Is $Nd_{2-x}Ce_xCuO_4$ a High-Temperature Superconductor?

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(Received 27 January 1995)

Single-crystalline $Nd_{1.84}Ce_{0.16}CuO_4$ with a superconducting transition temperature of 19.3 K has been studied above and below T_c using polarized Raman scattering. Electronic, crystal-field, and vibrational excitations have been detected. In the superconducting state, the formation of an almost isotropic gap 2Δ is observed which varies between 4.1 and 4.9 in units of kT_c. This indicates that $Nd_{1.84}Ce_{0.16}CuO_4$ is different from the other cuprate systems.

PACS numbers: 74.25.Gz, 74.72.Hs, 78.30.Er

Apart from the unexpectedly low superconducting transition temperature, $Nd_{2-x}Ce_xCuO_4$ (NCCO), along with the La_2CuO_4 family, seems optimally suited for systematic studies, since the whole phase diagram can be accessed easily by appropriate doping. It is therefore considered as one of the model systems for the high-T_c compounds. However, in addition to the low T_c, there are several other properties which do not fit into the established picture. In contrast to the other cuprates, the charge carriers are probably electrons [1]. The in-plane normal-state resistivity $\rho_{a\text{-}b}(T)$ varies almost quadratically [2] and not linearly with temperature. The temperature dependence of the penetration depth [3] and the tunneling conductance below T_c [4] are closer to classical superconducting behavior than in any other high-T_c material. In addition, the electron-phonon spectral function $\alpha^2F(\omega)$ could be obtained and was found to be in fair agreement with the generalized phonon density of states measured by neutron scattering [4]. From the latter results there arise basically two questions: Is the superconducting ground state significantly different from that of other cuprates and, secondly, can we get some idea of how electron-electron coupling works in this material class? In the hole-doped systems the mechanism of superconductivity is not at all clear, but the results from several independent experiments can be interpreted with an energy gap which depends strongly on the momentum $\mathbf{k}$ and which may even have a reduced symmetry [5]. It is a challenge to find an answer for NCCO since the measurement of gap anisotropies within the copper-oxygen plane is a nontrivial task using traditional methods. Among other problems the resolution of angle-resolved photoemission spectroscopy (ARPES) is, at the moment, of the same size as the expected gap energy and therefore hinders a measurement similar to that in $Bi_2Sr_2CaCu_2O_8$ [6]. Partly due to the short coherence length, directional electron tunneling into high-T_c superconductors does not reveal consistent results to date and quantum interference experiments such as for $YBa_2Cu_3O_7$ [7] do not exist for NCCO to our knowledge. We therefore tried to get some more insight into the structure of the energy gap of this system by electronic Raman scattering, since according to recent work a $\mathbf{k}$ dependence of the gap is found to produce Raman spectra which vary significantly and characteristically with polarization [8].

We also look briefly at other excitations which couple to light, particularly to detect possible anomalies at T_c. The interaction of phonons with the conduction electrons has already been studied in classical superconductors [9,10] and extensively in $YBa_2Cu_3O_7$ [11]. In the latter material a signature of electron-phonon interaction was found by light scattering, but not by electron tunneling. The opposite situation occurs apparently in NCCO [12], where only the tunneling spectra provide evidence for electron-phonon coupling [4]. It is noted, however, that the transition to superconductivity was not previously identified in this material by Raman scattering.

In this paper the polarization and temperature dependence of Raman spectra from superconducting NCCO will be studied systematically. Although the main focus of the paper is the investigation of the electronic continuum, we will also address the other excitations observed since there are still some open questions which deserve further clarification.

The samples were grown as described previously [2]. The final reduction anneal was done in a partial pressure mass flow controller system with 100 ppm oxygen in argon at 950 °C for two days. Crystals from the same batch show very similar properties when examined by energy dispersive spectroscopy of electrons. The sample studied here has a cerium concentration of $x = 0.16 \pm 0.01$. The onset of the magnetically measured transition is at 20.5 K; almost complete shielding is observed at 18 K. The crystal structure is tetragonal (D_{4h}), the Nd positions have the reduced C_{4v} symmetry. Standard Raman scattering equipment was used for the experiments with the spectral resolution set at 6 cm^{-1} in most of

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the measurements. For excitation the Ar^+ laser line at 476 nm was selected. The laser heating was minimized by adjusting the incident power appropriately between 0.5 and 2 mW and was determined experimentally to be 1.5 K/mW near T_c. The polarization directions of the incident ($\mathbf{e}_i$) and the scattered ($\mathbf{e}_s$) photons are nearly perpendicular to the c axis in all experiments and are indicated by ($\mathbf{e}_i, \mathbf{e}_s$) with $x = [100]$, $y = [010]$, $x' = [110]$, and $y' = [\bar{1}10]$.

Spectra were measured at temperatures below 210 K with emphasis on the range between 3 and 25 K. The response for frequencies less than 800 cm^{-1} turns out to be very similar to the one found in compounds with high T_c (Fig. 1). There are broad continua at all polarizations with only little dependence on frequency and temperature. Superimposed on the continua, several narrow lines are observed, depending strongly on the polarizations (Fig. 1). The structures at 167 and 206 cm^{-1} with A_{2g} and B_{1g} selection rules, respectively, can be attributed to crystal-field (CF) excitations of the Nd^{3+} ions similarly as in pure Nd_2CuO_4 [13]. A weak line with A_{2g} symmetry appears at 100 cm^{-1}, the intensity of which is enhanced compared to the corresponding one at 119 cm^{-1} in the undoped material. Accordingly, it is found by inelastic neutron scattering that partial substitution of Nd by Ce causes the lowest CF transition to shift down in frequency from 121 to 97 cm^{-1} and to increase in intensity [14]. The two lines with B_{1g} symmetry at 207 and 340 cm^{-1} are clearly asymmetric and, similar to the CF excitations at 100 and 170 cm^{-1}, gain intensity upon cooling. For the temperature dependence of both the intensities and the frequencies, it is likely that there exists a coupling between the CF transition at 207 cm^{-1} and the vibration of the oxygen atoms sandwiched between the ND layers (O2) along the c axis at 340 cm^{-1} as studied in detail for $NdBa_2Cu_3O_7$ by Heyen and co-workers [15]. The phonon at 340 cm^{-1} exhibits a small deviation from pure tetragonal B_{1g} to orthorhombic A_g symmetry which manifests itself as a tiny peak at the $x'x'$ polarization (see Fig. 1) and may originate from the doping with cerium. The line at 480 cm^{-1} shows up in the yy, $x'x'$, and $x'y'$, but not in the xx and xy polarized spectra as a consequence of polarization leakage and can be identified as a vibration of the O2 atoms perpendicular to the c axis with E_g symmetry [16]. Finally there is a strong line at 590 cm^{-1} with pure tetragonal A_{1g} symmetry, which due to the high frequency probably involves oxygen vibrations. It has been reported that this phonon is very weak in Ce-free samples but gains intensity upon doping and shows a dominant zz component of the Raman tensor hinting at a vibration along the c axis [12]. Because of the frequency and the symmetry selection rules, it has already been proposed that vibrations of oxygen atoms in apex position could be one possible explanation for the unexpected line [12]. Recently it was indeed found by neutron scattering on pure Nd_2CuO_4 and at least 5% of the normally empty apex positions are occupied by oxygen independent of the sample history [17]. As the Raman line at 590 cm^{-1} is stronger in doped samples, it is natural to assume that replacing Nd by Ce favors the occupation of the apex instead of the O2 position by leaving the overall oxygen content almost unchanged. As we have seen in the discussion of the Raman line at 340 cm^{-1}, the O2 sublattice does not have the full translational symmetry of the crystal. This scenario offers an explanation not only for the strong zz component of the Raman tensor but also for the doping dependence of the 590 cm^{-1} phonon and, as we will see later, may also help to better understand the electronic spectra. Upon cooling below T_c, no change in the vibrational response was observed.

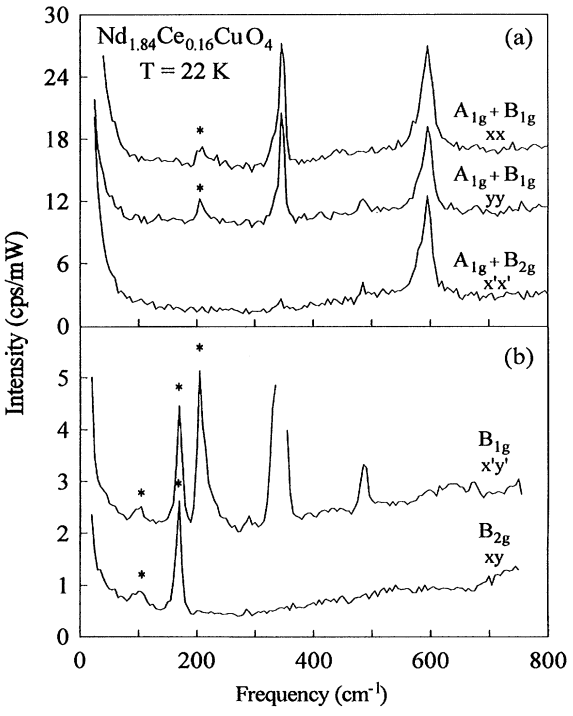

FIG. 1. Raman spectra of $Nd_{1.84}Ce_{0.16}CuO_4$ just above T_c. The polarizations and the respective symmetry components projected out are indicated. Crystal-field (CF) excitations are marked by asterisks. In (a) constants of 7 and 14 units are added to yy and xx polarized spectra, respectively. In (b) a constant of 1 unit is added to the $x'y'$ polarized spectrum.

For the discussion of the scattering from the conduction electrons, we will restrict ourselves to the energy range below 250 cm^{-1} and to temperatures lower than 25 K. In the normal state just at T_c the continuum is almost flat, showing the usual increase close to the exciting line which is particularly strong in this material class. In the superconducting state the scattering intensity is redistributed in a characteristic way (Fig. 2). The new peaks in the Raman spectra can be understood as critical breaking of Cooper pairs induced by the absorbed photons. The positions of the pair breaking peaks ω_p at the B_{1g} and

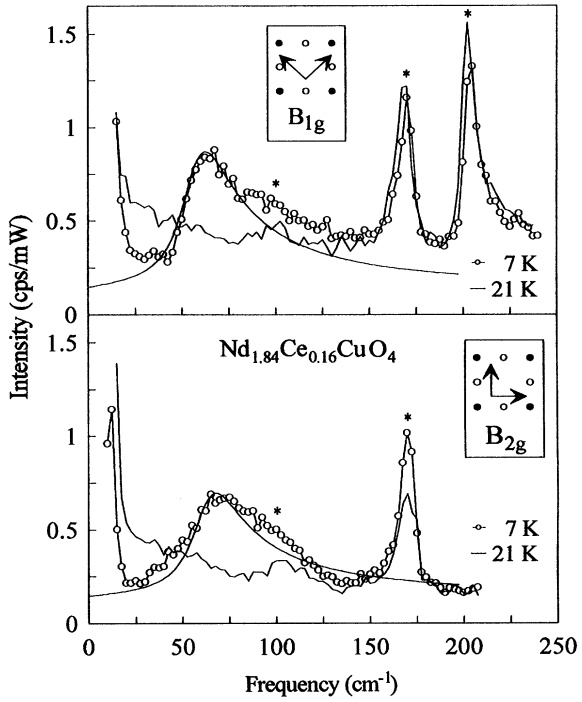

FIG. 2. Raman spectra of $Nd_{1.84}Ce_{0.16}CuO_4$ just above and well below T_c. The smooth lines are fits using a slightly anisotropic s-wave gap. Again, the CF excitations are asterisked.

B_{2g} polarizations do not differ by more than 5–10 cm^{-1}, with the frequency at the B_{2g} symmetry being the higher one. The onset of the structures does not depend strongly on the polarization and is close to that observed in classical superconductors like Nb_3Sn [18,19]. The intensity increase at the low energy side of the peaks occurs in a fairly small range and starts at a threshold which is as large as 3/4 of the energy of the maximum. The onset of the B_{2g} gap structure is not as sharp as that at the B_{1g} symmetry. Finally, the residual scattering intensity below the threshold is very much the same at both polarizations and is as high as 50% of the normal state one. This is not expected for an ordinary superconductor. However, we do not believe we have to deal with some kind of exotic physics such as gapless superconductivity, but rather with an experimental artifact originating from insufficient rejection of the exciting laser light, scattering from surface contaminations, or (and) nonsuperconducting material due to a degradation in the uppermost layers. For these reasons, in spectra measured with parallel polarizations gaplike features are superimposed on a strong background and the A_{1g} response could not be isolated in a useful way. To date, $Bi_2Sr_2CaCu_2O_8$ is the only compound which is very close to what is considered to be intrinsic as its surface is smooth on an atomic scale and, in contrast to all other cuprates and most of the normal metals, practically inert at ambient air.

The interpretation of the low temperature data makes use of a theoretical approach which has been proposed recently to interpret the Raman spectra of superconducting $Bi_2Sr_2CaCu_2O_8$ [8]. The basic idea is to expand the Raman vertex, which connects the band structure and the light polarizations, into Fermi-surface harmonics. It can be shown that the actual shape of the Fermi surface is of minor importance and influences predominantly the relative intensities but not the spectral response [20]. The B_{1g} vertex is maximal along the principal directions and zero along the diagonals, while at B_{2g} the sensitivity is just reversed. From the weak polarization dependence of the pair breaking maxima, it is clear that the gap $\Delta(\mathbf{k})$ can vary only slightly around the Fermi surface. We attempted to reproduce the spectra qualitatively by assuming a slightly anisotropic s-wave (or equivalently A_{1g}) gap given by $2\Delta(\phi) = (\Delta_{\max} + \Delta_{\min}) - (\Delta_{\max} - \Delta_{\min})\cos 4\phi$ with $2\Delta_{\min} = 56$ cm^{-1} or $4.1kT_c$ and $2\Delta_{\max} = 66$ cm^{-1} or $4.9kT_c$ (Fig. 3). ϕ is the azimuthal angle on a cylinderlike Fermi surface with $\phi = 0$ the direction along $\mathbf{k}_x$. A broadening $\Gamma/2\Delta = 0.3$ is used to account for the relatively large superconducting transition width and, phenomenologically, for the finite lifetime of the excited carriers.

If the temperature is increase, the spectra approach continuously, and the normal-state response and the pair breaking peaks at $\omega_p(T)$ shift to lower frequencies. The superconducting features vanish at sample temperatures between 20 and 21 K. As already observed in other cuprates [21], the temperature dependence of $\omega_p(T)$ is considerably weaker than predicted by the BCS theory (Fig. 3). In $Bi_2Sr_2CaCu_2O_8$ the peak maximum ω_p

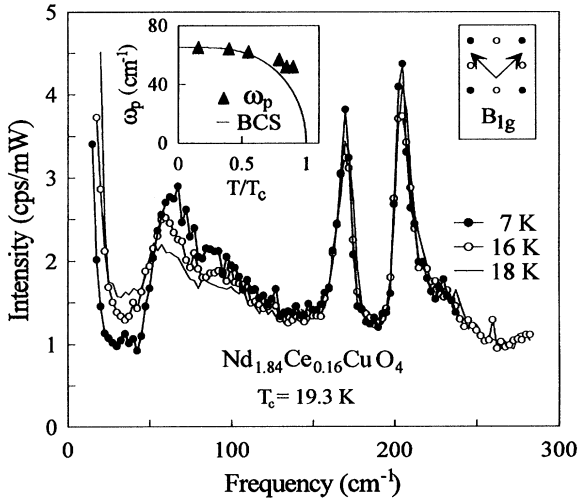

FIG. 3. Raw data for the B_{1g} polarization illustrating the temperature dependence of the gap features. Because of the larger slit widths, the overall intensity is higher here. The inset shows the peak frequencies ω_p for B_{1g} symmetry as a function of reduced temperature in comparison with the BCS prediction.

depends on the weaker the temperature the larger $\rho_c/\rho_{a\text{-}b}$ (and the two dimensionality) is [21]. In fact, $\rho_c/\rho_{a\text{-}b}$ in NCCO is of the same order of magnitude [2]. The anomalous temperature behavior seems therefore to be related to the layered structure and not to the mechanism of superconductivity in the cuprates, the signature of which is more likely the strong in-plane gap anisotropy found in the materials with high T_c [22].

What is new in NCCO which seems to be an ordinary cuprate system apart from the sign of the carriers? In a compound like $Bi_2Sr_2CaCu_2O_8$ the peak positions ω_p differ by 40% with the B_{1g} maximum at the highest energy of approximately $8kT_c$. The intensities increase continuously over a range of some 300 cm^{-1} starting from zero in the B_{1g} spectra and exhibit frequency power laws characteristic for each polarization. These features have been found to be similar in several other cuprates with high transition temperatures [22] and can be accounted for quantitatively if an energy gap with $d_{x^2-y^2}$ symmetry is assumed [8]. Very recently $La_{1.83}Sr_{0.17}CuO_4$ was found to fit into the same picture [23]. NCCO, on the other hand, is the first cuprate which hardly shows any anisotropy of the gap in Raman spectroscopy. In addition, the low-temperature limiting value of $2\Delta_{\max}$ is as small as $4.9kT_c$. Along with other studies probing the gap [3,4] without, however, being directly sensitive to its **k** dependence, we arrive consistently at the conclusion that NCCO is an almost isotropic s-wave superconductor by looking at the **k** variation of the order parameter.

There remains the question for the role of electron-phonon coupling in NCCO which is particularly favorable in a system with s-wave symmetry of the gap. Indeed, some strong-coupling effects are observed in tunneling spectra, which reveal a coupling parameter λ of order 1 [4]. On the other hand, in contrast to NCCO, in some classical superconductors with $1 < \lambda < 2$ and comparable transition temperatures, strong phonon anomalies at T_c are found by Raman scattering [10]. The two arguments combined give $\lambda \leq 1$ and, by applying the appropriate formula for the transition temperature [24], yield a mean phonon frequency $\langle\omega\rangle$ between 200 and 400 cm^{-1}, which is very realistic for the copper oxides in general. To obtain T_c's of at least 100 K by simply increasing λ would require unprecedently large coupling strengths and, accordingly, strong phonon anomalies at T_c and particularly weak gap anisotropied [25]. This implies that NCCO is different from the other high-T_c superconductors and seems to be an intermediately coupling almost two-dimensional BCS superconductor. One might speculate that the superconductivity is closely related to excess oxygen in apex position via a mechanism which has been proposed recently [26].

In summary, we have extended the Raman experiments in NCCO to the superconducting state which is unambiguously identified in the electronic response. It is found that NCCO is an almost isotropic superconductor with a minimum gap of approximately $4.1kT_c$ which is also observed via activated behavior in penetration-depth and surface-resistance measurements [3] and a maximum gap of $4.9kT_c$. These values and their anisotropy are significantly smaller than those measured in other cuprates. The temperature dependence of the gap structures deviates from the BCS prediction as already observed in other CuO_2 superconductors. We conclude that the superconductivity in NCCO is mediated by phonons. The occupation of the normally empty apex position may play a crucial role, but finally the very delicate balance between oxygen and cerium doping makes some of the samples superconducting in a way which needs further clarification.

Enlightening discussions with Dietrich Einzel and Tom Devereaux are gratefully acknowledged. J. L. C. and J. T. M. would like to thank the U.S. National Science Foundation (Grant No. DMR-9158089) and the Robert A. Welch Foundation (Grant No. F-1119) for financial support. We express our gratitude to the Bayerische Forschungsstiftung which supported this work via the Forschungsverbund Hochtemperatur-Supraleiter (FORSUPRA).

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