

## Phonon Self-Energies and 4*f*-Electron-Phonon Interaction in Ce<sub>c</sub>La<sub>1-c</sub>F<sub>3</sub>

K. Ahrens and G. Schaack

*Physikalisches Institut der Universität, D-8700 Würzburg, Germany*

(Received 27 February 1978)

In Ce<sub>c</sub>La<sub>1-c</sub>F<sub>3</sub> we have observed frequency shifts of optical phonons depending on the concentration *c* of the 4*f* ions and on temperature. It is shown that these effects are due to a resonant 4*f*-electron-phonon interaction via photon-induced virtual quadrupole transitions to excited crystal-field states of Ce<sup>3+</sup>. These shifts are related to the magnetic phonon splitting of doubly degenerate phonons. Both effects can be quantitatively interpreted with the same coupling constant.

The most conspicuous consequences of electron-phonon interactions studied recently have been found on fields related with lattice dynamics. Of relevance to the following are examples where a change of the phonon-self-energy is observed due to the interaction with the conduction electrons especially near the Fermi surface. The phonon anomalies in transition-metal carbides and nitrides may be mentioned,<sup>1</sup> the frequency shift due to the self-energy of the phonon-deformation-potential interaction in heavily doped *n*-Si,<sup>2</sup> and the effects due to valence instabilities in rare-earth (R.E.) metals and intermetallic compounds.<sup>3</sup>

In systems with localized electrons the self-energy of a phonon state due to its interaction with 3*d* or 4*f* electrons is usually not known. In the following we present experimental and theoretical results on this type of interaction. Using Raman spectroscopy, we have studied the frequency shift of optical phonons in the ionic R.E. compound Ce<sub>c</sub>La<sub>1-c</sub>F<sub>3</sub> ( $0 \leq c \leq 1$ ) and give a quantitative interpretation of these results in terms of the theory of Thalmeier and Fulde<sup>4</sup> on the magnetoelastic interaction. It turns out that this shift is intimately related to the magnetic phonon splitting<sup>5,6</sup> and can be understood assuming a dynamic quadrupolar deformation of the 4*f* shell by the phonon.

The Ce-La trifluorides form trigonal crystals (*D*<sub>3*d*</sub><sup>4</sup>); however, the deviations from the more symmetrical hexagonal structure *D*<sub>6*h*</sub><sup>4</sup> are small.<sup>7</sup> In the following discussion we shall use the higher symmetry because of simplicity.

The light scattering experiments have been performed at 2 K or at higher temperatures using standard Raman techniques. We have studied in detail three doubly degenerate optical-phonon modes (Fig. 1) which typically represent other modes in this material. The modes at 391 and 204 cm<sup>-1</sup> show a considerable magnetic phonon splitting<sup>5,8</sup>; the mode at 310 cm<sup>-1</sup> does not split. The *c*-dependent zero-field frequency shifts are

considerably for the phonons at 391 cm<sup>-1</sup> and at 310 cm<sup>-1</sup> but small for the phonon at 204 cm<sup>-1</sup>. The magnetic phonon splitting follows the paramagnetic saturation of the lowest Kramers doublet [ $\sim \tanh(\text{const } H/T)$ ]. The split phonon components are orthogonally circularly polarized.<sup>9</sup>

Before entering the theoretical discussion we have to subtract from the data of the zero-field shift that part which is due to the reduction of the unit-cell volume on going from La<sup>3+</sup> to Ce<sup>3+</sup> because of the lanthanide contraction. The contribution to the frequency shift due to the mass difference between the two cations is of minor importance, because the high-frequency phonons comprise essentially motions of only the fluorine ions.<sup>7</sup>

We have used two methods to determine the Grüneisen parameters for a calculation of this lattice contribution. First, we have used data on the thermal frequency shift of phonons in LaF<sub>3</sub> and on the thermal expansion to extrapolate to CeF<sub>3</sub>; second, we have used the bulk compressibilities (Rehwald<sup>10</sup>) and the pressure dependences of the mode frequencies (Dultz<sup>11</sup>) both in CeF<sub>3</sub> to calculate these shifts. In Table I, the average results of these calculations have been compiled; the discrepancies were largest (4.8 cm<sup>-1</sup>) for the *E*<sub>2*g*</sub> mode at 391 cm<sup>-1</sup>. In conclusion, we see that about one half of the observed shift of the 391-cm<sup>-1</sup> phonon is due to unit-cell contraction while the shift of the 204-cm<sup>-1</sup> phonon produced by this "trivial" effect is larger than the observed value, i.e., the zero-field shift is obviously negative.

For a quantitative interpretation we follow Ref. 4, where the magnetic phonon splitting in CeCl<sub>3</sub> was calculated. The interaction Hamiltonian is of the usual bilinear Jahn-Teller type:

$$H_{\text{int}} = \sum_{\rho, \Gamma_i} g_{\Gamma_i}(\rho) \varphi_{\Gamma_i}(\rho) O_{\Gamma_i}(\rho). \quad (1)$$

Here  $\varphi$  is phonon coordinate at a R.E. site trans-

TABLE I. Experimental and calculated values for the diagonal (zero-field shift,  $S_{\Gamma',\Gamma'}$ ) and off-diagonal (magnetic phonon splitting  $S_{\Gamma',\Gamma''}$ ) elements of the phonon self-energy and of the coupling constants  $g$  in  $\text{CeF}_3$ . The values of  $S_{\Gamma',\Gamma'}^{\text{expt}}$  have been corrected for effects of the lanthanide contraction  $\Delta\bar{\nu}_{j,L}$  (see text). The coupling constant for the near-resonant phonon at  $310 \text{ cm}^{-1}$  has been determined from the results plotted in Fig. 2.

$\bar{\nu}$ ( $\text{cm}^{-1}$ )	$\Delta\bar{\nu}_{j,L}$ ( $\text{cm}^{-1}$ )	$g$ ( $\text{cm}^{-1}$ )	$S_{\Gamma',\Gamma'}^{\text{expt}}$ ( $\text{cm}^{-1}$ )	$S_{\Gamma',\Gamma'}^{\text{calc}}$ ( $\text{cm}^{-1}$ )	$S_{\Gamma',\Gamma''}^{\text{expt}}$ ( $\text{cm}^{-1}$ )	$S_{\Gamma',\Gamma''}^{\text{calc}}$ ( $\text{cm}^{-1}$ )
391	$12 \pm 2$	6.34	11.0	10.5	14	14.6
310	$4 \pm 4$	3.61	20	...	0 (<4)	...
204	$4 \pm 4$	4.30	-2.2	-2.6	8.0	6.8

forming according to the i.r.  $\Gamma_i$  of the site group,  $g$  is a magnetoelastic coupling constant, and  $\rho = 1, \dots, 6$  numbers the six  $\text{Ce}^{3+}$  sites in the unit cell. The quadrupolar Stevens operators  $O_{\Gamma_i}$  have been grouped together according to their factor-group symmetry properties  $\Gamma_i$ .<sup>12</sup> Only those operators have to be considered in (1) which at the same time transform according to a particular i.r.  $\Gamma_i$  of the site group and the i.r.  $\Gamma$  of the fac-

tor group which characterizes the phonon being considered. The frequency shift and mode splitting are calculated by solving Dyson's equation for the Green's function of the  $E$  phonon at zero wave vector.<sup>4</sup> The Green's function and the phonon self-energy  $S(\bar{\nu})$  are  $2 \times 2$  matrices with the elements labeled by the  $\Gamma', \Gamma''$  transforming as one of the subvectors of  $\Gamma$ .  $S(\bar{\nu})$  is calculated to lowest order in perturbation theory:

$$S_{\Gamma',\Gamma''}(\bar{\nu}) = 2 \sum_{\substack{N, N', \rho, \\ \Gamma_i, \Gamma_j}} g_{\Gamma_i} g_{\Gamma_j} \frac{(n_{N'} - n_N) \langle N | O_{\Gamma_i}(\rho) | N' \rangle \langle N' | O_{\Gamma_j}(\rho) | N \rangle}{\bar{\nu} - \bar{\nu}_{NN'}} \quad (2)$$

Here  $N, N' = 1^+, 1^-, 2^+, 2^-, 3^+, 3^-$ , are the three Kramers-degenerate crystal-field states at wave numbers  $\bar{\nu}_N$  of the lowest multiplet component  ${}^2F_{5/2}$  of  $\text{Ce}^{3+}$  with the thermal occupation numbers  $n_{N'}$ , and  $\bar{\nu}_{NN'} = \bar{\nu}_N - \bar{\nu}_{N'}$ . The composition of the crystal-field states  $|N'\rangle$  at  $0, 142 \pm 2, 290_{-20}^{+30} \text{ cm}^{-1}$  in terms of the free-ion states  $|\gamma JM\rangle$  of  ${}^2F_{5/2}$  has been determined<sup>13</sup> from electronic magneto-Raman-scattering experiments in  $\text{CeF}_3$  in high magnetic fields ( $B < 12 \text{ T}$ ).

By separating the real and imaginary parts of the phonon self-energy matrix elements and summing up over  $\rho$ , the following general expressions are obtained:

$$S_{\Gamma',\Gamma'}(\bar{\nu}) = g^2 \left[ \frac{(n_2 - n_1) \bar{\nu}_{12}}{\bar{\nu}^2 - \bar{\nu}_{12}^2} Z_{12}^{(\Gamma',\Gamma')} + \frac{(n_3 - n_1) \bar{\nu}_{13}}{\bar{\nu}^2 - \bar{\nu}_{13}^2} Z_{13}^{(\Gamma',\Gamma')} + \frac{(n_3 - n_2) \bar{\nu}_{23}}{\bar{\nu}^2 - \bar{\nu}_{23}^2} Z_{23}^{(\Gamma',\Gamma')} \right],$$

$$S_{\Gamma'',\Gamma''}(\bar{\nu}) = S_{\Gamma',\Gamma'}(\bar{\nu}); \quad (3a)$$

and

$$S_{\Gamma',\Gamma''}(\bar{\nu}) = ig^2 \bar{\nu} \left[ \frac{(n_1^- - n_1^+)}{\bar{\nu}^2 - \bar{\nu}_{12}^2} Z_{12}^{(\Gamma',\Gamma'')} + \frac{(n_1^- - n_1^+)}{\bar{\nu}^2 - \bar{\nu}_{13}^2} Z_{13}^{(\Gamma',\Gamma'')} \right],$$

$$S_{\Gamma'',\Gamma'}(\bar{\nu}) = -S_{\Gamma',\Gamma''}(\bar{\nu}), \quad (3b)$$

where  $kT \ll hc\bar{\nu}_{12}$  and the  $Z_{NN'}^{(\Gamma',\Gamma')}$  are sums of products of the  $\langle N | O_{\Gamma_i}(\rho) | N' \rangle$  quadrupolar matrix elements. Except where explicitly stated, the Zeeman splitting has been neglected ( $1^+, 1^-, \dots, -1$ , etc.). Calculating the frequency shift  $\delta\bar{\nu}$  of the perturbed phonon  $\bar{\nu}_{\text{ph}}$  against the uncoupled

$\bar{\nu}_0$  we find that

$$\delta\bar{\nu} = \bar{\nu}_{\text{ph}} - \bar{\nu}_0 = S_{\Gamma',\Gamma'}(\bar{\nu}) \pm |S_{\Gamma',\Gamma''}(\bar{\nu})|, \quad (4)$$

assuming  $\delta\bar{\nu} \ll \bar{\nu}_{\text{ph}}, \bar{\nu}_0$ . This approximation is equivalent to replacing the phonon wave number

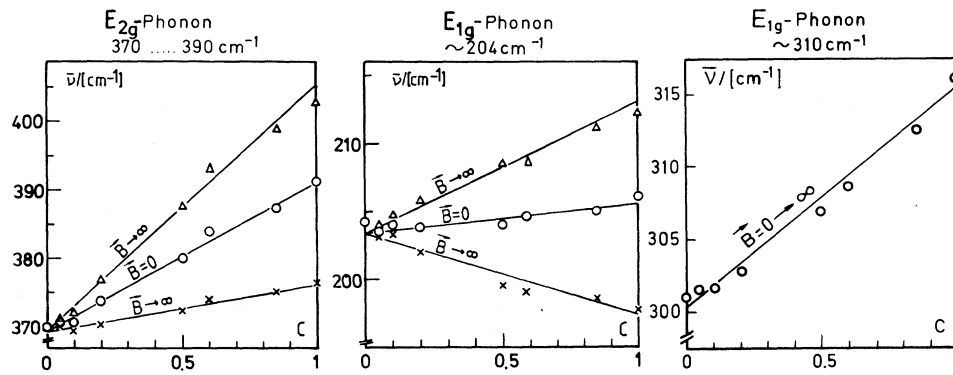


FIG. 1. Zero-field shift of optical phonons and magnetic phonon splitting as a function of concentration  $c$  in  $Ce_c La_{1-c} F_3$  at  $T=2$  K. The  $E_{1g}$  phonon near  $310\text{ cm}^{-1}$  does not split in a magnetic field.

$\bar{\nu}$  in the denominator of (2) by  $\bar{\nu}_0$ , which is admissible in the nonresonant case.  $S_{\Gamma'\Gamma''}(\bar{\nu})$  is slowly temperature dependent; the weak magnetic-field dependence of the  $n_i$  can be neglected;  $S_{\Gamma'\Gamma''}(\bar{\nu})$  varies, however, strongly with temperature and is proportional to the paramagnetic magnetization, vanishing at zero field. Thus the zero-field shift is due to the diagonal elements of the self-energy matrix and the magnetic phonon splitting is determined by the off-diagonal elements.<sup>4</sup>

We have determined values of the magnetoelastic coupling constants  $g$  for both phonons at  $391\text{ cm}^{-1}$  and at  $204\text{ cm}^{-1}$  by simultaneously fitting calculated values of the zero-field shift and the magnetic phonon splitting to the experimental data (Fig. 1). As Table I demonstrates, a good

fit is possible which indicates that both the zero-field shift and the magnetic phonon splitting have a common origin.

For the near-resonant phonon at  $310\text{ cm}^{-1}$  our approximation (4) is invalid. Instead of solving the Dyson equation exactly and considering poorly understood damping mechanisms,<sup>14</sup> we have included<sup>15</sup> reasonably guessed terms  $i\gamma_{NN'}$  in the denominators of (2) which take the finite linewidths of the excited electronic states into account and we have recalculated Eqs. (3) accordingly. Thus the self-energies of the phonon at  $310\text{ cm}^{-1}$  can be interpreted as in qualitative agreement with the experimental results (zero-field shift large as compared to the magnetic phonon splitting).

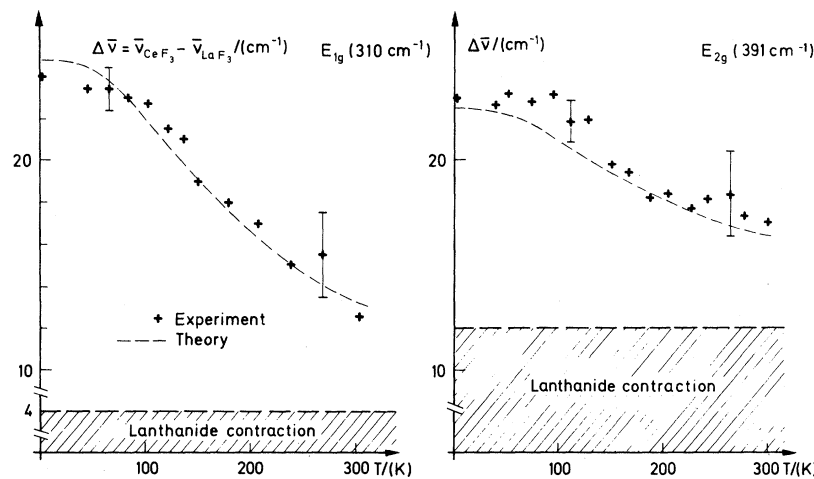


FIG. 2. Temperature dependence of the difference  $\Delta\bar{\nu}$  of optical-phonon frequencies in  $CeF_3$  and  $LaF_3$ . The contribution of the varying unit-cell size has been marked. The theoretical curve for the  $E_{2g}$  mode has been calculated using the coupling constant taken from Table I, and no fitting to the experimental data in this plot has been tried; the  $E_{1g}$  data, however, have been fitted to the theory to determine the coupling constant given in Table I.

According to Eq. (3a) the zero-field shift should diminish with increasing temperature, the exact temperature dependence is determined by the thermal occupation numbers  $n_N$ . This is demonstrated in Fig. 2, where we have plotted for various temperatures the wave numbers of the phonons near 391 and 310  $\text{cm}^{-1}$  in  $\text{CeF}_3$  with the strongly  $c$ -dependent zero-field shifts and numerical results calculated from Eq. (3a). The phonon at 204  $\text{cm}^{-1}$  in  $\text{CeF}_3$ , however, with a small zero-field effect, shifts between 2 and 300 K only by two wave numbers essentially due to anharmonicity and nearly coincides with the same phonon in  $\text{LaF}_3$ .<sup>16</sup>

It is interesting to discuss Eq. (2) in terms of a quadrupolar response of the R.E. ion to the phonon field. The phonon induces virtual transitions to excited crystal-field states, or equivalently the  $4f$  shell experiences at low temperatures a multipolar (even parity) dynamical deformation or reorientation by the phonon-modulated crystal field. Such compounds might be interesting candidates for the investigation of the role of deformable shells in lattice dynamics. We note that phonon-induced quadrupolar deformations of ions have been identified before in the silver halides  $\text{AgCl}$  and  $\text{AgBr}$ .<sup>17</sup>

The authors are indebted to W. Rehwald (Zürich) and W. Dultz (Regensburg) for communicating their data prior to publication. They acknowledge gratefully the encouragement of P. Fulde and P. Thalmeier (Max Planck Institut, Stuttgart) and of G. Abstreiter and M. Berger (Grenoble). The Deutsche Forschungsgemeinschaft has supported this investigation financially.

<sup>1</sup>W. Hanke, J. Hafner, and H. Bilz, *Phys. Rev. Lett.* **37**, 1560 (1976).

<sup>2</sup>M. Chandrasekhar, J. B. Renucci, and M. Cardona, *Phys. Rev. B* **17**, 1623 (1978).

<sup>3</sup>F. Weling, *Solid State Commun.* **26**, 913 (1978).

<sup>4</sup>P. Thalmeier and P. Fulde, *Z. Phys. B* **26**, 323 (1977).

<sup>5</sup>G. Schaack, *Solid State Commun.* **17**, 505 (1975), and in *Proceedings of the Third International Conference on Light Scattering in Solids, Campinas, Brazil, 1975*, edited by M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, 1976), p. 372.

<sup>6</sup>G. Schaack, *Z. Phys. B* **26**, 49 (1977), and *Physica (Utrecht)* **89B**, 195 (1977).

<sup>7</sup>R. P. Bauman and S. P. S. Porto, *Phys. Rev.* **161**, 842 (1967).

<sup>8</sup>K. Ahrens and G. Schaack, in *Proceedings of the International Conference on Lattice Dynamics, Paris, 1977*, edited by M. Balkanski (Flammarion, Paris, 1978), p. 257.

<sup>9</sup>G. Schaack, *J. Phys. C* **9**, L297 (1976); K. Ahrens and G. Schaack, *Ind. J. Pure Appl. Phys.* **16**, 311 (1978).

<sup>10</sup>W. Rehwald, private communication.

<sup>11</sup>W. Dultz, private communication.

<sup>12</sup>Multipolar operators of order 4 and 6 have been neglected.

<sup>13</sup>K. Ahrens, to be published.

<sup>14</sup>G. A. Toombs and F. W. Sheard, *J. Phys. C* **6**, 1467 (1973).

<sup>15</sup>Y. Toyozawa, *J. Phys. Chem. Solids* **25**, 59 (1964).

<sup>16</sup>It is assumed that the effects due to anharmonicity in the  $\text{CeF}_3$  and the  $\text{LaF}_3$  lattice are identical. In  $\text{LaF}_3$  all frequency shifts of phonons in the temperature interval  $2 \text{ K} < T < 300 \text{ K}$  are found  $< 2 \text{ cm}^{-1}$ .

<sup>17</sup>K. Fischer, H. Bilz, R. Haberkorn, and W. Weber, *Phys. Status Solidi (b)* **54**, 285 (1972); B. Dorner, W. von der Osten, and W. Bührer, *J. Phys. C* **9**, 723 (1976).