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Infrared study of $R\mathrm{Ba_2Cu_4O_8}$ (R =Y,Er,Dy,Gd)

R. G. Buckley
The New Zealand Institute for Industrial Research, P.O. Box 31-310, Lower Hutt, New Zealand

M. Ziaei* and B. P. Clayman
Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

E. M. Haines
The New Zealand Institute for Industrial Research, P.O. Box 31-310, Lower Hutt, New Zealand

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Temperature-dependent far-infrared reflectivity of rare-earth substituted ceramic $R\mathrm{Ba_2Cu_4O_8}$ with R =Y, Er, Dy, and Gd is reported. The same number of modes are observed in the rare-earth substituted compounds as in previously reported $\mathrm{YBa_2Cu_4O_8}$ and, except for the Y–rare-earth mode, the shifts in the mode frequencies are small. The temperature-dependent behavior of the phonons and the electronic background in all the samples is also similar to earlier reports of $\mathrm{YBa_2Cu_4O_8}$. Modes near 310 and 500 $\mathrm{cm^{-1}}$ soften significantly with decreasing temperature beginning 30 or 40 K above the zero-resistance T_c. Other modes display little sensitivity to temperature. There is an enhancement in the reflectivity in the superconducting state relative to the normal state for frequencies less than 600 $\mathrm{cm^{-1}}$ that grows in magnitude rapidly below T_c. The spectral range of the enhancement is independent of temperature, rare-earth substitution, and T_c, a behavior that cannot be described by weak-coupling BCS theory.

I. INTRODUCTION

Infrared (IR) reflectance spectroscopy is a useful tool in the study of the lattice vibrations of curprate superconductors and their electronic properties in both the superconducting and normal states. Moreover, the temperature dependence of the phonon frequencies and linewidths can be employed to probe the electronic system. That a number of the phonons in these layered cuprates are coupled to the electronic system is illustrated by the anomalous broadening and softening at T_c of the Raman-active[1] 340-$\mathrm{cm^{-1}}$ phonon of $\mathrm{YBa_2Cu_3O_7}$ and the softening, again near T_c, of a number of the IR-active modes.[2] Inelastic neutron-scattering measurements have also demonstrated that phonons with nonzero wave vectors also soften at T_c.[3,4] These superconductivity-induced changes, in particular the softening of the 340-$\mathrm{cm^{-1}}$ Raman mode, have provided within strong-coupling theory an estimate of the superconducting gap.[1,5,6] Hastreiter and co-workers[7] have shown that the softening of the IR-active phonons can be understood within the same framework by including interband transitions in the theory.

An interesting recent observation[8] is that the temperature-dependent softening of the IR-active mode near 300 $\mathrm{cm^{-1}}$ occurs above T_c for oxygen-depleted $\mathrm{YBa_2Cu_3O_{7-\delta}}$ (δ=0.43 and 0.37) and $\mathrm{YBa_2Cu_4O_8}$ (1:2:4) which have hole concentrations on the $\mathrm{CuO_2}$ planes lower than the optimum required to maximize T_c. Moreover, Litvinchuk, Thomsen, and Cardona[8] have noted a correlation between the temperatures at which phonon softening and anomalies in the spin susceptibility occur, whether it is at T_c or significantly above T_c, and drew the conclusion that magnetic order (opening of a gap in the spin excitation spectrum) above T_c affects the phonon energy rather than the transition to superconductivity. Bucher *et al.*[9] have also noted for 1:2:4 a correlation in temperature between the deviation from the usual linear temperature-dependent behavior of the a-axis resistivity above T_c and the spin dynamics. Superconducting fluctuations above T_c have also been invoked to account for the observed mode softening.[10] There is considerable evidence in the literature that underdoped cuprates display fluctuation behavior above T_c.

In addition to information about the phonons, the electron system can also be probed directly by studying the temperature-dependent low-frequency reflectivity. The infrared reflectance of $\mathrm{YBa_2Cu_3O_7}$ (1:2:3) is anomalous, particularly at low hole doping, in both its frequency and temperature dependence. In the superconducting state there appears to be an absorption onset near 500 $\mathrm{cm^{-1}}$ whose magnitude is strongly temperature dependent particularly below T_c but which persists into the normal state.[11] Two approaches are usually considered in interpreting infrared data from superconducting cuprates.[12] First, in terms of two sets of charge carriers comprising a set of Drude-like free carriers and a set of bound carriers, or secondly, as a single carrier with a frequency-dependent scattering rate due to coupling between the carriers and optically inactive excitations, such as spin excitations. The first approach has been widely employed for superconducting cuprates,[12] including $\mathrm{Y_2Ba_4Cu_7O_{15}}$ (2:4:7),[13] and the latter derives some support in the light of the phonon softening discussed above, NMR data,[14] resistivity data,[9] and inelastic neutron-scattering[15] data for both 1:2:4 and underdoped 1:2:3. These measure-

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ments have all been linked to the opening of a gap in the spectrum of spin excitations above T_c.

Here we present the results of a temperature-dependent infrared reflectance study of ceramic samples of $RBa_2Cu_4O_8$, where R is Y, Er, Dy, and Gd. 1:2:4 is the third member of a homologous series of compounds, namely $R_2Ba_4Cu_{6+n}O_{14+n-\delta}$ with $n=0$, 1, and 2, with superconducting transition temperatures for $R=\mathrm{Y}$ near 92, 92, and 80 K, respectively.[16] These compounds are characterized by two copper-oxide substructures, a CuO_2 plane, and a $CuO_{1-\delta}$ chain of variable oxygen stoichiometry, and differ in that the chain structure in $n=0$ (1:2:3) is replaced by a double chain of fixed oxygen stoichiometry in $n=2$ (1:2:4). $n=1$ (2:4:7) is an ordered intergrowth of $n=0$ and 2. The structure of 1:2:4 is illustrated in Fig. 1. Electronic structure calculations[17,18] indicate that the extra chain in 1:2:4, when compared to 1:2:3, introduces differences which are largely restricted to the environment of the chain atoms. 1:2:4 has a fixed oxygen stoichiometry, is underdoped, and T_c can be raised by increasing the hole concentration on the planes, for instance, by substituting Ca^{2+} for Y^{3+}.[19] Rare-earth substitution for Y lowers T_c from 80 K to 75, 65, and 60 K for Er, Dy, and Gd, respectively.

The double-chain structure running parallel to the b axis in 1:2:4 results in structural asymmetry between the in-plane a and b directions that is also observed in the conductivity. The b-axis dc resistivity is about one-third of the a-axis resistivity and displays a typical metallic temperature dependence considered to be dominated by the conductivity of the chains. The a-axis resistivity has the linear temperature dependence typical of cuprate superconductors above about 200 K but it falls faster than linearly below this temperature. This anomalous behavior has been correlated with the opening of a spin gap on the planes of 1:2:4 which is underdoped. The c-axis resistivity has not been measured but would be expected to display a metallic temperature dependence similar to 1:2:3 but larger due to the higher density of carriers on the double chains. The phase diagram of the Y-Ba-Cu-O system indicates that 1:2:4 is adjacent to a liquidus only at very high pressures so that growing single crystals from the melt requires 600 atmospheres of oxygen pressure.[9] These high-pressure preparation conditions have restricted the size and availability of crystals so that to date the only reported IR measurements on single crystals are those of Bucher *et al.*[9] for frequencies greater than about 1500 cm^{-1}. They observe that the ab-plane anisotropy is preserved with the a- and b-axis plasma frequencies at 1.145 and 1.76 eV, respectively.

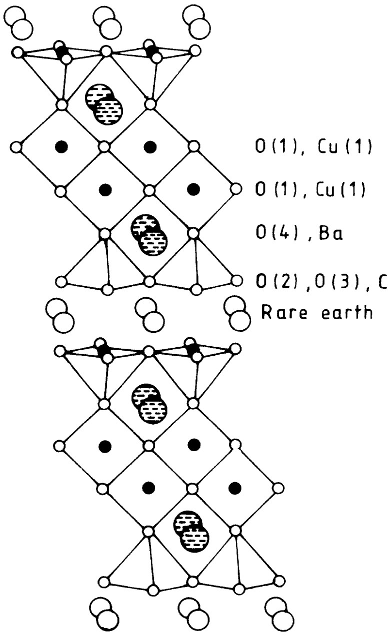

FIG. 1. Structure of 1:2:4. The small solid circles are copper, the small open circles oxygen, the large open circles yttrium, and the shaded circles barium.

Because of the small size of the available crystals far-infrared studies have been restricted to polycrystalline materials which are difficult to interpret.[8,20–24] For wavelengths much larger than the average crystal size, which is the present situation, the optical response is determined by some average of the three orthogonal components of the conductivity and without measuring them separately their relative contributions must be assumed. In a previous report[23] we used an effective medium approximation, along with assumptions regarding the contribution of these components, as a guide to understanding the temperature dependence of the conductivity of 1:2:4 and Ca-substituted 1:2:4 and we will follow the same procedure in Sec. III below.

To date a number of studies of the far-infrared reflectivity of ceramic Y-1:2:4 have been reported with general agreement on the assignment of the dominating features of the spectra.[8,20–24] In an earlier publication we assigned seven features in the measured spectra to the expected seven B_{1u} modes of 1:2:4. This is the same number predicted for 1:2:3, but when the spectra of the two compounds are compared, the IR modes associated with the chain structure differ. We observe the same number of modes in the rare-earth substituted compounds as Y-1:2:4, and except for the Y–rare-earth mode, at very nearly the same frequencies. The temperature dependence of the modes in Y-1:2:4 have also been published with the notable result that the strong mode near 310 cm^{-1} displays considerable softening (12 cm^{-1}) with decreasing temperature beginning about 30 K above the zero-resistance T_c. The mode at 500 cm^{-1} displays a smaller softening (2.5 cm^{-1}), again beginning above T_c. Rare-earth substituted compounds display the same behavior for both the 310- and 500-cm^{-1} modes suggesting that the anomalous softening of these modes is a general feature of underdoped $Y_2Ba_4Cu_{6+n}O_{14+n-\delta}$ superconductors. This result differs from the behavior reported for the Raman-active modes in rare-earth substituted 1:2:4.[25] In this case no modes were reported to soften unlike the behavior of the 340-cm^{-1} phonon in fully loaded 1:2:3. This mode is observed to soften at T_c, the degree depending on oxygen stoichiometry and diminishing as the oxygen content decreases.[5] Litvinchuk *et al.*[26] have recently reported IR spectra for Dy- and Ho-1:2:4 which are similar to the data discussed here. The spectral range of the enhancement in reflectivity below T_c is observed to be independent of rare-earth substitution, T_c, and temperature a behavior that is unlike weak-coupling BCS.

II. SAMPLE PREPARATION AND EXPERIMENT

Ceramic samples were prepared by first decomposing a stoichiometric mixture of oxides and nitrates at 700 °C for 30 min in air.[16] The partial melt that results ensures an intimate contact between the reactants and thus a better final product. This was followed by reacting the reground mixture at 930 °C in oxygen at 6 MPa for 3 days with repeated regrinding. The phase purity of the samples with larger rare-earth ions was improved by reacting at a slightly lower temperature, near 910 °C.

X-ray powder diffraction patterns (XRD) showed, in general, that the samples were nearly phase pure but the quality varied within the series. The Y-1:2:4 pattern was essentially phase pure, the Er pattern displayed some weak unidentified impurity lines, the Dy pattern displayed a small amorphous background, and the Gd pattern displayed a somewhat larger amorphous background. Lattice parameters for these samples have been reported earlier[25] and were found to agree closely with values in the literature.[27] As would be expected there is an increase in the size of the unit cell with increasing rare-earth ion size and it is interesting to note that the orthorhombic distortion drops by a factor of more than 2 when the rare-earth ion size is increased by 10%. It may be significant that for Dy and larger ions the a axis is equal to, or larger than, the a axis is tetragonal YBa$_2$Cu$_3$O$_6$ which suggests that oxygen may be able to occupy the interchain O(5) site. This would result in an increase in oxygen disorder and ultimately to the instability of 1:2:4 with respect to 1:2:3. This observation suggests that the integrity of the double chain is possibly being progressively lost with increasing ion size which would be consistent with problems we experienced in preparing phase-pure 1:2:4 with larger rare-earth ions.

IR reflectance spectra were measured on ceramic samples between 50 and 2000 cm^{-1} at 1-cm^{-1} resolution with a Bruker IFS-113v interferometer employing a pyroelectric detector. Temperature-dependent measurements were made between room temperature and 15 K with a flow-through cryostat. Because light scattering losses from the ceramic samples dominate the magnitude of the reflectivity we have simply taken the mode frequency as the frequency of the peak in the reflectivity spectra.

Four-terminal resistance measurements were performed between room temperature and 20 K. With an increase in ion size the superconducting transition temperature, T_c, is observed to decrease from about 80 to 60 K, with a tendency for the transition to broaden. This is typically observed in cuprate superconductors as the hole doping on the copper-oxide planes decreases.[28]

III. RESULTS AND DISCUSSION

A. Phonon spectra at room temperature

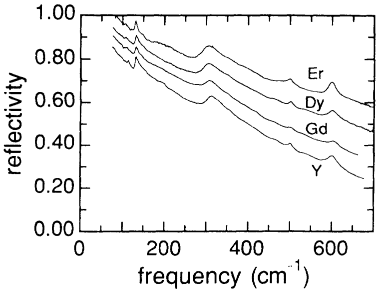

FIG. 2. Room-temperature IR reflectance of YBa$_2$Cu$_4$O$_8$, ErBa$_2$Cu$_4$O$_8$, DyBa$_2$Cu$_4$O$_8$, and GdBa$_2$Cu$_4$O$_8$ from 0 to 700 cm^{-1}. Note that the Y spectra have been displaced down by 5% and Dy and Er spectra have been displaced upwards by 5 and 10 %, respectively.

Displayed in Fig. 2 are the room-temperature infrared spectra of Y-, Er-, Dy-, and Gd- 1:2:4. The spectra of all three rare-earth substituted compounds are very similar to that reported for Y-1:2:4.[8,20–24] It is generally thought that the IR-active phonons, involving motion parallel to the highly conducting CuO$_2$ planes, are screened in these systems so that only the B_{1u} modes are observed. Group theory predicts seven B_{1u} modes[29] and five features can be identified in the spectra in Fig. 2 that are readily associated with vibrational modes near 110, 130, 310, 500, and 600 cm^{-1}. A sixth weak mode can be observed near 280 cm^{-1} in all the rare-earth substituted spectra similar to the mode observed in Y-1:2:4 and La-substituted 1:2:4.[21] As will be discussed in the next section an additional seventh mode can be observed in the spectra of Y-, Er-, and Gd-1:2:4. We have employed IR mode assignments made elsewhere[21] on the basis of lattice dynamic calculations[29] and by comparison with 1:2:3. Although there is general agreement in the literature regarding mode assignments the rather weak feature at 280 cm^{-1} has only been identified as a 1:2:4 mode by ourselves.[21,23]

Figure 3 displays for the five most prominent modes the shifts in mode frequency relative to Y-1:2:4 at room temperature plotted against the cube root of the cell

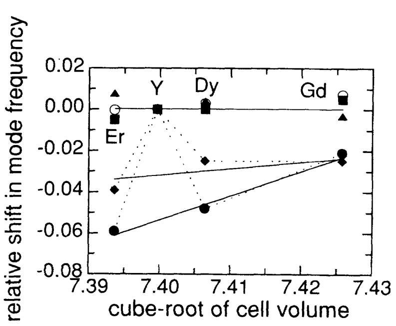

FIG. 3. Relative shifts at room temperature in the IR modes as a function of the cube root of the cell size showing that there are two distinct behaviors that depend on the atoms involved in each mode. Open circle, 600 cm^{-1}; solid triangles, 500 cm^{-1}; solid diamonds, 310 cm^{-1}; solid squares, 130 cm^{-1}; solid circle, 110 cm^{-1}. The solid lines demonstrate the linear shifts within the rare-earth series. The dashed lines connect all the points for the 110- and 310-cm^{-1} modes only.

volume. The shifts fall strongly into two classes, those with a shift of less than 1% (130, 500, and 600 cm^{-1}) and those with a shift greater than 2% (110 and 310 cm^{-1}). Relative to Y the shifts cannot be simply related to the expansion of the lattice but, as illustrated by the lines in Fig. 3, there is, within the rare-earth series, an approximately linear relationship between the shifts for the 110- and 310-cm^{-1} modes and the cube root of the cell volume. However, the observed hardening accompanying the expansion of the lattice indicates that the shift cannot simply be related to the dilation. Moreover, the shifts within the rare-earth series are too large to be accounted for by the change in mass. These observations imply that the shifts result largely from changes in the force constants associated with the substitution of Y by the rare-earth ion with the implication that this difference is related to the partially filled f shell of the rare-earth ions when compared to the lack of f electrons for Y. This is a rather interesting result as band-structure calculations usually assume that Y does not participate strongly in the bonding levels.[30,31] This picture would thus seem to be inappropriate for rare-earth substituted 1:2:4. Moreover, the different bonding of the rare-earth ions may alter the hole concentration on the $\mathrm{CuO_2}$ planes and thus account for the observed variation in T_c.

In seeking to understand the separation of the modes into two distinct classes it is instructive to discuss the modes in detail. The 130-cm^{-1} feature is a complex mode that involves all the atoms in the unit cell except the $\mathrm{CuO_2}$ plane oxygens. The mode at 500 cm^{-1} involves mainly motion of the double-chain O(1) oxygen but also significant motion of all the other oxygens and Y while the 600-cm^{-1} mode involves largely out-of-phase motion on the apical O(4) and chain O(1) oxygens. These three modes, which display little sensitivity to rare-earth substitution, are dominated by motion of the chain atoms. On the other hand, the modes at 110 and 310 cm^{-1} display significant shifts with rare-earth substitution. The mode at 110 cm^{-1} involves out-of-phase motion of Cu(2) and Ba while the 310-cm^{-1} mode involves motion of all the oxygens and Y. The mode at 280 cm^{-1} is too weak and too close to the 310-cm^{-1} mode for us to be confident of its dependence on rare-earth substitution. Based on expectations and similar to 1:2:3 we have previously[21,23] assigned it to involve solely motion on O(2) and O(3). With the exception of this latter mode, phonons which involve largely motion of the $\mathrm{CuO_2}$ plane atoms, Cu(2), O(2), and O(3), and the rare-earth atom display large shifts while the modes that have significant contributions from the double-chain atoms or O(4) are relatively insensitive to rare-earth substitution. The separation of the B_{1u} modes into two classes is broadly consistent with their assignments and understood, as noted above, in terms of the difference between the bonding of Y and the bonding of the rare-earth ions.

B. Temperature dependence of the phonons

The mode near 190 cm^{-1} in Y-1:2:4, which does not appear in any of the rare-earth substituted compounds, has been assigned to involve largely motion of Y and is clearly visible only below T_c. An equivalent mode would be expected for all the rare-earth compounds but at a lower frequency. Spectra for Y-, Er-, and Gd-1:2:4, recorded below T_c, are displayed in Fig. 4. In Er-1:2:4, and again below T_c; a weak broad feature is observed at 157 cm^{-1}. Assigning the 157-cm^{-1} mode to motion of Er seems reasonable given that this is close in frequency to the mode identified as involving largely Er motion in 1:2:3.[32] Two weak features at 147 and 164 cm^{-1} are visible in the Gd spectra and again by comparison with 1:2:3 the latter could be expected to be due to vibration of the Gd ion.[33] No comparable feature can be reliably associated with motion of the Dy ion although a mode would be expected near 160 cm^{-1},[32] as is observed by Litvinchuk *et al.*[26] The softening in frequency is not simply based on the increase in mass suggesting again that the force constants for bonding of Y and the rare-earth ions are different.

Figure 5 compares the temperature dependence of the spectral position of the 310-cm^{-1} mode and the resistance for all four samples. Clearly some temperature-dependent mode softening occurs above T_c. The resistance displays behavior similar to the a-axis resistivity reported for single crystal 1:2:4 in that the resistance is approximately linear in temperature down to about 200 K and then falls faster than linear dropping sharply to zero resistance at T_c in a manner suggestive of a three-dimensional superconducting transition. In a polycrystalline sample there are, of course, other contributions to the conductivity such as intergranular resistance which prevent a quantitative comparison. Bucher *et al.*[9] have shown experimentally that there is an approximate correlation between the temperature at which the resistivity deviates from linear behavior and the temperature at which a gap opens in the spectrum of spin excitations. Measurements of the spin relaxation rate in 1:2:4 indicate that this temperature is approximately 160 K, a little higher than the phonon softening temperature.

Turning now to the softening of the 310-cm^{-1} mode displayed in Fig. 5 it can be seen that the size of the softening measured between room temperature and 20 K is about 12 cm^{-1} for Y-1:2:4, close to reported values.[22,23] The 310-cm^{-1} mode also narrows consider-

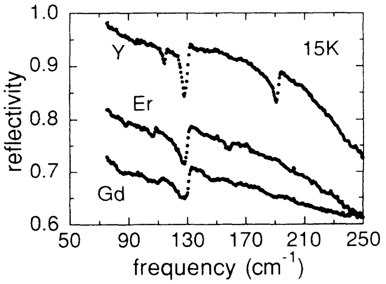

FIG. 4. Reflectance at 15 K for Y-, Er-, and Gd-1:2:4 illustrating, when compared to Fig. 2, the changing response of these low-frequency phonons to lowering the temperature below T_c. The Er and Gd spectra have been displaced downwards by 0.1 and 0.2, respectively, for clarity.

ably as the temperature drops below T_c. For Er- and Gd-1:2:4 the softening is about 8 cm^{-1} while for Dy-1:2:4 the softening is about 6 cm^{-1}. The value for Dy-1:2:4 is the same as that reported by Litvinchuk *et al.*[26] The softening sets in below 120 K and up to 50% of the softening occurs above the zero-resistance T_c. Given that the equivalent mode also exists in 1:2:3 and 2:4:7 and has been observed to soften in underdoped 1:2:3 (Ref. 8) with and without atomic substitution,[34,35] Y-2:4:7,[26] Y-1:2:4,[22] Ca-substituted Y-1:2:4 (Ref. 23) and now rare-earth substituted 1:2:4 this softening appears to be a general feature of the underdoped $\text{Y}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n-\delta}$ system.

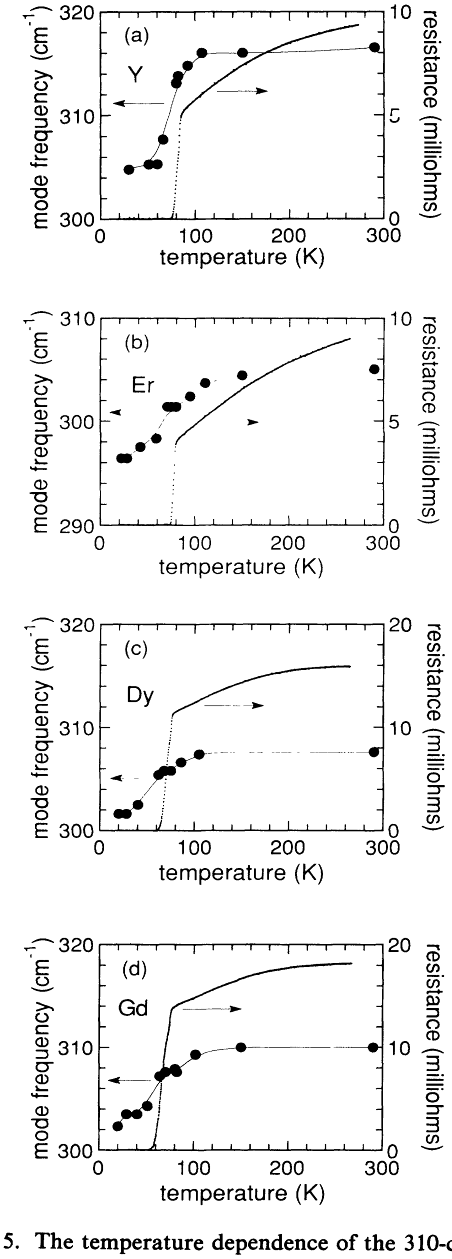

FIG. 5. The temperature dependence of the 310-cm^{-1} mode for Y and the rare-earth substitutions. Errors in the mode position are ±1 cm^{-1}. The line is simply to guide the eye. Also shown is the temperature-dependent resistance, demonstrating that the phonon softening begins in all cases above the zero-resistance T_c. The unusual nonlinear temperature-dependent behavior of the resistance is evident for each sample.

The temperature-dependent softening of the 500-cm^{-1} mode is illustrated for Dy- and Y-1:2:4 in Fig. 6 and is about 2.5 cm^{-1} for all the samples studied. Again the softening begins above T_c. It is interesting that this mode is dominated by motion of the double-chain O(1) oxygen but does have a significant contribution from the plane oxygens so that the smaller but similar response to the 310 cm^{-1} is as expected.

The mode at 280 cm^{-1} is too weak to determine its temperature dependence. The rare-earth mode, seen at 190 cm^{-1} in Y-1:2:4, is visible only below T_c and the other B_{1u} modes harden with decreasing temperature but the variation is in general weak.

A number of authors have argued[20,22] that the IR mode softening can be understood in terms of Zeyher and Zwicknagl's[6] strong-coupling theory when extended to include interband transitions. The problem with this approach is that the theory does not apply above T_c where significant softening is observed. Obhi and co-workers[24] have argued that the softening is caused by superconducting fluctuations which would be expected to increase as the hole doping is reduced in these anisotropic systems. There is evidence from both heat capacity and resistivity measurements[36] on 1:2:3 that as the hole doping is decreased, by reducing the oxygen stoichiometry, that this material becomes more two-dimensional (2D) and that superconducting fluctuations appear to contribute increasingly at temperatures above the zero resistance T_c. Recently[26] a link has been made between the onset temperature of mode softening and ordering of the spin system for Y-1:2:4. Moreover, Loram *et al.*[36] have suggested that large 2D superconducting fluctuations may account for the observed spin-gap effects, at least in 1:2:3. Clearly further experiments are required to sort out this interesting question.

C. Temperature dependence of the electronic background

Figure 7 displays, for Y and rare-earth substituted 1:2:4, the reflectivity ratios of spectra recorded below T_c

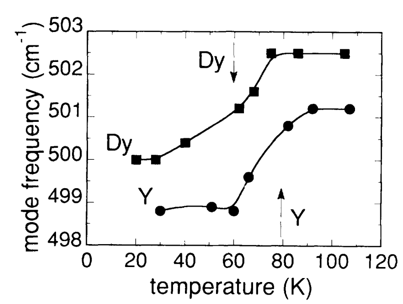

FIG. 6. The temperature dependence of the 500-cm^{-1} mode for Y and Dy displaying softening near T_c. The other rare-earth substitutions, namely, Er and Gd, soften by a similar amount. The zero-resistance T_c is indicated by the upward and downward arrows for Y and Dy, respectively. The softening is observed to begin above T_c. The lines are a guide to the eye. The absolute error in mode position is ±1 cm^{-1} and the relative error between points is ±0.2 cm^{-1}.

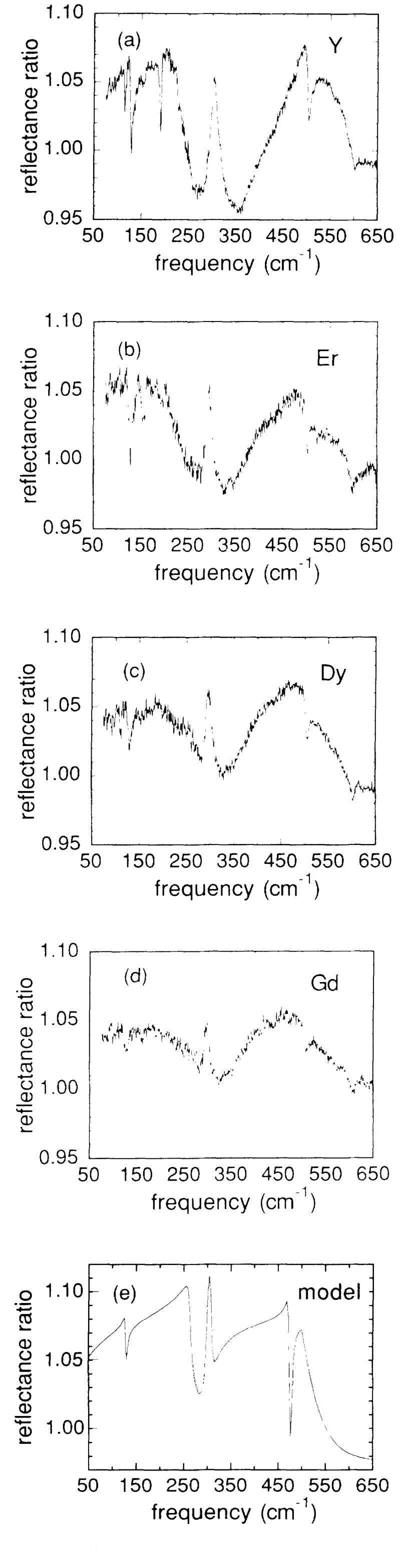

FIG. 7. Reflectivity ratios for Y and rare-earth substituted 1:2:4 illustrating that the enhancement in reflectivity is localized at two frequency ranges near 175 and 500 cm^{-1} separated by a strongly temperature-dependent phonon at 310 cm^{-1}. The ratios are generated by dividing spectra collected at 20 K (except for Y which was collected at 30 K) by spectra recorded at 92, 80, 85, and 82 K for (a) Y, (b) Er, (c) Dy, and (d) Gd, respectively. Also displayed (e) is the result of the model calculation discussed in the text.

to a spectrum near but above T_c. For all samples there are two spectral regions of strong reflectivity enhancement associated with the electronic background that grows as the temperature is decreased below T_c, saturating at about 30 K. They are centered near 175 and 500 cm^{-1} and appear to be asymmetric although this is hard to define due to the complication of superimposed phonons. Broadly the behavior of the rare-earth substituted compounds is independent of composition and very similar to that observed for Y although the magnitude of the response alters with rare-earth substitution. The difference in the magnitude of the enhancement between samples does not correlate with other trends within the series, such as ion size, and may be related to sample quality.

The observed enhancement in the reflectivity below T_c is the behavior expected when the real part of the conductivity decreases in association with the formation of a superconducting gap. We have previously demonstrated[23] that for Y-1:2:4 the appearance of two regions of enhancement in the reflectivity below T_c can be qualitatively modeled with an effective medium approach incorporating a single BCS-like gap near 500 cm^{-1} and a strongly temperature-dependent phonon at 300 cm^{-1}. To interpret the measured reflectivity ratios using this model it is important to make some reasonable estimates of the three orthogonal components of the conductivity, i.e., the conductivity parallel to the *a*-, *b*-, and *c*-crystallographic axes. As noted in the Introduction, polarization-dependent reflectivity measurements of 1:2:4 have not been made on single crystals in the far IR so we have been guided in estimating the three components by measurements made on 1:2:3. An enhancement in the reflectivity at temperatures below T_c is observed in the IR spectra of single crystals of 1:2:3 measured with the electric vector parallel to the *a* and *b* axes. Measurements made with the electric vector parallel to the *a* axis, which largely probes the response of the carriers on the CuO_2 planes, demonstrate that the conductivity decreases with decreasing temperature below T_c as expected for a transition to the superconducting state.[11,38] On the other hand, measurements with the electric vector parallel to the *b* axis (parallel to the chains) have been analyzed in terms of a separate plane and chain contribution where the chain contribution to the conductivity increases with decreasing temperature down to 6 K (Ref. 38) typical of metallic conductivity. The plane contribution to the *b*-axis conductivity is observed to decrease below T_c consistent with a superconducting transition on the CuO_2 planes.[11,38] The metallic conductivity measured with the electric vector parallel to the *c* axis in 1:2:3 is very low[37] and a number of phonons are readily apparent. As noted above the IR measurements above about 1500 cm^{-1} on 1:2:4 by Bucher *et al.*[13] indicate that 1:2:4 displays a similar asymmetry in the *ab*-plane conductivity as 1:2:3 and the observation of phonons in ceramic samples indicates that the electronic component parallel to the *c* axis is also low. On the basis of the similarity between 1:2:3 and 1:2:4 we have assumed in our modeling of the temperature-dependent reflectivity of ceramic 1:2:4 that the enhancement results largely from the response of carriers on the $\mathrm{CuO_2}$ planes to the superconducting transition and that we an ignore any temperature-dependent changes of the carrier systems on the chains or parallel to the c axis.

The effective medium model assumes that the polycrystalline samples used consist of randomly oriented uniaxial crystallites much smaller than the wavelength and that the effective conductivity is composed of two components: a term from Leplae theory below T_c describing the conductivity within the $\mathrm{CuO_2}$ planes and a Drude function above T_c and a second term describing conductivity parallel to the c axis that is insulating and simply consists of a series of Lorentz oscillators and a frequency-independent dielectric constant. The model, with parameters appropriate for Y-1:2:4, is compared with the reflectivity ratios in Fig. 7. As is illustrated, and as we reported earlier,[23] this model qualitatively describes the data well. In particular, the double-peaked enhancement is accounted for if we assume, as is observed in Fig. 5, that the phonon at 310 $\mathrm{cm^{-1}}$ softens and narrows with decreasing temperature near T_c. Differences in the shape of the ratios for the rare-earth substituted ions are then related largely to the differences to the softening and narrowing of this mode. Other structure in the ratio results from changes in the electronic background and the temperature-dependent narrowing of the phonons other than the 310-$\mathrm{cm^{-1}}$ mode. As the spectral range of the enhancement is the same as for all the samples the model describes their behavior with the same gap parameter.

Figure 7 illustrates a striking feature of the data, namely, that the spectral range of the enhancement (≤ 600 $\mathrm{cm^{-1}}$) is independent of rare-earth ion and thus T_c. Another significant aspect, not seen in Fig. 7, is that the spectral range of the reflectivity enhancement is also independent of temperature. This is demonstrated for Y-1:2:4 in Fig. 8(a). On the other hand, the magnitude of the enhancement is temperature dependent and as illustrated in Fig. 8(b) is the same for Y and all the rare-earth substitutions. Since the enhancement is defined relative to the reflectivity at T_c, Fig. 8(b) may not show the actual enhancement relative to the normal state but it does illustrate the common temperature dependence of the enhancement. Although the effective-medium model described above accounts for the temperature-dependent enhancement in a qualitative way the BCS theory employed cannot account for the lack of temperature dependence of the spectral range of the reflectivity enhancement nor the independence of T_c. These results are similar to measurements on single crystals of 1:2:3 (Refs. 11 and 38) where the spectral range of the measured reflectivity enhancement for light polarized parallel to the a axis is observed to be independent of temperature and oxygen stoichiometry and consequently T_c. Thus, if the response of the carriers on the $\mathrm{CuO_2}$ planes of ceramic 1:2:4 solely determines the reflectivity enhancement then the condensation into superconducting state is clearly non-BCS-like.

In developing the assumptions used in the modeling described above we have not only been influenced by the spectra of the ceramic samples but also guided by measurements of the reflectivity of single crystals of $\mathrm{YBa_2Cu_3O_7}$ and found that the observed temperature-dependent reflectivity enhancement in ceramic 1:2:4 could be understood in terms of a single but non-BCS response of the carriers on the $\mathrm{CuO_2}$ planes to the superconducting transition. The justification is largely in terms of the similarities of the structure and the spectral range over which an enhancement can be observed. In contrast it is interesting to note that the spectral range over which an enhancement in reflectivity is observed in ceramic 1:2:3 is below 400 $\mathrm{cm^{-1}}$ (Ref. 39), a smaller spectral range than that observed in single crystals of $\mathrm{YBa_2Cu_3O_7}$ and less optimally doped ceramic 1:2:4. Moreover, recent measurements by Homes *et al.*[40] of the c-axis reflectivity of underdoped 1:2:3 ($T_c = 63$ K) display an unidentified broad reflectivity enhancement below T_c centered around 450 $\mathrm{cm^{-1}}$ similar to the high-frequency enhancement seen in less than optimally doped 1:2:4. In an unrelated superconducting cuprate,[41] $\mathrm{Tl_2Ba_2Ca_2Cu_3O_{10}}$, a similar reflectivity enhancement around 450 $\mathrm{cm^{-1}}$ is also observed at temperatures below T_c. Thus, given the existence of these features and the difficulties of separating the three orthogonal components of the conductivity from measurements on ceramic samples the reflectivity enhancement observed in 1:2:4 may well result from the temperature-dependent response of carriers other than those on the $\mathrm{CuO_2}$ planes assumed in the effective medium modeling discussed above. It seems that the answer to the question of whether the reflectivity enhancement below 600 $\mathrm{cm^{-1}}$ in ceramic 1:2:4 results from one or two responses will need to wait until either appropriate single crystals or c-axis-oriented thin films become available.

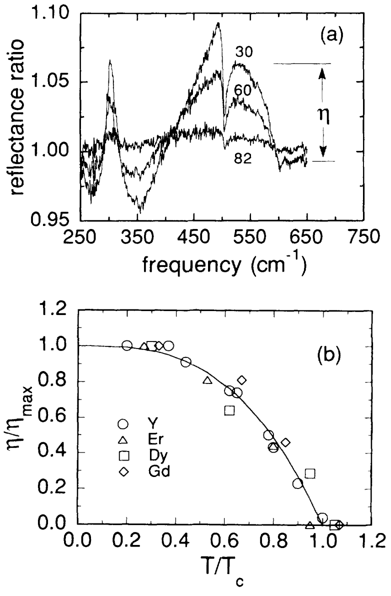

FIG. 8. (a) Reflectivity ratios for Y-1:2:4 at a number of temperatures as illustrated in the figure divided by a spectra collected at 92 K. (b) Normalized η [defined in (a)] plotted against reduced temperature demonstrating that the magnitude of the reflectivity enhancement has a temperature dependence that is common to Y and all the rare-earth substitutions. The line is simply a guide to the eye.

IV. CONCLUSION

We have reported the temperature-dependent IR reflectance of a series of ceramic rare-earth substituted 1:2:4 compounds and compared the results with earlier measurements on Y-1:2:4. Qualitatively the data are very similar to Y-1:2:4. The modes near 310 and 500 cm^{-1} soften significantly as the temperature is lowered through T_c. The softening begins 30–40 K above T_c, a behavior that appears to be a general feature of the underdoped $Y_2Ba_4Cu_{6+n}O_{14+n-\delta}$ system and has, in part, been correlated by others to either the opening of a spin gap or to superconducting fluctuations. At low temperatures a temperature-dependent enhancement in reflectivity is observed for frequencies below 600 cm^{-1}. The spectral range of the enhancement is independent of temperature, rare-earth substitution and T_c, behavior that is inconsistent with a weak-coupling BCS superconductor.

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[*] Present address: Northern Lights College, Box 1000, Fort St. John, BC V1J 6K1, Canada.

[1] B. Friedl, C. Thomsen, and M. Cardona, Phys. Rev. Lett. **65**, 915 (1990).

[2] L. Genzel, A. Wittlin, M. Bauer, M. Cardona, E. Schönherr, and A. Simon, Phys. Rev. B **40**, 2170 (1989).

[3] N. Pyka, W. Reichardt, L. Pintschovius, G. Engel, J. Rossat-Mignod, and J. Y. Henry, Phys. Rev. Lett. **70**, 1457 (1993).

[4] H. A. Mook, B. C. Chakoumakos, M. Mostoller, A. T. Boothroyd, and D. McK Paul, Phys. Rev. Lett. **69**, 2272 (1992).

[5] E. Altendorf, J. C. Irwin, R. Liang, and W. N. Hardy, Phys. Rev. B **45**, 7551 (1992).

[6] R. Zeyher and G. Zwicknagl, Z. Phys. B **78**, 175 (1990).

[7] G. Hastreiter, U. Hofmann, J. Keller, and K. F. Renk, Solid State Commun. **76**, 1015 (1990).

[8] A. P. Litvinchuk, C. Thomsen, and M. Cardona, Solid State Commun. **83**, 343 (1992).

[9] B. Bucher, P. Steiner, J. Karpinski, E. Kaldis, and P. Wachter, Phys. Rev. Lett. **70**, 2012 (1993).

[10] H. S. Obhi and E. K. H. Salje, J. Phys.: Condens. Matter **4**, 195 (1992).

[11] L. D. Rotter, Z. Schlesinger, R. T. Collins, F. Holtzberg, C. Field, U. W. Welp, G. W. Crabtree, J. Z. Liu, Y. Fang, K. G. Vandervoort, and S. Fleshler, Phys. Rev. Lett. **67**, 2741 (1991); Z. Schlesinger, R. T. Collins, F. Holtzberg, C. Field, S. H. Blanton, U. Welp, G. W. Crabtree, Y. Fang, and J. Z. Liu, *ibid.* **65**, 801 (1990); J. Orenstein, G. A. Thomas, A. J. Millis, S. L. Cooper, D. H. Rapkine, T. Timusk, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. B **42**, 6342 (1990).

[12] D. B. Tanner and T. Timusk, in *Physical Properties of High Temperature Superconductors III,* edited by D. M. Ginsberg (Singapore, World Scientific, 1992), p. 363.

[13] B. Bucher, J. Karpinski, E. Kaldis, and P. Wachter, Phys. Rev. B **45**, 3026 (1992).

[14] H. Zimmermann, M. Mali, I. Mangelschots, J. Roos, L. Pauli, D. Brinkmann, J. Karpinski, S. Rusiecki, and E. Kaldis, J. Less-Common. Met. **164-165**, 138 (1990).

[15] J. Rossat-Mignod, L. P. Regnault, C. Vettier, P. Bourges, P. Burlet, J. Bossy, J. Y. Henry, and G. Lapertot, Physica C **185-189**, 86 (1991).

[16] R. G. Buckley, D. M. Pooke, J. L. Tallon, M. R. Presland, N. E. Flower, M. P. Staines, H. L. Johnson, M. Meylan, G. V. M. Williams, and M. Bowden, Physica C **174**, 383 (1991).

[17] T. Oguchi, T. Sasaki, and K. Terakura, Physica C **172**, 277 (1990).

[18] J. Yu, K. T. Park, and A. J. Freeman, Physica C **172**, 467 (1991).

[19] R. G. Buckley, J. L. Tallon, D. M. Pooke, and M. R. Presland, Physica C **165**, 391 (1990).

[20] M. E. Ziaei, B. P. Clayman, R. G. Buckley, and M. P. Staines, Physica C **176**, 242 (1991).

[21] R. G. Buckley, M. P. Staines, and H. J. Trodahl, Physica C **193**, 33 (1992).

[22] A. P. Litvinchuk, C. Thomsen, P. Murugaraj, and M. Cardona, Z. Phys. B **86**, 329 (1992).

[23] M. E. Ziaei, B. P. Clayman, R. G. Buckley, and E. M. Haines, Phys. Rev. B **46**, 10 997 (1992).

[24] H. S. Obhi, E. K. H. Salje, and T. Miyatake, J. Phys: Condens. Matter **4**, 10 367 (1992).

[25] H. J. Trodahl, R. G. Buckley, and C. K. Subramaniam, Phys. Rev. B **47**, 11 354 (1993).

[26] A. P. Litvinchuk, C. Thomsen, M. Cardona, J. Karpinski, E. Kaldis, and S. Rusiecki, Z. Phys. B **92**, 9 (1993).

[27] D. E. Morris, J. H. Nickel, J. Y. T. Wei, N. G. Asmar, J. S. Scott, U. M. Scheven, C. T. Hultgren, A. G. Markelz, J. E. Post, P. J. Heaney, O. R. Veblen, and R. M. Hazen, Phys. Rev. B **39**, 7347 (1989).

[28] J. L. Tallon, R. G. Buckley, E. M. Haines, M. R. Presland, A. Mawdsley, N. E. Flower, and J. Loram, Physica C **185-189**, 855 (1991).

[29] K. K. Yim, J. Oitmaa, and M. M. Elcombe, Solid State Commun. **77**, 385 (1991).

[30] W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).

[31] H. Krakauer, W. E. Pickett, and R. E. Cohen, J. Supercond. **1**, 111 (1988).

[32] M. Cardona, R. Liu, C. Thomsen, M. Bauer, L. Genzel, W. König, A. Wittlin, U. Amador, M. Barahona, F. Fernandez, C. Otero, and R. Saez, Solid State Commun. **65**, 71 (1988).

[33] M. Cardona, L. Genzel, R. Liu, A. Wittlin, H. Mattausch, F. Garcia-Alvarado, and E. Garcia-Gonzalez, Solid State Commun. **64**, 727 (1987).

[34] R. Gajic, J. Shutzmann, J. Betz, T. Zetterer, H. H. Otto, P. E. Obermayer, and K. F. Renk, Solid State Commun. **78**, 65 (1991).

[35] R. Gajic, M. J. Konstantinovic, Z. V. Popovic, W. Konig, S. Zec, and I. Bradaric, Solid State Commun. **81**, 85 (1992).

[36] J. W. Loram, J. R. Cooper, J. M. Wheatley, K. A. Mirza, and

R. S. Liu, Philos. Mag. B **65**, 1405 (1992).

[37] Z. Schlesinger, R. T. Collins, F. Holtzberg, C. Field, G. Koren, and A. Gupta, Phys. Rev. B **41**, 11 237 (1990).

[38] J. Schützmann, B. Gorshunov, K. F. Renk, J. Münzel, A. Zibold, H. P. Geserich, A. Erb, and G. Müller-Vogt, Phys. Rev. B **46**, 512 (1992).

[39] W. Ose, P. E. Overmayer, H. H. Otto, T. Zetterer, H. Lengfellner, J. Keller, and K. F. Renk, Z. Phys. B **70**, 307 (1988).

[40] C. C. Homes, T. Timusk, R. Liang, D. A. Bonn, and W. N. Hardy, Phys. Rev. Lett. **71**, 1645 (1993).

[41] T. Zetterer, M. Franz, J. Schützmann, W. Ose, H. H. Otto, and K. F. Renk, Phys. Rev. B **41**, 9499 (1990).