gamma)}(q)$, i.e. again in the singularities of the density response function (2.3).

We intend to propose another type of microscopic formulation of the CDD picture, taking into account the specific features of rare-earth (RE) compounds with unstable f shell. In this case the peculiarities of the electron contribution to the dynamical matrix are determined by the numerator of force matrix (2.2) and the electronic states in the response function (2.3) are soft enough intermediate-range excitons. The band contribution for the RE compounds will also be briefly discussed.

The excitonic contribution to the phonon renormalisation can be obtained by means of standard procedure of Fourier transforming the force matrix (2.2) where charge-density response function is determined by the excitonic states $|P) = |B_q)$ (equation 2.5):

$$D^{(\text{CDD})}(q) = N^{-1} \sum_{mn} \sum_{\Gamma} \exp[iq(R_n - R_m)]$$

$$\times \frac{(0|\nabla_r H_{\text{ei}}(r - R_m)|B_q^\Gamma)(B_q^\Gamma|\nabla_r H_{\text{ei}}(r - R_n)|0)}{E_{\text{ex}}(q)}. \tag{3.1}$$

Then the second-order contribution to the energy shift of the phonon branch α is given by

$$\delta^{\text{ex}}(\hbar\omega_{q\alpha})^2 = -2h^2 \sum_{\Gamma} \left| \sum_{m} Q^{\Gamma}_{q\alpha}(R_m)F(R_m) \right|^2 \frac{E_{\text{ex}}(q)}{E^2_{\text{ex}}(q) - (\hbar\omega_{q\alpha})^2} \qquad (3.2)$$

with

$$Q^{\Gamma}_{q\alpha}(R_m) = \int d^3r\, \varphi^*_v(r)P^{\Gamma}_{q\alpha}(r)\varphi_c(r - R_m) \qquad (3.3)$$

$$P^{\Gamma}_{q\alpha}(r) = \sum_{st} M^{-1/2}_t \exp(iqR_s)e^t_{q\alpha}\nabla^{\Gamma}_r V(r - R_{st}) \qquad R_{st} = R_s + \rho_t. \qquad (3.4)$$

Here the symbol ∇^{Γ}_r stands for the projected gradient operator representing the distortion of the crystal potential with the given point symmetry Γ. This contribution reduces to the usual local CDD expression (2.16) only in the case of Frenkel exciton with envelope function $F(R_m) = \delta_{R_m,0}$. In such a situation the symmetry of the vibrational mode is in one-to-one correspondence with the symmetry of local exciton Γ_{ex}: for a non-degenerate ground state of the electronic subsystem $\Gamma = \Gamma_{\text{ex}}$. Hence the breathing mode, which is very popular in current theories of electron–phonon interaction, can be obtained only when the local monopole excitations of the valence electrons are soft enough. As a rule the intrasite Frenkel excitons in semiconductors and insulators are of multipole character; hence the local CDD contribution of this type can be expected as a rule only to the dipole, quadrupole and other low-symmetry distortions of tables 1 and 2.

The intermediate-radius excitons provide more diverse possibilities of charge distortions because of the composite structure of excitonic wavefunction (2.5). In particular, one may always construct a fully symmetric combination of Wannier functions in the conduction band obeying the condition

$$\Gamma_0 \subset \gamma_v \otimes \gamma_c \qquad (3.5)$$

where the valence state transforms along the irreducible representation γ_v of the point group, the combination $\Sigma_l F(l)\psi_{j+l,c}(r)$ of the Wannier function in the conduction band obeys the representation γ_c, and their direct product contains the unit representation Γ_0 of vibrational mode. But the non-local nature of the excitation (2.5) generates the formfactor $\Phi^{(\Gamma)}_1(q, \omega_{q\alpha})$ (cf (2.9)), which is absent in the conventional CDD theory.

Now we turn to calculating this formfactor in the simplest LCAO approximation for a two-band semiconductor. Here we take the 'prime' valence and conduction electron wavefunctions constructed from the atomic orbitals with given l, which transform along the given representation γ of the crystal point group, and introduce the interband mixing integral in nearest-neighbour (NN) approximation

$$V_{lt,l't'}(m) = \int d^3r\, \psi^*_{lt}(r - R_j)V(r)\psi_{l't'}(r - R_{j+m}) = V\chi(m) \qquad l \neq l'. \qquad (3.6)$$

Here $V_{lt,l't}(0) = 0$. Then the regular linear combination of these orbitals describing the valence and conduction states can be written in the lowest order in V as

$$\varphi_v(r - R_0) = A\psi_{lt}(r - R_0) \mp G_0 V \sum_{m} \chi^*(m)\psi_{l't'}(r - R_0 - R_m) \qquad (3.7a)$$

$$\varphi_c(r - R_0) = A\psi_{l't'}(r - R_0) - G_0 V \sum_{m} \chi(m)\psi_{lt}(r - R_0 - R_m). \qquad (3.7b)$$

Here G_0 is the well known diagonal lattice Green function

$$G_0 = N^{-1} \sum_k (\varepsilon_{lk} - \varepsilon_{l'k})^{-1} \tag{3.8}$$

and ε_{lk} are the initial energy bands; A is the normalising factor defined by the equation

$$A^2 + Z(VG_0)^2 = 1 \tag{3.9}$$

where Z is the number of the nearest neighbours. In (3.7) subindex t numbers the sublattices to which the orbitals l and l' belong, and $\chi(m)$ are the projection operators selecting the linear combinations of NN atomic orbitals $\psi_{l't'}$ of the 'alien' band obeying the given irreducible representation γ for the Γ point of the host band,

$$|\chi(m)| = 1 \qquad \chi(-m) = \mp \chi(m). \tag{3.10}$$

In lattices with an inversion centre the upper sign $(-)$ in equations (3.7a) and (3.10) corresponds to the different parity of conduction and valence bands, and the lower sign $(+)$ should be chosen for the bands with the same parity.

Now returning to equation (3.3) we retain only the strongest one-centre integrals in the matrix element $Q_{q\alpha}^\Gamma$,

$$I_{q\alpha}^{t\Gamma}(l, l') = \int d^3r \, \psi_{lt}^*(r) P_{q\alpha}^\Gamma(r) \psi_{l't}(r) \tag{3.11}$$

including the 'prime' atomic orbitals on the same site only.

First we consider the exciton with fully symmetrical envelope function $F(l)$ in (2.5), which has non-zero component in the central cell $F(0)$. In this case the main term in (3.2) proportional to $Q_{q\alpha}^\Gamma(0)$ inevitably contains integrals $I_{q\alpha}^{t\Gamma}(l, l + \Delta l)$ non-diagonal in ll', and the selection rules for the integral (3.11) allow only the CDD with Γ defined by the restriction

$$\Gamma \subset \gamma \otimes \gamma'. \tag{3.12}$$

For example the dipole CDD Γ_{15}^- is allowed for the exciton with fully symmetrical envelope function in sp semiconductors ($\gamma = \Gamma_{15}^-$, $\gamma' = \Gamma_1^+$). In the pd semiconductor (e.g. $\gamma = \Gamma_{15}^-$, $\gamma' = \Gamma_{25}^+$) four CDD modes are allowed, $\Gamma = \Gamma_2^-$, Γ_{12}^-, Γ_{15}^- and Γ_{25}^-, and so on. Neglecting the two-centre integrals in (3.2) one obtains

$$\Phi^\Gamma(q) = -\left(2h^2 F^2(0)/E_{ex}(q)\right) [A^2 I_{q\alpha}^{t\Gamma}(l, l') + (VG_0)^2 I_{q\alpha}^{t'\Gamma}(l, l') S(q)]^2 \tag{3.13}$$

where

$$S(q) = \sum_m^{(NN)} \cos(q \cdot R_m) $$

R_m are the positions of the sites with which hybridisation in (3.7) takes place.

The most interesting is the case of the exciton with angle-dependent envelope function, which has a node on the central site, $F(0) = 0$. Again, retaining only the one-centre integrals $I_{q\alpha}^{t\Gamma}$ (3.11) in $Q_{q\alpha}^\Gamma(R_m = 0)$, we find that this matrix element inevitably contains the diagonal terms $I_{q\alpha}^{t\Gamma}(l, l)$ and $I_{q\alpha}^{t\Gamma}(l', l')$. Hence in a two-band semiconductor the breathing mode according to the selection rule (3.12) is essentially non-local. Direct

calculations of $\Delta\omega_{q\alpha}^2$ gives in this case the expression

$$\Phi^{\Gamma_1^+}(q) = -\frac{2h^2}{E_{ex}(q)}(AVG_0F_1)^2 \left| \sum_m^{(NN)} \chi_{ex}(R_m)[\chi(-R_m)I_{q\alpha}^{t\Gamma_1^+}(l,l) \right.$$

$$\left. \mp \exp(iqR_m)\chi(R_m)I_{q\alpha}^{t\Gamma_1^+}(l',l')] \right|^2. \tag{3.14}$$

Here we introduce $F(m) = F_1\chi_{ex}(R_m)$ where $\chi_{ex}(R_m)$ are the phase factors defining the point symmetry of the envelope function similarly to the Wannier function (3.7); the $\mp$ sign is to be chosen for the valence and conduction states with the same and opposite parity, respectively. In a sense, the exciton contributing the breathing mode can be qualified as a fully symmetric excitation, because the final state of the electronic sub-system has the same symmetry as the ground state of the filled valence band. In this case $\chi_{ex}(R_m)$ and $\chi(R_m)$ have the same transformation properties and all phase factors cancel each other.

In the case of $t = t'$ and in simplifying approximation $I_{q\alpha}^{t\Gamma}(l,l) = I_{q\alpha}^{t\Gamma}(l',l')$ (which holds precisely for the highly localised normalised 'prime' orbitals), equations (3.13) and (3.14) can be reduced to the product (2.9). Thus we obtain for the mode obeying (3.12) the following formfactors

$$\Phi_0^{\Gamma}(q) = -2h^2 |I_{q\alpha}^{t\Gamma}(l,l')|^2 \tag{3.15a}$$

$$\Phi_1^{\Gamma}(q) = (F^2(0)/E_{ex}(q)) |A^2 + (VG_0)^2S(q)|^2 \tag{3.15b}$$

and for the Γ_1^+ mode

$$\Phi_0^{\Gamma_1^+}(q) = -2h^2 |I_{q\alpha}^{t\Gamma_1^+}(l,l)|^2 \tag{3.16a}$$

$$\Phi_1^{\Gamma_1^+}(q) = (F_1^2/E_{ex}(q))(AVG_0)^2 |Z - S(q)|^2. \tag{3.16b}$$

In the case of (3.15b) the additional dispersion introduced by $\Phi_1^{\Gamma}(q)$ only slightly changes the usual CDD renormalisation but for the Γ_1^+ mode dispersion of additional formfactor is essential (see also the next section).

4. Phonon renormalisation in RE semiconductors with stable and unstable valency

In this section we apply the general principles of the theory to the specific case of rare-earth (RE) semiconductors in which the CDD modes are induced by the excitations in the f shells of RE ions. We study the sequence of RE chalcogenides EuS—'black' SmS—'gold' SmS, which are akin in their lattice symmetry, ion masses and may be distinguished only by the lattice constants and the electronic properties. EuS is the conventional RE semiconductor with extremely narrow valence f band, wide f–d energy gap ($\Delta \simeq 1.12$ eV) and stable valency. 'Black' $SmS_{(B)}$ is also a conventional semiconductor, but with small enough f–d gap ($\Delta \simeq 0.23$ eV). Finally, 'gold' $SmS_{(G)}$ is a mixed-valence (MV) semi-conductor with extremely narrow gap (or pseudo-gap) ($\Delta \simeq 7$ meV) and anomalous electronic properties (see Kikoin 1983 and references therein).

These semiconductors demonstrate remarkable distinctions in their phonon spectra, particularly in [$\xi\xi\xi$] direction (see figure 4(b)): $SmS_{(B)}$ in comparison with EuS has a softened LO branch, and $SmS_{(G)}$ has a profound anomaly in LA branch and LO phonons, which are softer than TO phonons in the whole Brillouin zone (Mook et al 1982, Bilz et al 1979), an unusual situation for dielectrics with NaCl structure. Besides, in 'gold

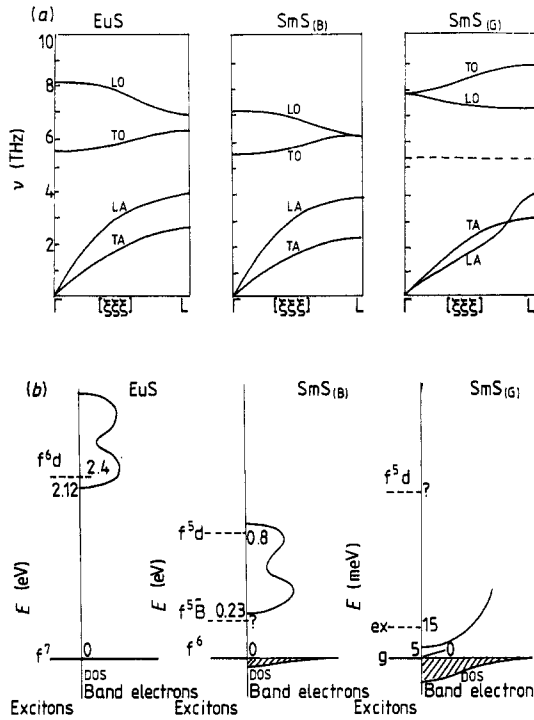**Figure 4.** (a) Phonon and (b) electronic excitations in EuS, $SmS_{(B)}$ and $SmS_{(G)}$.

$Sm_{0.75}Y_{0.25}$ S' the dispersionless resonance mode was discovered (Mook *et al* 1978), which is apparently connected with the MV in this system (Stuber *et al* 1982).

All these special features of phonon spectra can be explained by involving the distinctions in the structure of f-shell excitation spectra in the three compounds (figure 4(a)). 'Standard' EuS possesses only the conventional dipole fd excitations, which are hard enough ($\hbar\omega = 2.4$ eV; Guntherodt 1974). The same mode in $SmS_{(B)}$ is essentially softer ($\hbar\omega = 0.8$ eV; Guntherodt *et al* 1983). These excitations from the point of view of our theory are responsible for the dipole CDD mode, and one may search for the corresponding phonon softening in $SmS_{(B)}$ in comparison with EuS. On can also find the mechanism of forming the monopole exciton, which should be responsible for the 'breathing' CDD mode. According to the general theory this exciton ought to obey the selection rule (3.5) where $\Gamma = \Gamma_1^+$. But in the case of f ions the strong intrashell interaction forces one ought to formulate this selection rule in terms of irreducible representations of the atomic f shells as a whole rather than by using the one-electron valence and conduction states. The ground state of Sm^{2+} (f^6) in SmS transforms along the $^7F_0$ (Γ_1^+) representation. To form the excited states $f^5\tilde{B}^\gamma$ with $\tilde{B}^\gamma$ (2.5) having $F(0) = 0$ along the lines of the previous section, one must combine the lowest term $^6H_{5/2}$ (Γ_7^-) of the state f^5 with the linear combination (2.5) of t_{2g} adjacent orbitals in cation sublattice transforming along the same γ_7^- representation. Such combinations can always be found (Stevens 1976).

Monopole excitons were not detected in the optical spectra of $SmS_{(B)}$ because the corresponding transition is forbidden by the Laporte rule, but these excitons play the key role in explaining the phase transformation $SmS_{(B)}$–$SmS_{(G)}$ (Stevens 1976, Kikoin 1983, 1984). This transformation does not change the symmetry of the ground state, and
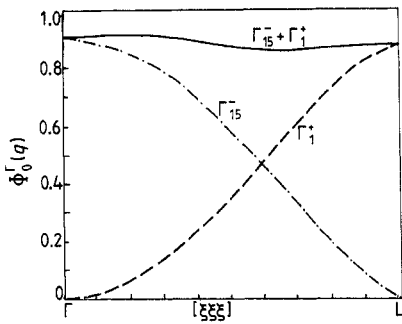
Figure 5. Optic phonon renormalisation in the ΓL direction for CDD modes Γ_1^+ (broken curve), Γ_{15}^- (chain curve) and their sum (full curve).
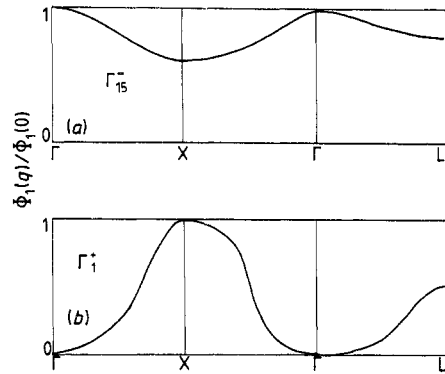

Figure 6. Covalent factors for the phonon renormalisation in black SmS: (a) dipolar mode; (b) monopolar mode.

the theory of excitonic instability proposed by those authors implies the mixing of the ground and excited states of the same symmetry in the 'black' phase to be the source of the instability. Hence the ground state of the new phase can be schematically represented as a linear combination

$$\Psi_{m,g} = \cos(\theta)|f_m^6, {}^7F_0\rangle + \sin(\theta)|f_m^5({}^6H_{5/2})\tilde{B}_{m,\Gamma_7^-}, {}^7F_0\rangle \qquad (4.1)$$

of the ground state of the ion f^6 and the non-local exciton in the black phase both having singlet wavefunctions. Apparently this 'bonding' combination demands the 'antibonding' partner

$$\Psi_{m,ex} = \cos(\theta)|f_m^5({}^6H_{5/2})\tilde{B}_{m,\Gamma_7^-}, {}^7F_0\rangle - \sin(\theta)|f_m^6, {}^7F_0\rangle \qquad (4.2)$$

which can be treated as the non-local fully symmetrical exciton in a new phase (the third column of figure 4(a)). Indeed, such excitations were registered by Travaglini and Wachter (1984) as f–f transitions with energies of 15 and 21 meV in the reflectivity spectra of $SmS_{(G)}$. It is clear that the similar spatial extent of the initial and final states (4.1) and (4.2) enhances the oscillator strengths of the monopole transition and facilitates its detection in optical spectra.

Thus we have the sources of the local (f–d) and non-local (f–f) CDD characteristic for systems with f ions close to valence instability, and in the final part of this paper we shall apply the general CDD theory to this specific case. Examining figures 1 and 2 and tables 1 and 2, we find that neither dipole nor monopole CDD mode can explain separately the softening of LO branch along the $[\xi\xi\xi]$ direction because the former nullifies in the L point and the latter gives no contribution to renormalisation in the Γ point. But the joint action of both modes gives the desired effect (figure 5). The origin of the dipole mode in $SmS_{(B)}$ is clear from the above discussion (f–d intra-atomic excitations), and the monopole contribution can be ascribed to the hypothetical exciton $|f^5\tilde{B}^\gamma, {}^7F_0\rangle$ (2.5) (f–$\tilde{f}$ transition). The final state of the latter transition is essentially non-local; hence the contribution of the covalent factors (3.15b) and (3.16b) should be included. However, the dipole covalent factor is practically dispersionless (figure 6(a)), and does not influence the form of the phonon curve. As to the monopole covalent factor, its contribution increases when approaching the zone boundary (figure 6(b)), but this dispersion is practically the same as that for the standard local formfactor for LO mode (type I of

figure 1), and cannot be distinguished experimentally. Turning to the LA mode we note that in the case of the polarisable heavy ions the CDD contribution to the LA mode is always smaller than that to the LO branch. Besides, the specific compensation mechanism due to the intersite CDD interaction leads to the additional reduction of LA branch renormalisation (Kikoin and Mishchenko 1988).

However, in gold SmS the interaction between the monopole CDD and the longitudinal branches is greatly enhanced due to the presence of extremely soft f–f̄ exciton (4.2) in the electron spectrum of MV semiconductor. In this case the monopole CDD renormalisation of LA branch (figure 1, type II) results in the deep 'sag' in the middle of $[\xi\xi\xi]$ direction (Bennemann and Avignon 1979), which describes roughly the character of renormalisation, but the careful analysis of the experimental data shows that really the formfactor of LA mode softening is asymmetrical with the maximum shifted towards the zone boundary (Matsuura *et al* 1980). This shift is excellently explained by the influence of the covalent formfactor $\Phi_1^{(\Gamma_1)}$, which has the form

$$\Phi_1^{(\Gamma_1)} = \frac{F_1^2}{E_{ex}(q)} \left[[12 - S(q)] \left(F_1[A^2 + (VG_0)^2] \frac{\sin(2\theta)}{2} + A|V|G_0 \cos(2\theta) \right) \right]^2 \quad (4.3)$$

in the case of the MV ground and excited states (4.1) and (4.2). Figure 7(*a*) presents the covalent formfactor for different values of the normalisation coefficient A. The full formfactor $\Phi^{(\Gamma_1^+)}$ in comparison with the experimental one extracted from the neutron scattering data (Mook *et al* 1982) by cancelling the rigid ion model contribution (Kikoin and Mishchenko 1988) is shown in figure 7(*b*). It is seen that inclusion of the covalent formfactor essentially improves the consistency of the theory with the experiment compared with the point CDD model.

The 'adiabatic' picture is invalid for the interaction between the excitonic CDD and optical phonon modes because these modes have very close frequencies. This is the reason for the failure of all attempts at describing both the optic and acoustic modes in MV SmS in a framework of adiabatic CDD theory (Bilz *et al* 1979, Entel *et al* 1979).
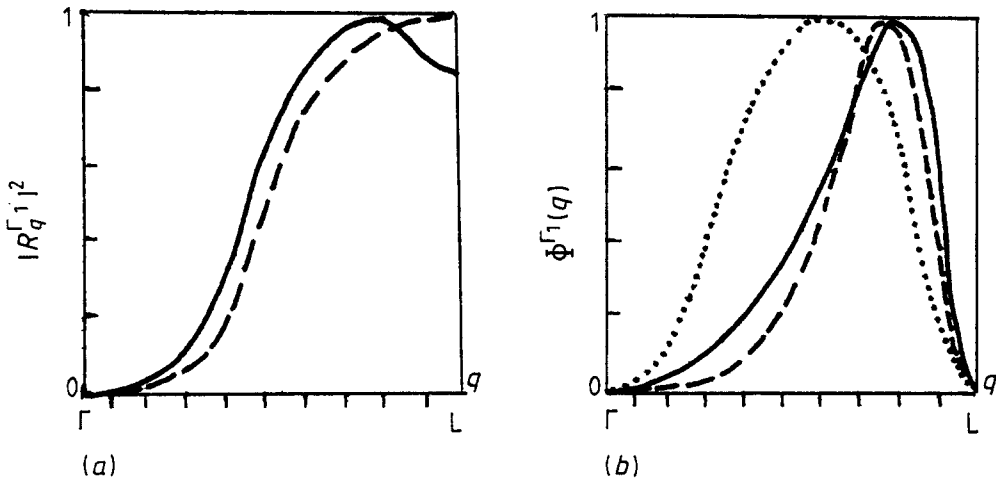

Figure 7. Formfactors of phonon frequency renormalisation in the 'gold' phase of SmS. (*a*) Covalent factor for $A^2 = 0.8$ (broken curve) and $A^2 = 0.6$ (full curve). (*b*) Phonon shifts $\Phi^{\Gamma_1}(q)$ in SmS$_{(G)}$: experiment (full curve), local CDD model (dotted curve) and CDD model with covalent factor taken into account (broken curve). All shifts are normalised to unity.

Actually, the different character of interaction of LA and LO modes with soft Γ_1 valence fluctuation mode leads to different types of phonon renormalisation and to the appearance of the resonance mode in the LO–LA gap in the optical and neutron spectra of gold SmS.

The same approach to the excitonic contribution can be checked for the CsCl symmetry. Figure 3 illustrates the CDD renormalisations in the local approximation for this case. Although there are no MV semiconductors possessing such symmetry, the famous mixed-valence samarium hexaboride with the CaB_6 crystal structure can be treated approximately as an example of CsCl MV semiconductor when neglecting the elastic forces within the boron octahedra. Recent neutron scattering measurements (Alekseev *et al* 1989) have revealed anomalies just in those directions. Moreover the resonance mode in LA–LO gap is also seen. Preliminary analysis shows that the excitonic theory of phonon renormalisation gives a satisfactory description of the experimental anomalies. It is interesting that in this case the covalent formfactor plays the decisive role in the renormalisation; no consistent explanation of the experiment can be obtained within the conventional local CDD theory for this system. The detailed description of the phonon spectra of both samarium-based MV semiconductors will be presented in a forthcoming paper.

References

Alekseev P A, Ivanov A S, Dorner B, Schober H, Kikoin K A, Mishchenko A S, Konovalova E S, Paderno Ju B, Lazukov V N, Rumyantsev A Yu and Sadikov I P 1989 *Europhys. Lett.* **10** 457
Allen P B 1977 *Phys. Rev.* B **16** 5139
Bennemann K H and Avignon M 1979 *Solid State Commun.* **31** 645
Bilz H, Guntherodt G, Kleppmann W and Kress W 1979 *Phys. Rev. Lett.* **43** 1998
Bilz H and Kress W 1979 *Phonon Dispersion in Insulators* (Berlin: Springer)
Brovman E G and Kagan Y 1974 *Dynamical Properties of Solids* (Amsterdam: North-Holland) p 191
Entel P, Grewe N, Sietz M and Kowalski K 1979 *Phys. Rev. Lett.* **43** 2002
Fischer K, Bilz H, Haberkorn R and Weber W 1972 *Phys. Status Solidi* b **54** 285
Guntherodt G 1974 *Phys. Kond. Mat.* **18** 37
Guntherodt G, Freeouf J L and Holtzberg F 1983 *Solid State Commun.* **47** 677
Ichinose S and Tamura I 1983 *Phys. Status Solidi* b **120** 703
Kikoin K A 1983 *Zh. Eksp. Teor. Fiz.* **85** 1000
—— 1984 *J. Phys. C: Solid State Phys.* **17** 6671
Kikoin K A and Mishchenko A S 1988 *Zh. Eksp. Teor. Fiz.* **94** (9) 237
Matsuura T, Kittler R and Bennemann K H 1980 *Phys. Rev.* B **21** 3467
Miura M, Kress W and Bilz H 1984 *Z. Phys.* B **54** 103
Mook H A, McWhan D B and Holtzberg F 1978 *Phys. Rev.* B **18** 2925
Mook H A, Nicklow R M, Penney T, Holtzberg F and Shafer M W 1982 *Phys. Rev.* B **25** 4321
Sham L J and Ziman J 1963 *Solid State Physics* vol 15, ed F Seitz and D M Turnbull (New York: Academic) p 223
Sinha S K 1969 *Phys. Rev.* **177** 1256
—— 1977 *Proc. Int. Conf. on Lattice Dynamics* (Paris: Flammarion) p 7
Stevens K W H 1976 *J. Phys. C: Solid State Phys.* **9** 1417
Stuber N, Guntherodt G, Jayaraman A, Fischer K and Holtzberg F 1982 *Valence Instabilities* ed P Wachter and H Boppart (Amsterdam: North-Holland) p 69
Travaglini G and Wachter P 1984 *Phys. Rev.* B **30** 5877
Varma C M and Weber W 1979 *Phys. Rev.* B **19** 6142
Wakabayashi N 1977 *Solid State Commun.* **23** 737
—— 1980 *Phys. Rev.* B **22** 5833
Weber W 1973 *Phys. Rev.* B **8** 5082
Woods A D, Cochran W and Brockhouse B N 1960 *Phys. Rev.* **119** 980