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Phonon frequencies and line widths at valence fluctuations: a simple vibronic model

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Abstract. It is shown that softening and broadening of the “phonon” line in the response spectrum of the coupled two-level atom–phonon system shows similar features as those observed for the intermediate valence $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ compound. An exact calculation of the phonon response, at different values of the atom–phonon coupling and at finite temperature, is presented for the two level atom–phonon (vibronic) system and an analysis of the modes, together with the shift of the spectral lines, is given.

1. Introduction

The pressure induced phase transition in SmS results in a metal of intermediate valence, with coexisting Sm^{2+} and Sm^{3+} states for the metal ions [1]. A similar phase occurs at normal pressure in mixed SmS – YS alloys [2] down until 200 K; further cooling leads to a semiconducting state with predominantly Sm^{2+} ions [2, 3]. Since the ion Sm^{2+} is larger than Sm^{3+} , it was expected that longitudinal phonon modes implying local compression-decompression of the metal ions are coupled with the valence fluctuations in the intermediate valence state, where Sm^{2+} and Sm^{3+} states are present with typically equal probability.

Experiments [3–5] on $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ indeed showed anomalous phonon behaviour as compared to similar but stable valence compounds, namely

- (i) the LO branch lies everywhere below the TO branch and has a deep minimum at the zone boundary L point ($\vec{q} = \pi/a(111)$);
- (ii) the LO phonon peaks are broadened, and the more the nearer they are to the L point, where the width is so large that “scattering can be seen all the way down to LA phonons” [5].

The consequences of a coupling between the electronic (f -shell) and vibrational modes have been treated by different theoretical techniques [6–11]. The two main arguments underlying these theories say that

- (1) the typical period of valence fluctuations, as deduced from a number of spectroscopical data [5, 12], is $\tau \sim 3 \times 10^{-13}$ s, which is a typical zone boundary phonon period in this and similar compounds;

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- (2) the most anomalous $LO(L)$ mode is precisely a vibration of S^{2-} planes in antiphase, compressing (decompressing) the Sm ion planes sandwiched in between.

The phenomenological approach includes lattice dynamical (shell) models with a “breathing deformability” parameter [6, 7], by which the phonon softening is well reproduced; on introducing a relaxation term [8] the broadening can also be described. The partly “*ab initio*” approaches start from the Anderson model completed with phonon interaction terms [9–11] and, by use of perturbation theory and of some parameter fitting, lead to reasonable agreement with experiment.

With these previous calculations in mind, we still find it instructive to study the phonon response of an *exactly soluble* coupled system: the two-level atom interacting, via a polaronic coupling, with a phonon mode. This model has already been used [13–16] to explain certain aspects of the intermedite valence state, like polaron-like behaviour of the excitations. More generally, the “vibronic” behaviour of coupled electronic and vibrational motion in molecules and the mathematically equivalent problem of a 2-level atom in radiation field have an extensive literature [17–23]. Yet, the question how the complicated dynamics of this relatively simple system appears in a one phonon absorption or emission experiment, e.g. in neutron scattering, has not been studied to our knowledge. The advantage of this model is that the frequencies and eigenstates of the system can, for all values of the relevant parameters (electron excitation Δ_0 , phonon frequency ω_0 , coupling λ), easily be determined numerically [17] so that the calculation of the spectral function related to a particular experiment becomes straightforward [18]. We use known methods in dealing with the 2-level atom–phonon system, novel is only the calculation of the spectral intensities (oscillator strengths) relevant for the phonon spectroscopic (neutron) experiment and the form of the spectrum at temperatures comparable to $\hbar\omega_0$. The results lead to a very transparent interpretation for both the shift in phonon frequency and for the observed broadening as a function of the relevant physical parameters.

2. Phonon response of the two-level atom–phonon system

The $LO(L)$ vibration in a NaCl-type lattice is the same as the zone-boundary mode in a diatomic chain, where the lighter anions (each standing for a (111) plane in the vibrating NaCl structure) oscillate in antiphase in adjacent cells and the metal ions (planes) are immobile, as seen in Figs 1a–1b.

We assume now that there is a mobile electron in each “doubled” unit cell, corresponding to the $q = \pi/a$ wavevector, and this electron prefers to hop from the momentarily compressed metal ion to the decompressed one. (In the absence of vibration we have a “fluctuating” hopping leading to the “homogeneous” intermedite valence state). This electron hopping, correlated to the lattice

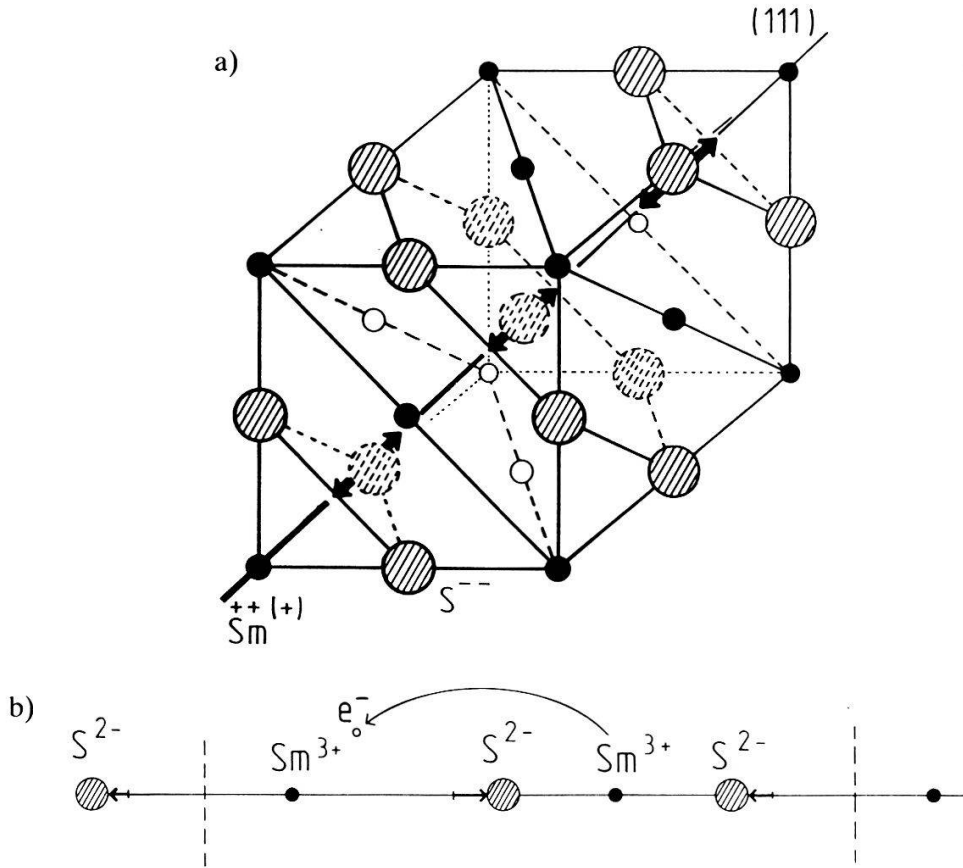


Figure 1

Vibration of the S^{2-} planes in the longitudinal $q = \pi/a(111)$ mode for the NaCl-type SmS (or $\text{Sm}_x\text{Y}_{1-x}\text{S}$) lattice. The small filled circles are metal ions, the anions (big circles) oscillate along the (111) direction; a) the elementary cube (elongated on the drawing, to point out the planes in phase); b) the equivalent linear chain.

vibration, is described by the Hamiltonian [14, 15]

$$\begin{aligned}
 H = & \varepsilon_0(c_A^+c_A + c_B^+c_B) - \frac{1}{2}\Delta_0(c_A^+c_B + c_B^+c_A) \\
 & + \hbar\omega_0 b^+b - \frac{\lambda}{2}(c_A^+c_A - c_B^+c_B)(b^+ + b)
 \end{aligned} \quad (1)$$

where c_A^+ and c_B^+ create electron occupation at sites A and B , b^+ and b are phonon emission and absorption operators and ε_0 , ω_0 , Δ_0 and λ are the energy of the occupied level, phonon frequency, hopping amplitude and coupling constant. This Hamiltonian describes a vibronic system. Since the electron number is fixed to 1, the first term can be omitted. The great simplification here is obviously that hybridization via the conduction band is replaced by the hopping between atoms of integer valence, and also that only one single phonon mode is taken into account. The dynamics of this system is still not trivial. It is known [13–15, 17] that for $\Delta_0 \ll \lambda$, the eigenstates are superpositions of coherent phonon states: the lattice follows the electron hopping (anti-adiabatic limit). In the other limiting case $\Delta_0 \gg \lambda$ the intermediate valence state is combined with given phonon number states. In our case $\Delta_0/\hbar\omega_0 \sim 1$ so that for the reasonably strong coupling $\lambda/\hbar\omega_0 \sim 1$ we are between these two limits. With pseudospin operators $S_i = \frac{1}{2}\sigma_i$ we

can rewrite equation (1) as

$$H = -\Delta_0 S_x - \lambda S_z (b^+ + b) + \hbar \omega b^+ b \tag{2}$$

where σ_i are the Pauli matrices and the state $|\frac{1}{2}\rangle = c_A^+ |0\rangle \equiv |A\rangle$ describes electron occupation at site A , similarly $|B\rangle \equiv |-\frac{1}{2}\rangle$. An equivalent form, obtained by a rotation,

$$H_R = \Delta_0 S_z - \lambda S_x (b^+ + b) + \hbar \omega_0 b^+ b \tag{3}$$

is known [22] as the Rabi Hamiltonian for an atom in a monochromatic radiation field. With the unitary transformation of Shore and Sander [17] we get

$$\tilde{H} = U H U^+ = -C \Delta_0 S_z + \hbar \omega_0 b^+ b - \frac{\lambda}{2} (b^+ + b) \tag{4}$$

where

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & 1 & C \\ & -1 & C \end{pmatrix}; \quad c = \cos(\pi b^+ b) \tag{5}$$

Now, \tilde{H} can simply be diagonalized in a finite space of phonon number states ($0 \leq n \leq N$), since the eigenvalues σ' of S_z are good quantum numbers with \tilde{H} . We have

$$\tilde{H} \tilde{\psi}_{\sigma' \nu} = E_{\sigma' \nu} \tilde{\psi}_{\sigma' \nu} = E_{\sigma' \nu} |\sigma'\rangle \sum_{n=0}^N C_n^{(\sigma' \nu)} |n\rangle \tag{6}$$

($\sigma' = \pm \frac{1}{2}, \nu = 1, 2, \dots$) and for the eigenstates of H

$$\psi_{\sigma' \nu} = \frac{1}{\sqrt{2}} \sum_{n=0}^N C_n^{(\sigma' \nu)} [2\sigma' |\frac{1}{2}\rangle + (-1)^n |-\frac{1}{2}\rangle] |n\rangle \tag{7}$$

The quantities $E_{\sigma' \nu}(d, q)$ and $C_n^{(\sigma' \nu)}(d, q)$ depend on two parameters $d = \Delta_0/\omega_0$ and $q = \lambda/\hbar\omega_0$. The ground state is always a $\sigma' = \frac{1}{2}$ (or ψ_+) state, and we study now the nearest ψ_- states in detail, since these are excited, from the $\psi_{+,1}$ ground state, in a phonon absorption experiment.

At weak coupling $d \gg q^2$ the ground state $\psi_{+,1} \sim (|A\rangle + |B\rangle) |n=0\rangle$ is symmetric in the electron occupation at A and, B with no phonon present; the first $\sigma' = -\frac{1}{2}$ excited state $\psi_{-,1}$ (for $d > 1$) is the same symmetric electronic state but with $|n=1\rangle$, the energy of excitation being $\Delta E_{-,1} \sim \hbar\omega_0$. The symmetry of $\psi_{-,1}$ is clearly due to the ‘‘phonon’’ factor $(-1)^n$ for $n=1$, compensating the ‘‘electronic’’ antisymmetry (via the factor $2\sigma'$) of all $\sigma' = -\frac{1}{2}$ states. In return, the antisymmetry in $A \rightleftharpoons B$ ‘‘remains’’ for the second excited state $\psi_{-,2} \sim (-|A\rangle + |B\rangle) |n=0\rangle$ having the energy $\Delta E_{-,2} \sim \Delta_0$.

For strong coupling $d \ll q^2$ the ground state is approximately $\tilde{\psi}_{+,1} \sim |A\rangle |\text{coh} \cdot A0\rangle + |B\rangle |\text{coh} \cdot B0\rangle$, where $|\text{coh} \cdot A0\rangle$ is a coherent, by the electron occupation at A ‘‘displaced’’ vibrational ground state,

$$|\text{coh} \cdot A0\rangle = e^{-q/2(b^+ - b)} |n=0\rangle = e^{-1/2(q/2)^2} \sum_n \frac{(q/2)^n}{\sqrt{n!}} |n\rangle \tag{8}$$

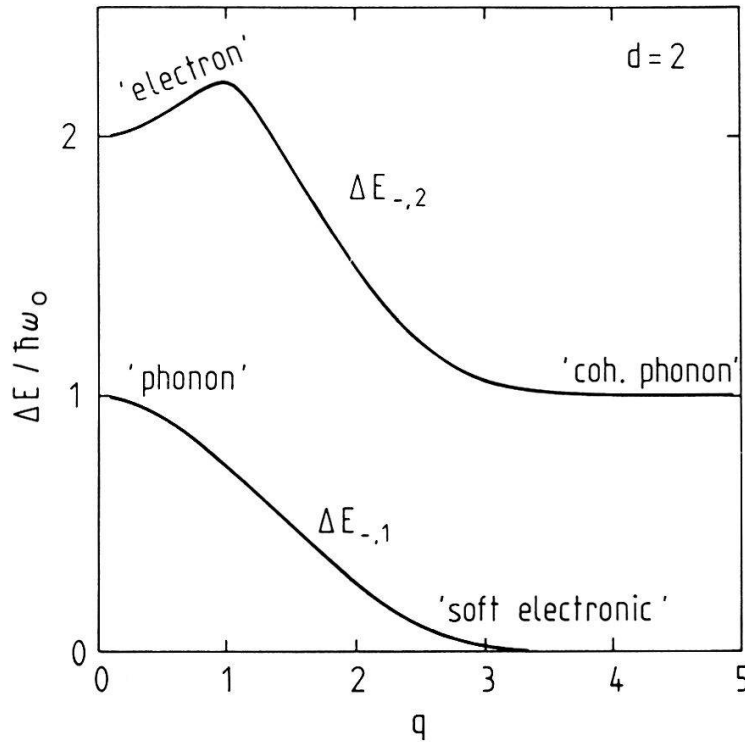


Figure 2

Energy of the first two $\sigma' = -\frac{1}{2}$ excited states, measured from the ground state energy E_{+1} , as a function of the vibronic coupling $q = \lambda/\hbar\omega_0$ for $d = 2.0$. The character of the modes changes with q , as described in the text.

and $|\text{coh} \cdot B0\rangle$ is the same with $q \rightarrow (-q)$. The first $\sigma' = -\frac{1}{2}$ excited state is approximately $\psi_{-,1} \sim (-|A\rangle |\text{coh} \cdot A0\rangle + |B\rangle |\text{coh} \cdot B\rangle)$ with excitation energy $\Delta E_{-,1} \sim \Delta_0 e^{-1/2(q/2)^2}$ [18] and the second, $\psi_{-,2}$, is the same but with “displaced” one-phonon states $|\text{coh} \cdot A1\rangle = (b^+ - q/2)e^{-(q/2)(b^+ - b)} |n=0\rangle$ and $|\text{coh} \cdot B1\rangle$, with the energy $\Delta E_{-,2} \sim \hbar\omega_0$.

The result for $\Delta E_{-,v}$ and $C_n^{(\sigma'v)}$ for arbitrary coupling strength are illustrated in Figs 2–3.

Note in Fig. 2 the change in character of the excitation as the coupling increases: the lower “phonon” branch transforms into the soft vibron-excitation and the phonon-free antibonding electron state goes over, in turn, to the coherent one-phonon state. Figure 3 shows the coefficients $C_n^{(\sigma'v)}$ for the ground state at weak and strong coupling, as compared to the coherent state limit $C_n \sim (q/2)^n / \sqrt{n!}$.

In a phonon absorption neutron experiment at momentum transfer $\vec{k} = \vec{q}_{ZB}$ the observed spectrum is proportional to the function

$$D(E) = \langle u(t)u(0) \rangle_E \quad (9)$$

where $u = b^+ + b$, $u(t)$ is a Heisenberg operator and $\langle \rangle_E$ indicates the Fourier transform of the quantum and statistical mechanical average. Simple analytical approximation for $D(E)$, valid for a general coupling and for non-zero temperatures could not be found. We calculate therefore $D(E)$ numerically, in the knowledge of $E_{\sigma'\alpha}$ and $C_n^{(\sigma'v)}$, equations (6–7). We note first that $\bar{u} = -2uS_X$ so

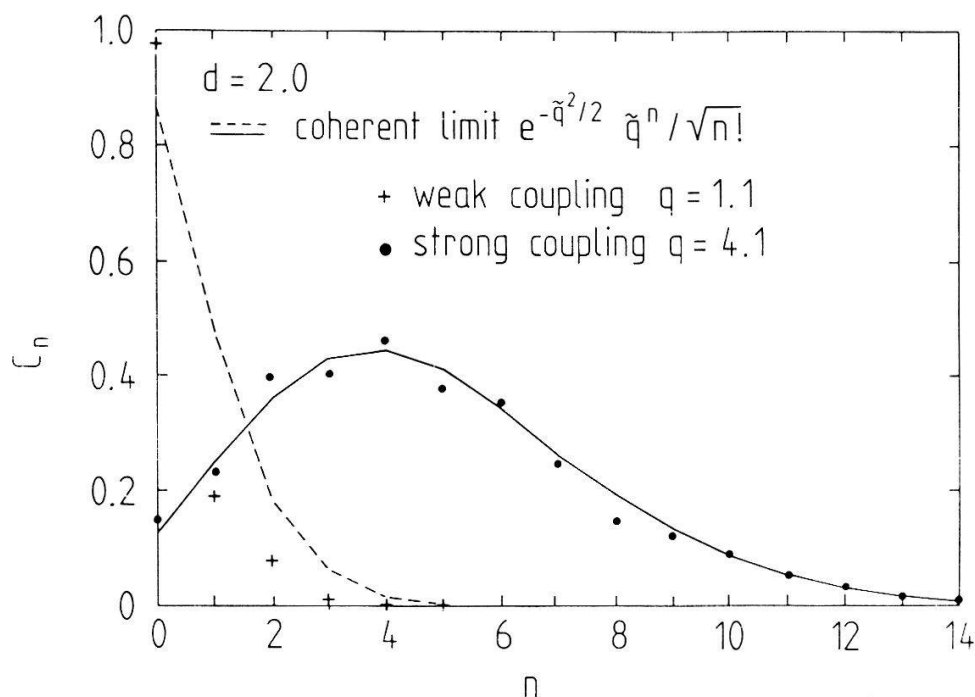


Figure 3
 The amplitude of states with different phonon numbers n in the composition of the vibronic ground state ψ_{+1} (equation (7)) for weak ($q = 1.1$) and strong ($q = 4.1$) coupling; $d = 2.0$ as in Fig. 2. The state for strong coupling is nearly a coherent phonon ground state with “displacement” parameter $\bar{q} = q/2$.

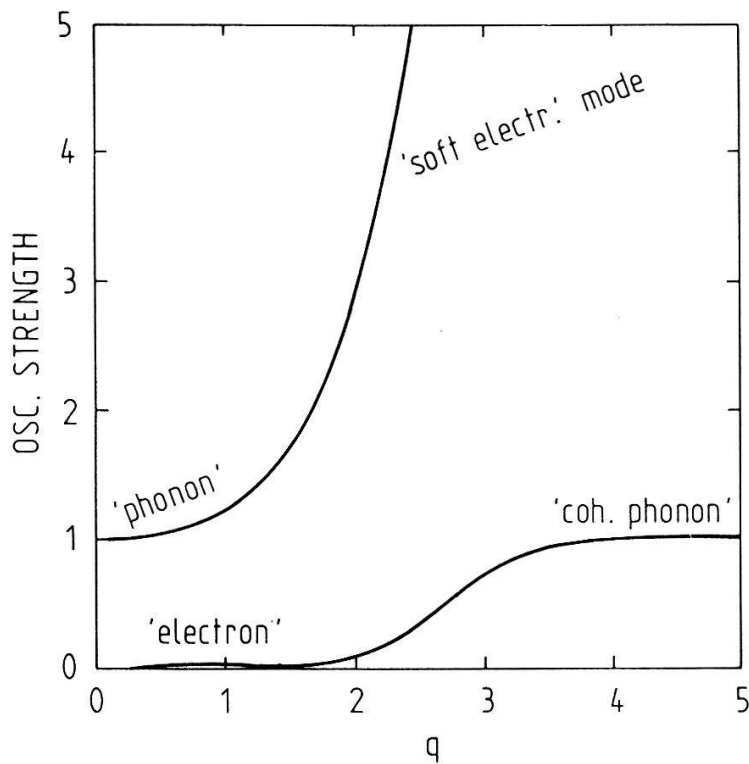


Figure 4
 Transition probabilities (oscillator strengths) for the first two excited $\sigma' = -\frac{1}{2}$ states, with the energies shown in Fig. 2, vs the coupling constant q . As in Figs 2-3, $d = 2.0$.

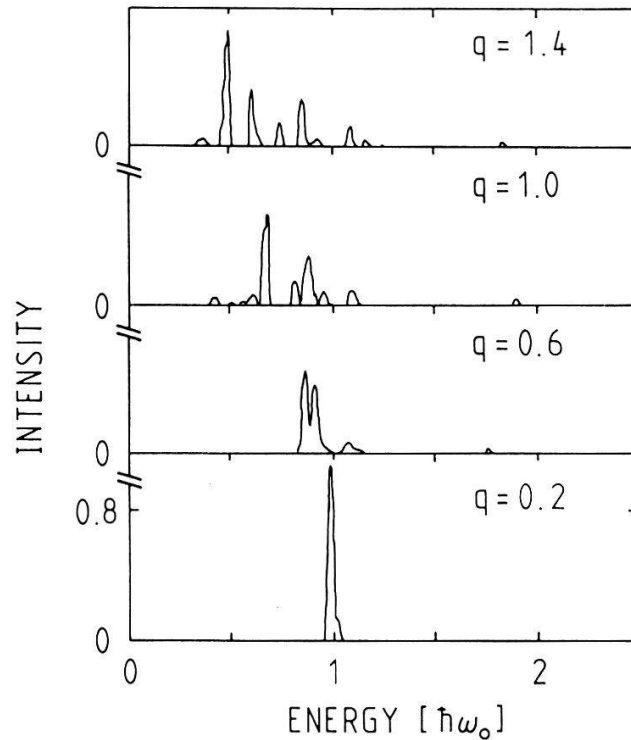


Figure 5

Predicted intensity $D(E)$ (equation (9)) in a neutron energy-loss experiment at $T = \hbar\omega_0$ on the vibronic system, for four values of the coupling strength q ; $d = 1.6$. At $q = 1.4$ the intensity of the “electronic” transition ($E \sim 1.8 \hbar\omega_0$) is still very small, in agreement with Fig. 4. Note the downward shift and the broadening of the “phonon” line ($I = (\bar{n} + 1)\delta(E - \hbar\omega_0)$ for $q = 0$), until a wide band of transitions appears for $q \geq 1$.

that it has matrix elements $\tilde{u}_{\sigma''}^{\sigma'}$ only for $\sigma'' = -\sigma'$. For $T \ll \hbar\omega_0$, the spectrum consists essentially from two lines, corresponding to the two energy branches plotted in Fig. 2, with the intensities (oscillator strengths) shown in Fig. 4.

Figures 2 and 4 show that with increasingly strong coupling the 1-phonon peak (at $q = 0$) goes more and more soft and a second, “electronic” peak appears at higher energy ($d > 1$) with growing intensity. At strong coupling the soft mode is very intensive and the other peak is stabilized at $E = \hbar\omega_0$.

In our model, broadening occurs at $T \sim \hbar\omega_0$ when, besides the $\psi_{+,1}$ ground state, other initial states are also available for the system.

We note that, in $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ [5], $\omega_0/2\pi = 7 \times 10^{13} \text{ s}^{-1}$, corresponding to $T/\hbar\omega_0 \sim 0.6$. The spectrum $D(E)$ is shown in Fig. 5 for $T/\hbar\omega_0 = 1$ for a few values of the coupling constant q . The low frequency line looks broadened with its centre of mass shifted toward lower ($< \omega_0$) frequencies, as an effect of the grouping of lines around the fundamental one, and both shift and broadening increase with increasing q . We note that an estimate for q has been given [13] as $|q|/2 \sim 2$.

Conclusion

For low temperatures, the neutron scattering experiment at the coupled vibronic system should result in a two-line spectrum: the line at lower frequency

has a pure phonon character at weak coupling and it goes over to a soft antibonding vibron excitation; the intensity of the second, "electronic" (at $q = 0$) line starts from zero, but it increases with increasing coupling as the mode becomes of mixed character. The energy of the low frequency line is less than $\hbar\omega_0$ for all coupling. At $T \sim \hbar\omega_0$ this line looks as broadened, with its centre of mass still shifted toward lower frequencies, due to a number of transitions with nearly the same energy. Bearing in mind the experimental resolution washing together closely grouped peaks, we can conclude that the phonon response of the two-level vibronic system is similar to that actually observed for the intermediate valence $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ system. However, no observation of the weaker, large-frequency peak has been reported. An explanation for that can be the small overall intensity for the $LO(L)$ line [3–5]: in fact, the line shape of this broadened peak is not known at all. Future experiments may show if the doublet structure, present in our results and pronounced especially at lower temperatures, really exists.

Acknowledgments

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