

## Determination of the Superconducting Gap in $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$

B. Friedl, C. Thomsen, and M. Cardona

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany

(Received 25 May 1990)

The anomalous broadening of the  $B_{1g}$ -like phonon of  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  observed in Raman scattering is studied as a function of phonon frequency by substituting various rare earths for  $R$ . The onset of broadening starts abruptly at a phonon energy which allows us to unambiguously determine a single, sharp superconducting gap at  $2\Delta = 316 \text{ cm}^{-1}$ .  $2\Delta/kT_c = 4.95 \pm 0.10$ , i.e.,  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  is a strong-coupling superconductor. We find qualitative and quantitative agreement with theory.

PACS numbers: 74.70.Vy, 71.10.+x, 78.30.Er

The high-temperature superconductors have given rise to questions concerning the pairing mechanism and the nature of their gap. In particular, it is still open whether at  $T=0$  there is only one gap or whether for different regions of the Fermi surface one could speak of different energy gaps. Even a so-called zero-gap structure in the superconducting state has been considered in view of the nonvanishing electronic scattering background observed in Raman scattering near  $T=0 \text{ K}$ .<sup>1,2</sup> The classical spectroscopic method<sup>3</sup> for the investigation of superconducting energy gaps—far-infrared reflectivity—has yielded a broad range of possible values for the ratio of gap to transition temperature. Values in the range of  $0 < 2\Delta/kT_c < 8$  have been reported by different groups.<sup>4-8</sup> Tunneling measurements have yielded values between 4.0 and 7.6 (Refs. 9 and 10) and, more recently, two distinct values.<sup>11</sup> Other methods for determining the gap energy find values of  $2\Delta/kT_c = 8$  (photoemission)<sup>12</sup> and  $2\Delta/kT_c$  near 3 and 9 (nuclear magnetic resonance, depending on Cu site).<sup>13,14</sup>

We will show here that Raman scattering is able to provide precise information about the superconducting gap through the dependence of the phonon self-energy on the difference between phonon frequency and the value of  $2\Delta$ .

The anomalous softening and linewidth increase of the  $B_{1g}$ -like Raman-active mode at  $340 \text{ cm}^{-1}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  below the transition temperature indicates a sizable coupling of the phonon to the electronic system.<sup>1,15-17</sup> It also suggests that the superconducting gap  $2\Delta$  should lie in the neighborhood of the phonon frequency. This motivated Zeyher and Zwicky's strong-coupling theory for the gap formation.<sup>18</sup> They calculated the change of the complex self-energy  $\Delta\Sigma = \Delta\omega - i\Delta\gamma$  of zone-centered phonons due to superconductivity [ $\Delta\omega$  is the change in frequency and  $\Delta\gamma$  the change in linewidth (half width at half maximum)]. Their theory predicts a characteristic dependence of the self-energy on the ratio of the phonon frequency  $\omega$  (at  $T_c$ ) to the gap  $2\Delta$ . The most drastic effects should be seen for  $\omega \approx 2\Delta$ .

We have recently investigated the frequency changes below  $T_c$  of the  $B_{1g}$ -like mode and the  $A_g$  mode near  $440 \text{ cm}^{-1}$  for different  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  superconductors ( $R$  is

a rare earth). We found good agreement with the theory by assuming a gap  $2\Delta$  between  $310$  and  $420 \text{ cm}^{-1}$  and using a coupling constant obtained from an *ab initio* local-density-approximation (LDA) calculation<sup>19</sup> of  $\lambda_v = 0.02$  and  $0.01$  for the two modes under consideration.<sup>20</sup> A significantly more precise value of  $2\Delta/kT_c$  may, however, be obtained by considering the imaginary part of the self-energy. The physical reason for the higher sensitivity to a gap is that for phonon energies lower than the gap, the decay channels disappear below  $T_c$ . Excitation energies above the gap, on the other hand, experience an increase in the density of states below  $T_c$  resulting in a broadening of phonons with overlapping frequencies.

In this Letter, we investigate the superconductivity-induced changes in linewidth  $\Delta\gamma$  of the Raman-active  $\text{CuO}_2$ -plane modes of  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ . By using materials with different rare earths  $R$  we can tune the phonon frequencies around the gap. We exploit the fact that the frequency of the  $B_{1g}$ -like mode in  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  (out-of-phase vibration of the plane oxygen) depends roughly linearly on the radius of the rare earth  $R$  while  $T_c$  (and presumably the gap) remains nearly the same.<sup>21,22</sup> Another possibility to change the phonon frequency of an oxygen vibration in a given  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  is to replace  $^{16}\text{O}$  by  $^{18}\text{O}$ . The phonon frequency is then lowered by about 6%. The onset of broadening, we find, starts abruptly at an energy which allows us to (a) ascertain that a single, sharp, well-defined gap exists in the energy range of observation and (b) determine this gap value to be  $2\Delta/kT_c = 4.95 \pm 0.10$ .

The setup for the Raman experiments is the same as described in Ref. 19. The experiments were performed on ceramic samples of  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $R = \text{Eu}, \text{Dy}, \text{Er}, \text{Tm},$  and  $\text{Y}$ ) and on a 90%-isotope-exchanged ( $^{18}\text{O} \leftrightarrow ^{16}\text{O}$ ,  $R = \text{Y}$ ) sample. The samples were fully oxygenated, i.e.,  $\delta \approx 0$ , as was determined by thermogravimetry, and the transition temperatures were about 92 K.

In Fig. 1 we show the Raman spectra of the  $B_{1g}$ -like phonon of (a)  $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and (b)  $\text{YBa}_2\text{Cu}_3^{18}\text{O}_{7-\delta}$  for 90 and 10 K. The spectra show clearly a Fano line shape, which is the signature of the interaction between

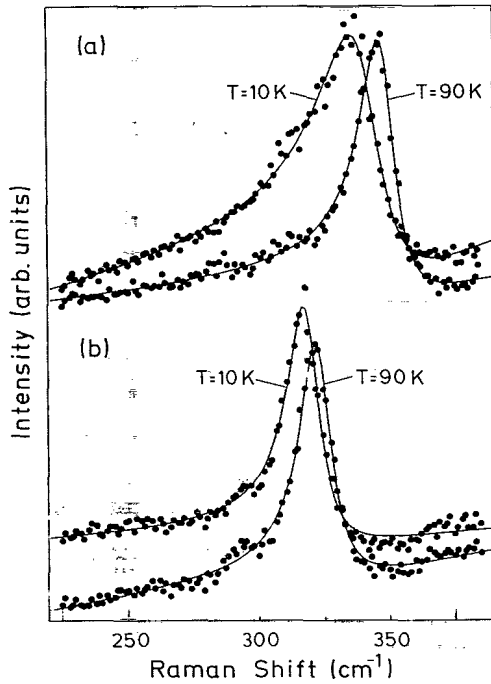


FIG. 1. The  $B_{1g}$ -like mode of (a)  $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and (b)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  for  $T=90$  and  $10$  K. The lines are fits to the experimental points with a Fano profile plus a linear background. ( $R=\text{Er}$ :  $\omega_v=348.0$   $\text{cm}^{-1}$ ,  $\gamma=7.7$   $\text{cm}^{-1}$ ,  $q=-3.8$  at  $90$  K;  $\omega_v=340.5$   $\text{cm}^{-1}$ ,  $\gamma=13.8$   $\text{cm}^{-1}$ ,  $q=-2.3$  at  $10$  K.  $R=\text{Y}$  ( $^{18}\text{O}$ ):  $\omega_v=323.0$   $\text{cm}^{-1}$ ,  $\gamma=7.2$   $\text{cm}^{-1}$ ,  $q=-6.2$  at  $90$  K;  $\omega_v=318.5$   $\text{cm}^{-1}$ ,  $\gamma=7.7$   $\text{cm}^{-1}$ ,  $q=-4.9$  at  $10$  K.) Note the difference in broadening and softening of this mode for the two materials.

the discrete (phonon) state and a broad (electronic) continuum.<sup>23</sup> The Raman intensity is then

$$I(\omega) \sim \frac{(\epsilon+q)^2}{1+\epsilon^2} + \text{background}, \quad (1)$$

where  $\epsilon=(\omega-\omega_v)/\gamma$ , with  $\omega_v$  the phonon frequency, and  $q$  the parameter which defines the asymmetry. We determined  $\omega_v$  and  $\gamma$  by fits with Eq. (1). When cooling from  $90$  to  $10$  K, the  $B_{1g}$ -like mode of  $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\omega_v=348$   $\text{cm}^{-1}$  at  $90$  K) shows a large softening ( $\approx 7.5$   $\text{cm}^{-1}$ ) accompanied by a tremendous broadening ( $\Delta\gamma=6.2$   $\text{cm}^{-1}$ , i.e., almost a doubling in linewidth). The  $B_{1g}$ -like mode of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $323$   $\text{cm}^{-1}$  at  $90$  K), on the other hand, softens by a rather large amount ( $\approx 4.5$   $\text{cm}^{-1}$ ) but shows only a small broadening of  $\Delta\gamma=0.5$   $\text{cm}^{-1}$  (i.e., 7%).

The anomalous frequency shifts and linewidth broadenings occur not only for the  $B_{1g}$ -like mode in  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ , but also for the phonon with  $A_g$  symmetry at  $440$   $\text{cm}^{-1}$  (with Lorentzian line shape), which is the in-phase vibration along  $z$  of the oxygen plane. This phonon exhibits substantial anomalous hardening by up to  $5.5$   $\text{cm}^{-1}$  in some of the  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ .<sup>20</sup>

In the upper part of Fig. 2 the linewidth of the  $A_g$

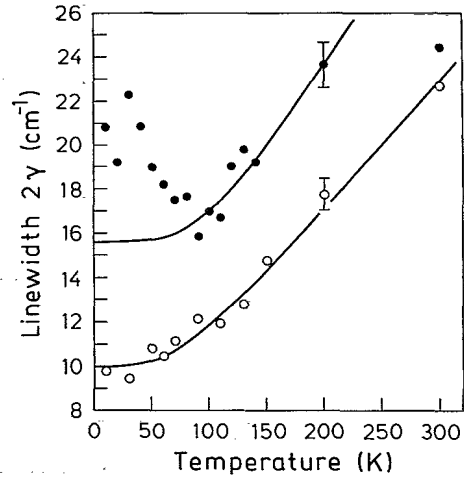


FIG. 2.  $T$ -dependent linewidth of the  $A_g$  phonon at  $440$   $\text{cm}^{-1}$  of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (upper part) and of the  $B_{1g}$ -like mode of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The solid lines describe anharmonic decay into two phonons.

phonon at  $440$   $\text{cm}^{-1}$  of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is shown for temperatures between  $300$  and  $10$  K. In the range from  $200$  K to  $T_c$ , the decrease in linewidth can be well described by a temperature-dependent anharmonic decay of the Raman-active phonon with frequency  $\omega_v$  and zero  $\mathbf{q}$  vector into two phonons with opposite  $\mathbf{q}$  vectors, each having a frequency close to  $\omega_v/2$ . The linewidth is then given by<sup>24</sup>

$$\gamma(\omega_0, T) = \gamma(\omega, 0)[1 + 2n(\omega_v/2)] + \text{const}, \quad (2)$$

where the constant stands for a temperature-independent contribution and  $n$  is the thermal occupation factor.

The solid lines in Fig. 2 are fits by Eq. (2) with  $\gamma(\omega, 0)$  as an adjustable parameter and they are seen to give an adequate description of the data above  $T_c$ . Below  $T_c$  the linewidth deviates significantly from that behavior. For  $T=10$  K the anomalous broadening amounts to more than  $5$   $\text{cm}^{-1}$  (full width at half maximum).

The lower part of Fig. 2 shows for comparison the linewidth of the  $B_{1g}$ -like mode of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$  as a function of temperature.<sup>25</sup> In this case no anomalies occur below  $T_c$ . Table I lists the experimental results for

TABLE I. Broadening  $\Delta\gamma$  (HWHM) of the  $B_{1g}$ -like and the  $A_g$  modes at  $440$   $\text{cm}^{-1}$  for different  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  from  $90$  to  $10$  K. All values given in  $\text{cm}^{-1}$ .

$R$	$\omega_v$	$\Delta\gamma$	$\omega_v$	$\Delta\gamma$
	$B_{1g}$		$A_g$	
Eu	309	0	a	
Y ( $^{18}\text{O}$ )	323	0.5	a	
Dy	338.5	2.4	433.5	1.8
Y ( $^{16}\text{O}$ )	344	3.7	434.5	2.7
Er	348	6.1	436	1.3
Tm	341.5	3.6	438	1.8

<sup>a</sup>Line too weak for precise work.

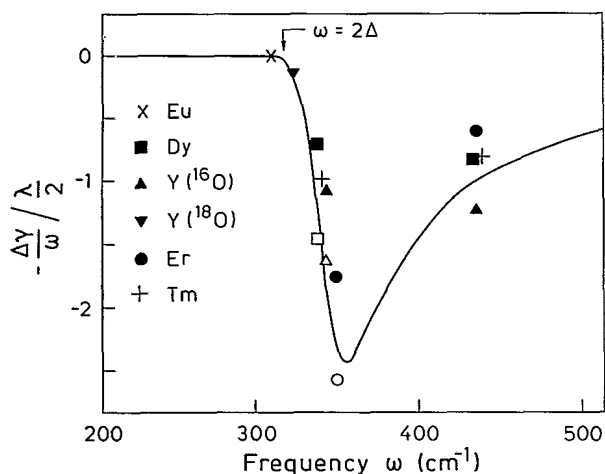


FIG. 3. Broadenings of two phonons between 90 and 10 K in  $RBa_2Cu_3O_{7-\delta}$  for various rare-earth elements  $R$ . The data have been normalized to  $\lambda_v \omega_v/2$  ( $\lambda_v=0.02$  and  $0.01$ , Ref. 19) which allows quantitative comparison with strong-coupling theory (solid line). The onset of broadening (arrow) defines the gap energy. For an explanation of open symbols, see text.

all  $R$  studied.

To compare the experimentally observed linewidth changes  $\Delta\gamma$  with the imaginary part of the polarization calculated by Zeyher and Zwicky,<sup>18</sup> we normalized the experimental  $\Delta\gamma$  by  $\lambda_v \omega_v/2$  since  $\Delta\gamma = (\lambda_v \omega_v/2) \times \text{Im}(\Pi/N)$  (with  $\Pi$  the polarization and  $N$  the density of states per spin). We plotted the normalized  $\Delta\gamma$  in Fig. 3 as a function of the respective phonon frequencies  $\omega_v$ . As coupling constants  $\lambda_v$  for the  $B_{1g}$ -like and the  $A_g$  modes we used values obtained by an LDA frozen-phonon calculation,  $\lambda_v=0.02$  ( $B_{1g}$ ) and  $\lambda_v=0.01$  ( $A_g$ ).<sup>19</sup> The solid curve is the theoretical result for  $T/T_c=0.16$  (i.e.,  $T=14$  K), an impurity scattering rate of  $\tau^{-1}=2\Delta$  (taken from recent ir-reflectivity measurements<sup>8</sup>), and assuming a gap of  $2\Delta=316$   $\text{cm}^{-1}$  (after Fig. 6 for Ref. 18).

The excellent agreement between theory and experiment allows us to draw three important conclusions: (1) Strong-coupling pairing seems to be applicable to the high- $T_c$  superconductors  $RBa_2Cu_3O_{7-\delta}$ . (2) The LDA-calculated coupling constants of the  $B_{1g}$ -like and  $A_g$  phonons have the correct magnitude. (3) The value for the gap, as seen by our phonons, can be confined to a very narrow interval.

The physical principle behind the determination of the gap from the broadening is evident: The gap must lie between the frequency of a phonon which exhibits no change in linewidth below  $T_c$  and the frequency of a phonon which has a frequency high enough to break a Cooper pair (i.e.,  $\omega_v > 2\Delta$ ) and thus shows broadening below  $T_c$  due to the opening of new relaxation channels. It turns out that this interval is defined extremely well in the  $RBa_2Cu_3O_{7-\delta}$  system. For the  $B_{1g}$ -like mode of  $EuBa_2Cu_3O_{7-\delta}$  (at  $309$   $\text{cm}^{-1}$ ),  $\Delta\gamma=0 \pm 0.25$   $\text{cm}^{-1}$ ,

whereas for the  $B_{1g}$ -like mode of  $YBa_2Cu_3^{18}O_{7-\delta}$  (at  $323$   $\text{cm}^{-1}$ ),  $\Delta\gamma=0.5 \pm 0.25$   $\text{cm}^{-1}$ . Therefore,  $309 < 2\Delta < 323$   $\text{cm}^{-1}$  and we conclude  $2\Delta/kT_c = 4.95 \pm 0.10$ .

The manifestation of a single sharp gap seems to be in contradiction with the nonvanishing low-energy background observed in Raman scattering, which is commonly attributed to electronic states inside the gap or to a gap distribution.<sup>1,2,26</sup> A gap distribution should smear out the curve in Fig. 3 considerably. It is possible that the phonons investigated here couple only to a certain region in  $k$  (or real) space where a single superconducting gap exists. The redistribution of electronic scattering below  $T_c$  would then result from an average over the Brillouin zone (or laser spot).

A second, low-energy gap, as was reported by Gurvitch *et al.*<sup>11</sup> ( $2\Delta=8$  meV, tunneling measurements), cannot be ruled out by our measurements because the distance of the second gap to the phonon frequencies is too large. The value for the high-energy gap of Ref. 11 ( $2\Delta=38$  meV) is in good agreement with our results.

If the real part of the self-energy is strongly dispersive, the measured linewidths below  $T_c$  may deviate from that given by the imaginary part. A correction is obtained by expanding the real part of the self-energy  $\Sigma_r(\omega)$  in the neighborhood of  $\omega_v$ . This leads to an experimentally observed linewidth  $\gamma'(\omega_v)$ , which is related to the true linewidth  $\gamma(\omega_v)$  by<sup>24</sup>

$$\gamma'(\omega_v) = \frac{\gamma(\omega_v)}{1 - [d\Sigma_r/d\omega]_{\omega_v}} \quad (3)$$

For  $T < 90$  K, the investigated phonons lie in a region where  $\Sigma_r$  varies strongly with frequency and Eq. (3) has to be used. In order to evaluate Eq. (3) we have taken values of  $d\Sigma_r/d\omega$  for  $RBa_2Cu_3O_{7-\delta}$  from Ref. 19. For the  $B_{1g}$ -like mode of  $EuBa_2Cu_3O_{7-\delta}$  the correction is negligible, because  $\Sigma_r(\omega)$  is flat in this frequency range. For the  $B_{1g}$ -like modes slightly below  $350$   $\text{cm}^{-1}$ ,  $d\Sigma_r/d\omega$  is negative ( $\approx -0.2$ ), which enhances the change in linewidth. For the  $A_g$  modes at  $440$   $\text{cm}^{-1}$ ,  $d\Sigma_r/d\omega$  is positive ( $< +0.1$ ), so that the change in linewidth is reduced somewhat. The overall shape of the curve in Fig. 3, however, remains the same. We have included in the figure the values for the  $B_{1g}$ -like modes of Dy, Y ( $^{16}O$ ), and Er  $Ba_2Cu_3O_{7-\delta}$  corrected with Eq. (3) by using  $d\Sigma_r/d\omega = -0.2$  (open symbols).

In conclusion, we have reported Raman measurements which pinpoint a superconducting gap: We obtain  $2\Delta/kT_c = 4.95 \pm 0.10$ . The anomalous linewidth increase below  $T_c$  of a mode as a function of its frequency can be described by the strong-coupling theory of Zeyher and Zwicky. The magnitude of the linewidth broadening is given by the electron-phonon coupling constant of the respective mode. The experimental values are reproduced well by coupling constants obtained by an LDA frozen-phonon calculation. However, we do not imply that the electron-phonon coupling alone can account for

the high transition temperature. Using coupling constants similar to those given above for all modes would give a  $\lambda_{\text{tot}}$  of around 0.6, much smaller than the value required by Zeyher and Zwicknagl ( $\lambda_{\text{tot}}=2.9$ ) to explain the observed  $T_c=92$  K. If only a subset of specific phonons were responsible for the superconductivity, they would have to have an even stronger coupling constant. However, regardless of the mechanism producing the gap  $2\Delta$  around  $316\text{ cm}^{-1}$  we can observe it through phonon self-energy effects (the electron-phonon coupling is not zero) provided it has a structure similar to that predicted by the BCS-Eliashberg theory.

We acknowledge expert technical help from H. Hirt, M. Siemers, and P. Wurster and financial support from the Bundesminister für Forschung und Technologie and the European Community.

<sup>1</sup>S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Rice, and D. M. Ginsberg, *Phys. Rev. B* **37**, 5920 (1988).

<sup>2</sup>R. Hackl, W. Gläser, P. Müller, D. Einzel, and K. Andres, *Phys. Rev. B* **38**, 7133 (1988).

<sup>3</sup>R. E. Glover, III, and M. Tinkham, *Phys. Rev.* **108**, 243 (1957).

<sup>4</sup>T. Timusk, S. L. Herr, K. Kamarás, C. D. Porter, D. B. Tanner, D. A. Bonn, J. D. Garrett, C. V. Stager, J. E. Greedan, and M. Reedyk, *Phys. Rev. B* **38**, 6683 (1988).

<sup>5</sup>G. A. Thomas, J. Orenstein, D. H. Rapkine, M. Capizzi, A. J. Millis, R. N. Bhatt, L. F. Schneemeyer, and J. V. Waszczak, *Phys. Rev. Lett.* **61**, 1313 (1988).

<sup>6</sup>L. Genzel, A. Wittlin, M. Bauer, M. Cardona, E. Schön-herr, and A. Simon, *Phys. Rev. B* **40**, 2170 (1989).

<sup>7</sup>R. T. Collins, Z. Schlesinger, F. Holtzberg, and C. Feild, *Phys. Rev. Lett.* **63**, 422 (1989).

<sup>8</sup>Z. Schlesinger, R. T. Collins, F. Holtzberg, C. Feild, S. H. Blanton, U. Welp, G. W. Crabtree, Y. Fang, and J. Z. Liu, *Phys. Rev. Lett.* **65**, 801 (1990).

<sup>9</sup>A. Fournel, I. Oujia, J. P. Sorbier, H. Noel, J. C. Levet, M.

Potel, and P. Gougeon, *Europhys. Lett.* **6**, 653 (1988).

<sup>10</sup>J. Geerk, X. X. Xi, and G. Linker, *Z. Phys. B* **73**, 329 (1988).

<sup>11</sup>M. Gurvitch, J. M. Valles, Jr., A. M. Cucolo, R. C. Dynes, J. P. Garno, L. F. Schneemeyer, and J. V. Waszczak, *Phys. Rev. Lett.* **63**, 1008 (1989).

<sup>12</sup>J.-M. Imer, F. Patthey, B. Dardel, W.-D. Schneider, Y. Baer, Y. Petroff, and A. Zettl, *Phys. Rev. Lett.* **62**, 336 (1989).

<sup>13</sup>W. W. Warren, Jr., R. E. Walstedt, G. F. Brennert, G. P. Espinosa, and J. P. Remeika, *Phys. Rev. Lett.* **59**, 1860 (1987).

<sup>14</sup>D. Brinkmann, *Physica (Amsterdam)* **153-155C**, 75 (1988).

<sup>15</sup>R. M. Macfarlane, H. J. Rosen, and H. Seki, *Solid State Commun.* **63**, 831 (1987).

<sup>16</sup>C. Thomsen, M. Cardona, B. Gegenheimer, R. Liu, and A. Simon, *Phys. Rev. B* **37**, 9860 (1988).

<sup>17</sup>T. Ruf, C. Thomsen, R. Liu, and M. Cardona, *Phys. Rev. B* **38**, 11985 (1988).

<sup>18</sup>R. Zeyher and G. Zwicknagl, *Z. Phys. B* **78**, 175 (1990).

<sup>19</sup>C. O. Rodriguez, A. I. Liechtenstein, I. I. Mazin, O. Jepsen, O. K. Andersen, and M. Methfessel, *Phys. Rev. B* **42**, 2692 (1990).

<sup>20</sup>C. Thomsen, M. Cardona, B. Friedl, C. O. Rodriguez, I. I. Mazin, and O. K. Andersen, *Solid State Commun.* **75**, 219 (1990).

<sup>21</sup>M. Cardona, R. Liu, C. Thomsen, M. Bauer, L. Genzel, W. König, A. Wittlin, U. Amador, M. Barahona, F. Fernández, C. Otero, and R. Sáez, *Solid State Commun.* **65**, 71 (1988).

<sup>22</sup>H. J. Rosen, R. M. Macfarlane, E. M. Engler, V. Y. Lee, and R. D. Jacowitz, *Phys. Rev. B* **38**, 2460 (1988).

<sup>23</sup>M. V. Klein, in *Light Scattering in Solids I*, edited by M. Cardona (Springer-Verlag, Heidelberg, 1983).

<sup>24</sup>J. Menéndez and M. Cardona, *Phys. Rev. B* **29**, 2051 (1984).

<sup>25</sup>Similar results were obtained by R. M. Macfarlane, M. C. Krantz, H. J. Rosen, and V. Y. Lee, *Physica (Amsterdam)* **162-164C**, 1091 (1989).

<sup>26</sup>S. L. Cooper, F. Slakey, M. V. Klein, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, *Phys. Rev. B* **38**, 11934 (1988).