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Optical study of the superconductor-nonsuperconductor transition in $(L_1,\mathrm{Ce})_2(\mathrm{Ba},L_2)_2\mathrm{Cu}_3\mathrm{O}_{8+z}$ (L_1 and L_2 = rare earths)

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In order to clarify the origin of electronic change in $(L_1,\mathrm{Ce})_2(\mathrm{Ba},L_2)_2\mathrm{Cu}_3\mathrm{O}_{8+z}$ (L_1L_2 2:2:3) (L_1 and L_2 are rare-earth atoms), we have grown single crystals of EuEu 2:2:3, EuLa 2:2:3, and ErLa 2:2:3, and measured their Raman-scattering spectra and optical-reflectivity spectra. Comparing the spectra for superconducting EuEu 2:2:3 and nonsuperconducting ErLa 2:2:3, we can see no clear difference between them, whereas the reduced samples of EuEu 2:2:3 show a systematic change in both the Raman and the reflectivity spectra, as the oxygen content decreases. This implies that the hole concentration in nonsuperconducting ErLa 2:2:3 is large enough to realize superconductivity. It strongly suggests the possibility of superconductivity destruction for reasons other than a decrease in hole concentration, such as local lattice distortion.

I. INTRODUCTION

It is well known that the superconducting transition temperature (T_c) varies significantly with hole concentration in the high-T_c superconducting cuprates (HTSC).[1] Thus, hole concentration is surely a key parameter in determining the T_c value in individual material, although it cannot explain the difference in T_c among various HTSC. On the T_c determination factor, there have been a number of proposals such as the spacing between the CuO_2 planes,[2] the bond-valence sum,[3] the Madelung energy difference,[4] etc. Although superconducting carrier density n_s divided by effective mass m^*, which is determined by the muon relaxation rate, seems to scale well with T_c,[5] we cannot find any normal-state parameter which scales with n_s/m^*. Therefore, also in this case, the physical background dominating the T_c value is not clear.

Therefore, when T_c was found to decrease in a material, in most cases its origin has been attributed to a lack (or an excess) of hole concentration. Also in $(L_1,\mathrm{Ce})_2(\mathrm{Ba},L_2)_2\mathrm{Cu}_3\mathrm{O}_{8+z}$, L_1 and L_2 being rare-earth atoms (L_1L_2 2:2:3), where T_c decreases systematically with decreasing ionic radius of the rare-earth atom L_1,[6] it was first suspected that the reduction in T_c was caused by the reduction of hole concentration. However, chemical analysis of the oxygen content showed a negative result for such a simple speculation,[6] and the following intensive study of transport properties provided no evidence of a lack of hole concentration.[7,8]

The 2:2:3 compound, $(L_1,\mathrm{Ce})_2(\mathrm{Ba},L_2)_2\mathrm{Cu}_3\mathrm{O}_{8+z}$ is a relatively new family among a number of HTSC's.[9] Although its crystal structure is quite similar to $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_7$, the so-called 1:2:3 compound, T_c of 40 K for the 2:2:3 compound, is only half of that (90 K) for the 1:2:3 compound. The main differences in crystal structure between the 1:2:3 and the 2:2:3 compounds are the following: One is the existence of fluorite layers in the 2:2:3 compound instead of Y (or rare-earth elements) layers in the 1:2:3 compound. The other is that the oxygen around Cu(1) is deficient isotropically (50% occupancy). Thus, the crystal structure is tetragonal in the 2:2:3 compound, while in the 1:2:3 compound they are deficient only in the a direction, resulting in an orthorhombic structure with the CuO chain. The single phase of the 2:2:3 compound can be obtained for various rare-earth elements L, which is a common property in compounds with the fluorite layers. By changing the L atom, we can change the lattice parameters systematically.

As described above, it has been found that when an L atom changes from Eu to Er in the Periodic Table, T_c decreases and finally disappears. The purpose of this study is to know what happens in the electronic state at the time of this dramatic change. According to the systematic studies on transport properties for polycrystalline $(L_{2/3}\mathrm{Ce}_{1/3})_2(\mathrm{Ba}_{1/3}\mathrm{Sr}_{1/3}\mathrm{La}_{1/3})_2\mathrm{Cu}_3\mathrm{O}_{8+z}$ (L = Eu, Dy, Y, and Ho),[7,8] in spite of the drastic change in T_c with the decreasing ionic radius of the L atom, the resistivity above 100 K does not change significantly, but its value remains at the same order. The values of the Hall coefficient R_H above 100 K are the same among the materials, except a little larger value for the Ho compound. All these results strongly suggest that the hole concentrations are not substantially different among the materials with various L atoms. However, it has been pointed out that R_H does not necessarily indicate the inverse of carrier concentration in the case of HTSC. Interpretation of the anomalous temperature dependence of R_H is also an unsettled problem. Furthermore, since there are two Cu sites in the 2:2:3 structure, it is not clear whether R_H is responsible for the electronic state only in the Cu(2)-O plane.

In this study, to investigate the electronic change in the CuO_2 plane of this system, we have grown single crystals of $(L_1,Ce)_2(Ba,L_2)_2Cu_3O_{8+z}$ for various rare-earth atoms L_1 and L_2. The crystals for L_1L_2=HoLa, YLa, and DyLa were so small that we could measure only the lattice parameters and the composition ratios, while the crystals for L_1L_2=EuEu, EuLa, and ErLa were large enough for measurement of the Raman-scattering spectra and the optical reflectivity spectra. Focusing on the change in hole concentration at the transition from the superconducting to nonsuperconducting phase, we have studied the Raman spectra and the reflectivity spectra of these crystals. For comparison purposes, we also prepared the reduced samples of EuEu 2:2:3 with various oxygen contents to measure the spectral change derived from the change in hole concentration in the CuO_2 plane. In contrast to the systematic change in both Raman-scattering and optical reflectivity spectrum for a series of reduced EuEu 2:2:3, we cannot find any clear spectral difference between the superconducting EuEu 2:2:3/EuLa 2:2:3 and the nonsuperconducting ErLa 2:2:3. This implies that the hole concentration in the nonsuperconducting ErLa 2:2:3 is large enough to realize superconductivity. It strongly suggests the possibility of superconductivity destruction due to facts other than the decrease in hole concentration, such as, for example, the local lattice distortion.

II. EXPERIMENT

A. Sample preparation and characterization

The single crystals of EuEu 2:2:3 were grown by a CuO flux method. The details are described in Ref. 10. For other materials including the La atom, the nominal composition as well as the preparation process is a little different from that of EuEu 2:2:3. For the crystal growth of ErLa 2:2:3, the powder of 99.9% pure Er_2O_3, CeO_2, $BaCO_3$, La_2O_3, and CuO were mixed with the mole ratio of 2:2:4:1:12, that is, the ratio of $(Er_{2/3}Ce_{1/3})_2(Ba_{2/3}La_{1/3})_2Cu_3O_{8+z}$ and CuO being 1:1, and were melted in a Pt crucible at 1500 °C. After melting, it was slowly cooled down from 1350 °C to 1100 °C at the rate of 2 °C/h. As-grown crystals were annealed at 600 °C under the oxygen partial pressure of 400 atm by a hot isostatic pressing (HIP) technique.

The obtained crystals were thin plates with a typical size of $0.5\times0.5\times0.05$ mm^3. The shiny surface was confirmed to be an ab plane in the tetragonal symmetry by an x-ray Laue photograph. The lattice parameters

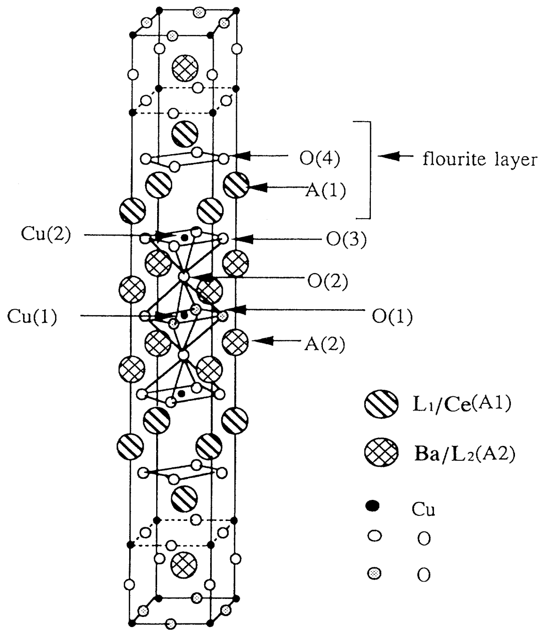

FIG. 1. Schematic picture of unit cell for $(L_1,Ce)_2(Ba,L_2)_2Cu_3O_{8+z}$.

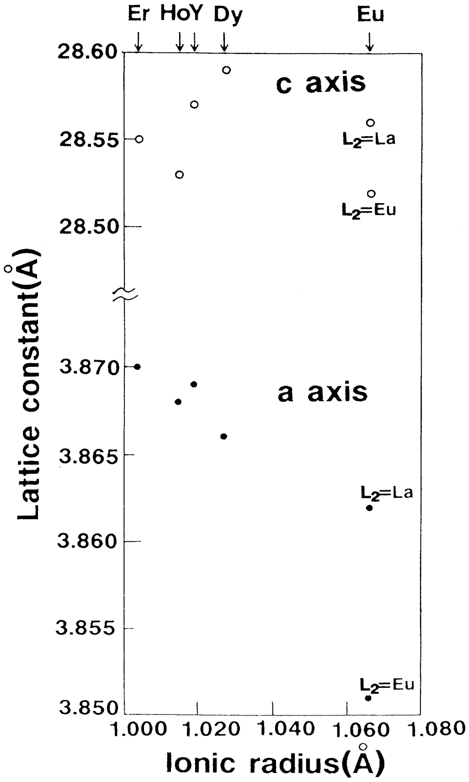

FIG. 2. Lattice parameters of grown crystals L_1L_2 2:2:3 for various rare-earth atoms L_1 and L_2, determined by x-ray-diffraction measurement using a four-circle x-ray diffractometer.

TABLE I. Composition ratios (at %) of the cations analyzed by EPMA, chemical formulas, and average Cu valences for the grown L_1L_2 2:2:3 crystals. The chemical formulas were expected from the composition ratios, assuming that the composition sum of all the cations other than Cu is 4. The average Cu valences were estimated from the composition ratios and/or the chemical formulas, assuming that the oxygen content $8+z$ is equal to 9.

L_1L_2	L_1	L_2	Ba	Ce	Cu	Pt	Chemical formula	Average Cu valence
EuEu	8.33		6.75	2.62	13.8	0.150	$(Eu_{0.704}Ce_{0.296})_2(Ba_{0.763}Eu_{0.237})_2Cu_{3.11}O_{8+z}$	+2.23
EuLa	7.92	4.77	6.19	1.99	17.4	0.086	$(Eu_{0.733}Ce_{0.184}La_{0.083})_2(Ba_{0.640}La_{0.360})_2Cu_{3.23}O_{8+z}$	+2.30
DyLa	6.98	8.34	6.44	1.54	17.3	0.749	$(Dy_{0.599}Ce_{0.132}La_{0.269})_2(Ba_{0.553}La_{0.447})_2Cu_{2.98}O_{8+z}$	+2.28
YLa	6.22	9.30	6.69	2.09	18.2	0.641	$(Y_{0.512}Ce_{0.172}La_{0.316})_2(Ba_{0.551}La_{0.449})_2Cu_{2.99}O_{8+z}$	+2.25
HoLa	5.00	9.71	6.50	3.03	18.1	0.373	$(Ho_{0.412}Ce_{0.250}La_{0.338})_2(Ba_{0.537}La_{0.463})_2Cu_{2.99}O_{8+z}$	+2.19
ErLa	4.72	10.8	6.59	2.18	17.8	0.945	$(Er_{0.388}Ce_{0.179}La_{0.433})_2(Ba_{0.542}La_{0.458})_2Cu_{2.92}O_{8+1}$	+2.24

were determined by an x-ray-diffraction measurement using a four-circle x-ray diffractometer. The results are plotted in Fig. 1.

The compositions in the obtained crystals were analyzed by an electron-probe-microanalysis (EPMA) technique. The results are summarized in Table I. Although the composition of EuEu 2:2:3 is close to the nominal one, i.e., $(Eu_{2/3}Ce_{1/3})_2(Ba_{2/3}Eu_{1/3})_3Cu_3O_{8+z}$, the composition ratio of Er to Ce and/or Ba to La in ErLa 2:2:3 is far from 2/1. In the latter case, the La atom with a large ionic radius is excessly substituted, that is, La occupies not only at the $A(1)$ site but also the $A(2)$ site in Fig. 2. This is probably in order to release the lattice distortion due to the occupation of the Er atom with a small ionic radius.

The dc magnetic susceptibility was measured by a SQUID magnetometer, in the magnetic field of 10*Oe* perpendicular to the plane. As shown in Fig. 3, the crystals of EuEu 2:2:3 and EuLa 2:2:3 exhibited superconductivity with $T_c=28$ and 20 K, respectively, whereas ErLa 2:2:3 did not show any superconductivity down to 4.2 K.

To compare the effect of a change of rare-earth atoms on the electronic state with that of a change in the oxygen content, we prepared samples of EuEu 2:2:3 with various oxygen contents by annealing the fully oxygenated crystals in the N_2 atmosphere for 2 days at various temperatures. The annealing temperatures were determined, based on the results of thermal gravimetry analysis (TGA) in N_2 atmosphere as shown in Fig. 4. After annealing the samples in N_2 up to 600 °C at the rate of 5 °C/min, the sample's weight decreased 0.45%, which corresponds to the reduction of oxygen content from $z=1$ to 0.74. The amount of decrease in the oxygen content with increasing temperature is less than that in YBCO. It means that in the 2:2:3 compounds the small amount of oxygen loss destroys the superconductivity. By reducing the samples at each temperature, we have obtained the crystals with various oxygen contents and thus with various T_c. The temperature dependence of magnetic susceptibility for these samples is shown in Fig. 5.

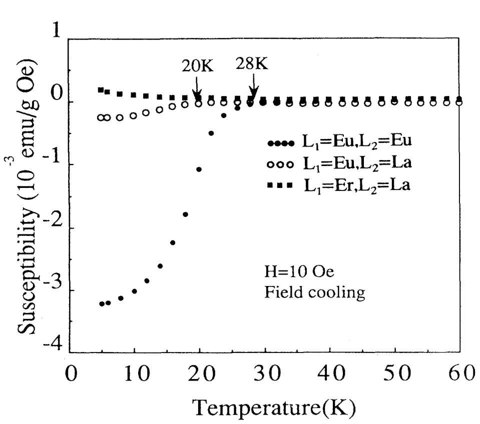

FIG. 3. Temperature dependence of magnetic susceptibility for EuEu 2:2:3, EuLa 2:2:3 and ErLa 2:2:3 single crystals with a magnetic field of 10*Oe*.

B. Optical measurements

The Raman-scattering spectra were measured in a backscattering configuration, using the 5145Å beam from an Ar laser as an excitation light. The incident beam with a power of 50 mW was focused on the sample surface with a diameter of 0.1 mm. The scattered light was monochromized by a double monochromator and detected by a photon counting detector.

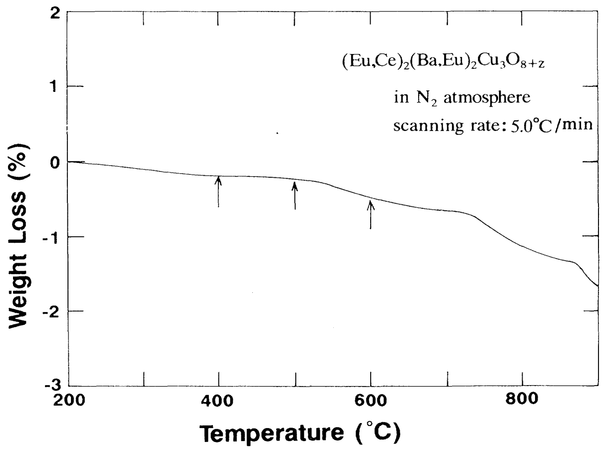

FIG. 4. Thermal gravimetry analysis curve in a N_2 atmosphere for fully oxygenated EuEu 2:2:3 crystals. The temperatures indicated by the arrows were chosen as the N_2 annealing temperatures for the reduction procedure.

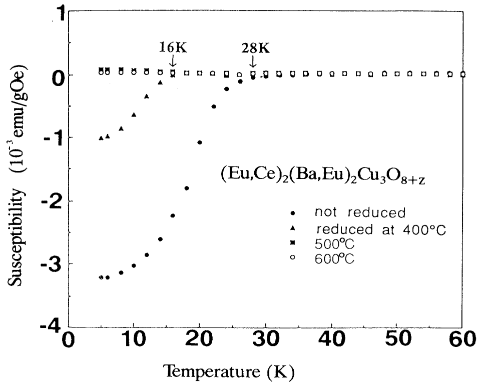

FIG. 5. Temperature dependence of magnetic susceptibility for EuEu 2:2:3 crystals reduced at various temperatures and thus with various oxygen contents.

The optical reflectivity spectra were measured by a Fourier-transformation-type spectrometer with a microscope in the infrared region and by a grating-type spectrometer in the visible and ultraviolet regions. The shiny as-grown surfaces were measured with the polarization of $E \perp c$. A gold-evaporated glass was used as a reference.

III. EXPERIMENTAL RESULTS

A. Raman-scattering spectra

Since we have previously reported on the phonon Raman-scattering spectra of the 2:2:3 compound in detail,[11] here we focus on the higher-energy scattering. From the phonon scattering spectrum we can reconfirm the orientation of the crystal axes. Figure 6 shows the room-temperature Raman spectra for the strongly reduced EuEu 2:2:3 with both A_{1g} and B_{1g} symmetry.

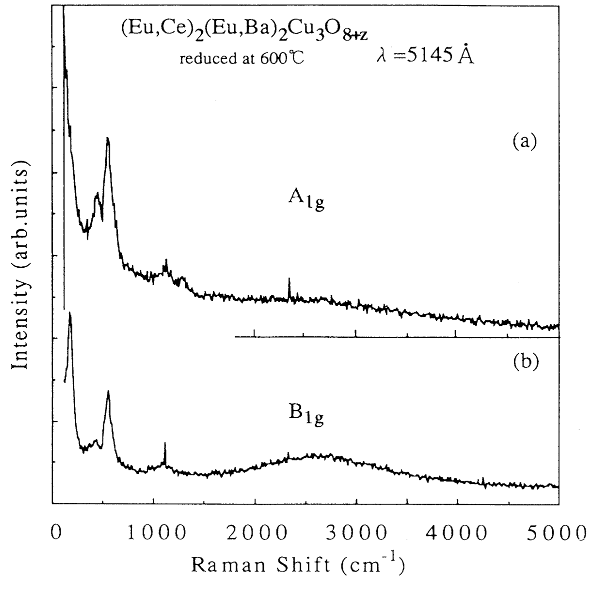

FIG. 6. Polarized Raman-scattering spectra of EuEu 2:2:3 reduced at 600 °C with A_{1g} and B_{1g} symmetry.

Only in the B_{1g} spectrum can we observe a broad peak centered at 2580 cm^{-1}, which is assigned to a two-magnon scattering peak due to the two-dimensional antiferromagnetic ordering. The magnon peak energy is close to that in YBa$_2$Cu$_3$O$_{6.1}$.[12] The exchange energy is estimated to be 960 cm^{-1}, assuming that the magnon peak energy corresponds to $2.7J$.

When the oxygen content increases, the intensity of this magnon peak decreases, shifting its center of gravity towards the lower energy, as shown in Fig. 7. For the highest oxygen content, i.e., the highest hole concentration with maximum T_c, no peak is seen except for the phonon scattering peaks. This spectral change implies that the doped holes destroy the antiferromagnetic ordering within the CuO$_2$ plane. A similar doping effect on the magnon scattering spectrum is observed in the other hole-doped cuprates such as La$_{2-x}$Sr$_x$CuO$_4$ (Ref. 13) and YBa$_2$Cu$_3$O$_y$.[12] By contrast, in the electron-doped cuprates such as Pr$_{2-x}$Ce$_x$CuO$_4$ the magnon scattering peak remains at the same energy although its intensity reduces with increasing electron concentration.[14] Therefore, it may be concluded that the behavior of the magnon scattering peak observed in this work is a common feature in a hole-doped HTSC. The difference in magnon behavior between a hole-doped and an electron-doped system may be attributed to the difference between a frustration and a dilution of spin ordering, as pointed out by Tomeno *et al.*[14]

Figure 8 shows the B_{1g} spectra for the oxygenated ErLa 2:2:3, EuLa 2:2:3, and EuEu 2:2:3. All the spectra

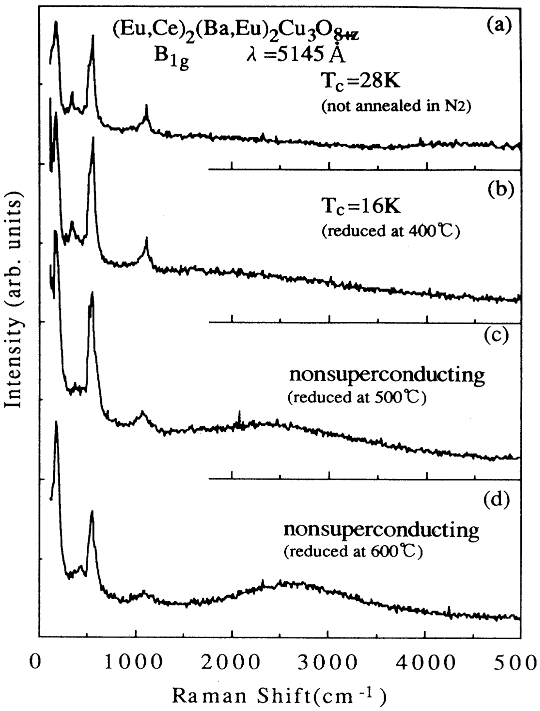

FIG. 7. B_{1g} Raman-scattering spectra for the EuEu 2:2:3 crystal not annealed (a), reduced at 400 °C (b), 500 °C (c), and 600 °C in N$_2$ atmosphere (d).

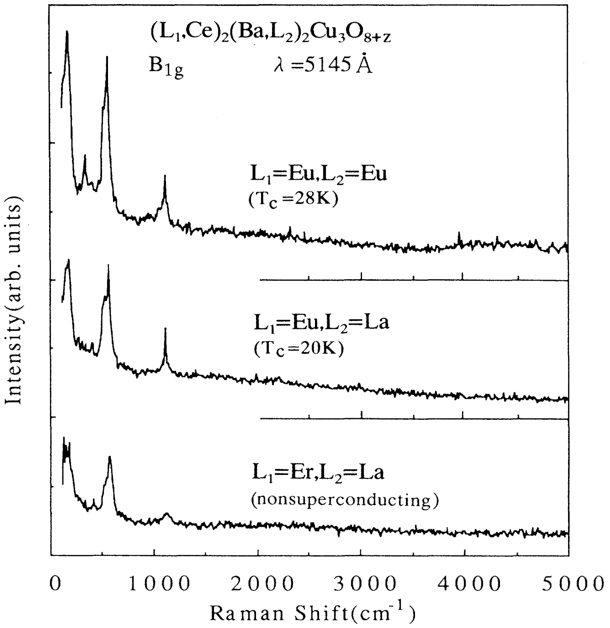

FIG. 8. B_{1g} Raman-scattering spectra for EuEu 2:2:3, EuLa 2:2:3, and ErLa 2:2:3 crystals annealed under high oxygen partial pressure.

have no peak above 1300 cm^{-1}. Comparing this result with Fig. 6, it is concluded that there is sufficient oxygen and thus sufficient holes in the CuO_2 planes of all these compounds, as suggested by the preceding Coulometric analysis for the ceramic samples. This indicates that the nonsuperconductivity of ErLa 2:2:3 does not originate from the lack of hole concentration.

Figure 9 shows the B_{1g} Raman spectra for ErLa 2:2:3 at low temperatures. In spite of a semiconductive temperature dependence of dc resistivity, there is no clear magnon peak in the Raman spectrum, indicating the existence of sufficient holes within the plane. The origin of a slight bump around 1700 cm^{-1} is not clear. It may be related to the restoration of a part of magnetic ordering due to the carrier localization.

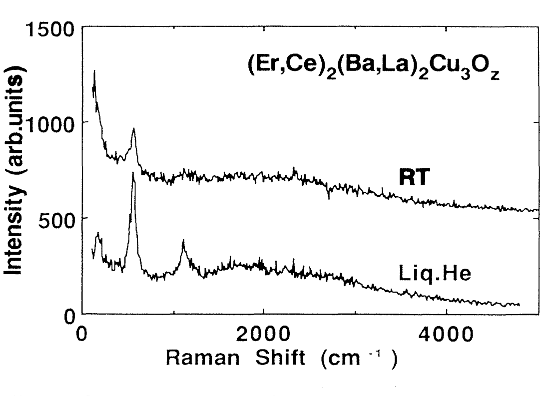

FIG. 9. B_{1g} Raman-scattering spectra of ErLa 2:2:3 measured at room temperature and liquid-He temperature. Since the temperature was monitored at the sample holder position, the actual sample temperature is expected to be 20 or 30 K higher than the monitored temperature.

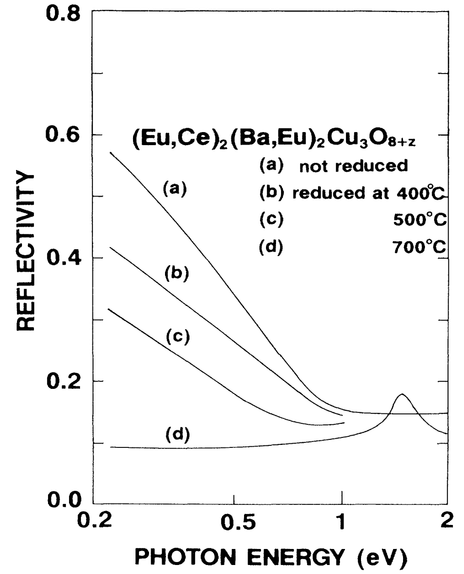

FIG. 10. Optical reflectivity spectra for EuEu 2:2:3 crystals not reduced (a), reduced at 400 °C (b), 500 °C (c), and 700 °C (d) in a N_2 atmosphere. Light was polarized within the *ab* plane ($E \perp c$).

B. Optical reflectivity spectra

The room-temperature reflectivity spectra of EuEu 2:2:3 are shown in Fig. 10 for various oxygen contents. Spectral reproducibility on the samples was excellent. Four crystals from the two different crucibles showed quite similar spectra to that in Fig. 10. For the most strongly reduced sample, i.e., the sample with the lowest hole concentration, the reflectivity is low and the spec-

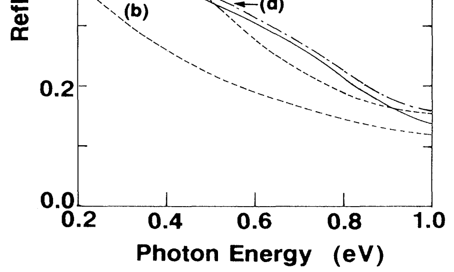

FIG. 11. Optical reflectivity spectra for fully oxygenated EuLa 2:2:3 and ErLa 2:2:3 with $E \perp c$. For comparison, the spectra for two superconducting EuEu 2:2:3 crystals [curves (a) and (b) in Fig. 10] are shown by dashed lines.

trum is almost flat from the far-infrared to the near-infrared region, which indicates that the sample is an insulator. The peak at 1.5 eV is associated with a charge-transfer (CT) excitation from the O 2*p* to Cu 3*d* orbital, which is commonly observed in all the parent insulators of HTSC.[15]

When the oxygen content increases, i.e., the hole doping proceeds, the CT excitation peak disappears and the reflectivity in the lower-energy region grows up, forming a reflectivity edge around 1 eV. Such a spectral change is a common doping effect on the in-plane spectrum among the HTSC.[16] Thus, it turns out that the value of in-plane reflectivity in the infrared region can be a measure of the doping level within the CuO_2 plane.

Figure 11 shows the room-temperature reflectivity spectra for superconducting EuLa 2:2:3 and nonsuperconducting ErLa 2:2:3, compared with the spectra for EuEu 2:2:3 in Fig. 10. These two spectra are quite similar to each other. The infrared reflectivity is high enough to be regarded as a metal; it is comparable to that of superconducting EuEu 2:2:3 with $T_c = 28$ K and is rather higher than that of lightly reduced EuEu 2:2:3 with $T_c = 16$ K. Also from this result we can judge that the hole concentration in ErLa 2:2:3 is large enough to realize superconductivity, which is consistent with the results of a Raman-scattering measurement.

However, concerning the detailed spectral profile, there remain some problems such as why the reflectivity of ErLa 2:2:3 and EuLa 2:2:3, as ω decreases, rises more rapidly in the near-infrared region and slows down in the far-infrared region, and why the reflectivity of ErLa 2:2:3 above 1 eV is lower than that of EuLa 2:2:3. This tendency of reflectivity saturation in the far-infrared region may be related to the low dc conductivity at low temperatures. The similarity between the spectra for ErLa 2:2:3 and EuLa 2:2:3 may indicate the possibility that the observed spectrum of EuLa 2:2:3 is dominated by a nonsuperconducting fraction of the crystal. However, this fact does not affect the above statement that the infrared reflectivity for the nonsuperconducting 2:2:3 compound is as high as that for superconducting one.

IV. DISCUSSION

From the results of the Raman-scattering spectra as well as the optical reflectivity spectra, it is concluded that the hole concentration in ErLa 2:2:3 with $T_c = 0$ K is not much smaller than that in the superconducting EuEu 2:2:3 and EuLa 2:2:3, but the carriers in the former compound localize at lower temperatures for some reason. Carrier localization at lower temperature is expected to be observed in an optical spectrum in the extremely far-infrared region. Since the crystal sizes are too small for resistivity measurement as well as far-infrared optical measurement at low temperatures, we could not directly observe the localization behavior for our crystals. However, the present optical results on the single crystals are consistent with the previous results of the Coulometric measurement and higher-temperature transport properties (resistivity, Hall coefficient, and Seebeck coefficient) for ceramic samples,[6–8] which indicate no clear difference in the doped hole concentration between the high-T_c EuEu 2:2:3 and the low-T_c, or nonsuperconducting YLa 2:2:3 and ErLa 2:2:3.

The present result is a striking contrast to the reflectivity spectra for $Pb_2Sr_2LCu_3O_8$, L being a rare earth (PbL 2:2:1:3).[17] In the PbL 2:2:1:3 system, the reflectivity decreases systematically from the superconducting PbDy 2:2:1:3 to the semiconducting PbPr 2:2:1:3. Therefore, it is clear that the semiconducting behavior of PbL 2:2:1:3 with a smaller element L, originates from a low hole concentration due to the cation deficiency.[18]

Other examples which show a similar systematic change in T_c with the change in the rare earth L are $Bi_2Sr_2(L,Ce)_2Cu_2O_{10+y}$ (Bi 2:2:2:2) (Ref. 19) and $(La,L,Sr)_2CuO_{4+y}$ (T^* 2:1:4).[20] It should be noted that in both of them the fluorite layers are included in a formula unit as in the 2:2:3 compound. Unfortunately, there is no intensive study on the single crystals for these two systems. Thus, in this case it is difficult to draw a definite conclusion that the decrease in T_c by changing the rare-earth atom is not caused by a decrease in hole concentration.

Next, we discuss several possible candidates for the origin of the T_c decrease in the 2:2:3 system. The first one is a structural phase transformation such as that observed in $La_{1.875}Ba_{0.125}CuO_4$,[21] where the metal-to-insulator transition at 60 K, accompanied with the structural phase transformation from the high-temperature-orthorhombic to the low-temperature-tetragonal phase, is closely related to the band filling of 1/8.[22] In the 2:2:3 system, we have measured the x-ray-diffraction pattern for the nonsuperconducting HoLa 2:2:3 ceramics at low temperature. The result showed no structural phase transformation down to 20 K.

The systematic change in lattice parameters is expected for the change in the rare-earth atom. In fact, such a systematic change in the lattice parameter *a* was observed in a previous study for the ceramics samples where the composition ratio was fixed.[6] However, in the present work, we obtained the crystals with more La content for the sample with a smaller ion L_1, as shown in the EPMA results of Table I. As a result, the lattice parameter *a* increases with the decreasing ionic radius of the L_1 atom as shown in Table I, which is the opposite tendency to the preceding ceramic data. This result implies that the change in the electronic properties does not depend on simple contraction or expansion of the lattice. Comparing the neutron-diffraction data for superconducting NdNd 2:2:3 and nonsuperconducting HoLa 2:2:3, Ichinose *et al.* suggested that the decrease of the distance *d* between the CuO_2 plane and the fluorite layer may be the origin of the T_c disappearance in HoLa 2:2:3.[23] Although there is no neutron-diffraction data for our single crystals, we expect that the distance *d* is larger in the nonsuperconducting ErLa 2:2:3 than in the superconducting EuEu 2:2:3, because both the lattice parameters (*a* and *c*) are larger in the former than in the latter. Therefore, the decrease in *d* cannot be an origin of nonsuperconductivity for ErLa 2:2:3 in this work.

The change in the Madelung energy and/or the bond-valence sum, which is one of the good parameters to determine the T_c value, is also a less possible candidate in the present case. This is because these parameters strongly depend on the structure parameters while the previous ceramic samples and the single crystals in this work have different structure parameters owing to different composition ratios but show similar electronic properties.

The most plausible candidate for the origin of the T_c decrease is a local distortion of the lattice around the fluorite layers. It is known that a fluorite-type structure AB_2 is stable when the ionic radius ratio r_A/r_B is larger than 0.73.[24] In the case of ceramic samples $(L_{2/3}Ce_{1/3})_2(Ba_{1/3}Sr_{1/3}La_{1/3})_2Cu_3O_{8+z}$, this ratio for the virtual ion $(L_{2/3}Ce_{1/3})$ is smaller than 0.73 for Dy, Y, Ho, and Er. Recently, Ikegawa *et al.* have measured the temperature dependence of the Seebeck coefficient and Hall coefficient for polycrystalline 2:2:3 samples. Comparing the results with that of T^* 2:1:4 compounds, they suggest that a disorder potential exists in the nonsuperconducting 2:2:3 compound and point out that the lattice distortion around the fluorite layers may induce this disorder potential.[8] In the case of single crystals, due to the requirement of structural stability, the La atom with a larger ionic radius occupies the A_1 site for the sample with a smaller L_1 atom. Due to this compensation for reduction of the A_1 site ionic size, the average ion size of the A_1 site atom becomes large enough for the construction of the 2:2:3 structure. However, the occupation of the large La atom and the small Er atom at the same site may introduce an additional local distortion which produces a disordered potential for holes within the CuO_2 plane and localizes the holes at a lower temperature.

A concrete form of disorder is beyond the scope of this work. It may be associated with the oxygen ordering in the CuO_2 plane which was observed by pulse neutron measurement,[25] or it may be another microscopic disorder which cannot be detected by experimental techniques based on the lattice periodicity.

The phenomenon observed here, the superconductivity destruction due to some local lattice distortion, may be related with the mysterious nonsuperconductivity in other materials, for example, in the metallic $Bi_2Sr_2CuO_y$ crystal with very low resistivity.[26] It might put a constraint on the mechanism of high-T_c superconductivity.

V. CONCLUSION

The single crystals of $(L,Ce)_2(Ba,L')_2Cu_3O_{8+z}$ for LL'=ErLa, EuLa, and EuEu were successfully grown. By annealing them under high oxygen partial pressure, the crystals of EuEu 2:2:3 and EuLa 2:2:3 exhibited superconductivity, whereas ErLa 2:2:3 did not, as expected from the previously reported results for the ceramic samples.

The differences in lattice parameters and composition among these crystals can be consistently understood by assuming that the La-atom occupation at the A_1 site increases as the ionic radius of rare earth at the A_1 site decreases, which is forced by the structural instability in the fluorite layer for small rare earth.

The Raman-scattering spectra and the optical reflectivity spectra were measured for the crystals of these three compounds as well as the lower T_c EuEu 2:2:3, reduced in N_2 atmosphere. In the reduced samples of EuEu 2:2:3, both the Raman-scattering spectrum and the optical reflectivity spectrum change, as commonly observed in the doping effect on all HTSC. However, the Raman spectrum and the optical reflectivity spectrum for nonsuperconducting ErLa 2:2:3 are not much different from those for superconducting EuEu 2:2:3 and EuLa 2:2:3. This implies that the hole concentration in ErLa 2:2:3 is not much different from that in EuEu 2:2:3 and EuLa 2:2:3. It strongly suggests that superconductivity destruction in ErLa 2:2:3 is not due to the reduction of hole concentration within the plane. Among the several possible origins for this superconductivity destruction, the local distortion around the fluorite layers introduced by the small rare-earth atom is most plausible.

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