Investigation of the Superconducting Order Parameter in $Bi_2Sr_2CaCu_2O_8$ Single Crystals

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(Received 28 August 1991)

Single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ with different oxygen concentrations were investigated by Raman scattering. Dependent on the polarizations of the incident and the scattered light, the electronic spectra measured well below T_c show either zero or finite intensity at small energy transfers. In oxygen-annealed crystals, the superconducting order parameter Δ is temperature dependent. In contrast, Δ is almost constant in the essentially two-dimensional argon-annealed samples.

PACS numbers: 74.70.Vy, 74.30.Gn, 78.30.Er

The energy gap in the quasiparticle excitation spectrum of superconductors $\Delta(\mathbf{k},T)$ reveals important information about the superconducting ground state. In classical superconductors the gap has been found to be completely developed over the whole Fermi surface. Remaining anisotropies are small and the temperature dependence obeys the prediction of the BCS theory [1]. In the heavy-fermion superconductor UPt_3 several properties indirectly suggest that the gap vanishes for certain directions of $\mathbf{k}$ space [2]. Metallic superconductors may be completely gapless in a certain impurity concentration range [2,3]. In the Cu-O superconductors, it is not clear whether these materials are fully gapped and which features are actually intrinsic. Contradictory results have been found for the low-temperature limiting value and for the temperature dependence of the energy gap or, more precisely, for the experimentally observable related quantities.

In this Letter, results of Raman scattering experiments on $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi 2:2:1:2) single crystals are presented. Spectra of as-grown superconducting samples have already been published [4], corroborating data and conclusions for $YBa_2Cu_3O_7$ (Y 1:2:3) [5,6]. We have taken spectra of freshly cleaved high-quality single crystals of Bi 2:2:1:2 with different oxygen doping and, consequently, different superconducting and normal-state properties. The question of the existence of a real gap will be addressed as well as the conditions which determine the temperature dependence of the superconducting order parameter.

The experiments were performed using standard Raman scattering equipment with single-channel detection. The spectral resolution was set at 10 cm^{-1}. For excitation the Ar^+ laser lines at 458 and 476 nm were selected. The angle of incidence for the exciting light was 60°, and the scattered light was collected along the surface normal of the a-b plane. The polarizations of the incident and scattered light are denoted in the usual way with $x=[100]$, $y=[010]$, $x'=[110]$, and $y'=[1\bar{1}0]$. Just before the samples were mounted into the cryostat, a thin surface layer was peeled off with an adhesive tape. In any case spot temperatures will be indicated.

The samples were prepared with a self-flux method [7] and characterized with x-ray and microprobe analysis as well as Raman scattering. The vibrational part of the spectra is in agreement with the data of single crystals published by other groups (cf. Ref. [4]). Several crystals were selected from one batch, a part of which was annealed in flowing Ar at 600 °C for 24 h; others were annealed in 10 bars of oxygen at 550 °C for 140 h [8]. The transition temperatures of the as-grown ($B1$), the Ar- ($B2$), and the O_2 ($B3$) annealed samples were 86, 86, and 79 K, respectively (see Table I). The c-axis resistivities ρ_c depended strongly on the annealing conditions. The temperature dependence of ρ_c was metallic in sample $B3$ and semiconductorlike in $B2$; the as-grown sample $B1$ became nonmetallic just above T_c. The anisotropy ρ_c/ρ_{ab} is approximately 3 orders of magnitude larger in $B2$ than in $B1$.

The data of sample $B3$ just above and well below T_c are shown in Figs. 1(a) and 1(b). Characteristic features of the superconducting state are (i) a decrease of scattering intensity to values below the normal conducting one for small frequency shifts, (ii) a maximum in the intermediate range, and (iii) an asymptotic approach of superconducting and normal spectra at high energy shifts. Since the surface is not perfectly flat, some diffuse elastic scattering occurs below 30 cm^{-1}. Nevertheless, the intensity below 50 cm^{-1} in the xy polarization at 20 K [Fig. 1(a)] is less than 3% of the one at 1000 cm^{-1}, where no difference between the normal and the superconducting states is observed. This result has been confirmed in a second sample with a similar oxygen con-

TABLE I. Magnetically measured transition temperatures T_c and widths ΔT_c, relative scattering intensities $I(50\ cm^{-1})/I(1000\ cm^{-1})$ at 20 K, and peak frequencies ω_{peak} of the spectra of Bi 2:2:1:2, samples $B1$–$B3$, at 20 K.

	T_c (K)	ΔT_c (K)	I_{50}/I_{1000} (%)				ω_{peak} (cm^{-1})			
			xx	xy	$x'x'$	$x'y'$	xx	xy	$x'x'$	$x'y'$
$B1$	86	2.5	47	7	30	39	365	510	390	475
$B2$	86	1.2	40	8	30	31	335	430	345	410
$B3$	79	3.5	50	3	···	···	325	375	···	···

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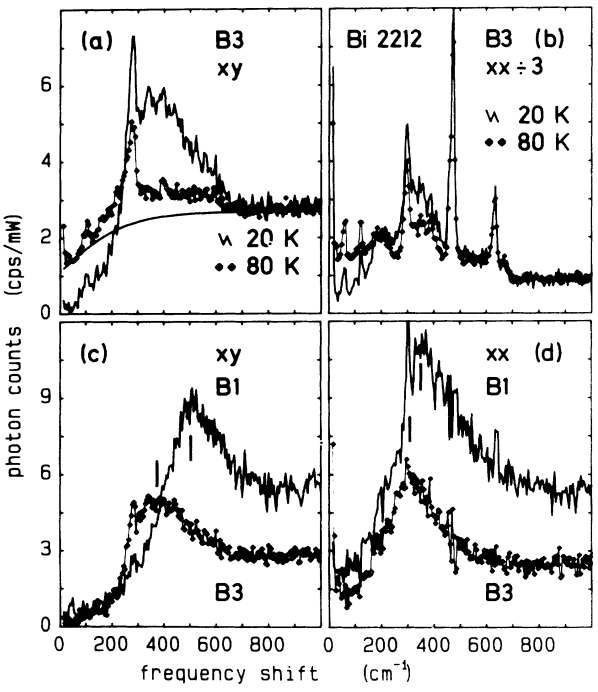

FIG. 1. (a),(b) Raman spectra for $Bi_2Ca_2SrCu_2O_8$ (T_c =79 K) above and below T_c. In xy symmetry the electronic continuum is constant at 190 K. The temperature dependence between 190 and 80 K (smooth line) is given by simply applying the Bose-Einstein thermal factors. (c),(d) Electronic spectra of samples $B1$ (T_c =86 K) and $B3$ (T_c =79 K) at 20 K.

tent. Therefore, the intrinsic scattering intensity can be considered to be actually zero at zero frequency shift. The residual scattering below 80 cm^{-1} increases slightly, if the oxygen concentration is reduced. The ratio $I(\omega=50\ cm^{-1})/I(\omega=1000\ cm^{-1})$ is approximately 8% in $B1$ and $B2$, showing no tendency to approach zero for small ω. At the xx polarization, the scattering intensity at low energies stays well above zero; independent of doping, I_{50}/I_{1000} at 20 K is approximately 40% [for sample $B3$ see Fig. 1(b)]. Similar values are found at $x'x'$ and $x'y'$ (Table I). In order to determine the electronic scattering below T_c, the superimposed vibrational excitations have to be removed. They are experimentally determined above T_c by substracting a smooth continuum [indicated in Fig. 1(a)]. In Figs. 1(c) and 1(d), the xy and the xx electronic spectra for sample $B3$ may be compared with the ones for $B1$. In sample $B3$, the intensity of the phonon mode at 285 cm^{-1} exhibits an anomalous temperature dependence below T_c which is most pronounced in the 20-K spectra and which vanishes in the vicinity of T_c. A similar anomaly exists in Y 1:2:3 (see, e.g., Refs. [5,6]). For determining the peak positions of the electronic spectra this excess intensity has been ignored (Table I).

In Fig. 2, normalized electronic cross sections, $I_s(\omega,T)/I_n(\omega,T)$, for samples $B1$ and $B3$ are shown. Here, $I_s(\omega,T)$ is the superconducting electronic scattering intensity, and $I_n(\omega,T)$ is the normal one at the same temperature T. Below T_c, $I_n(\omega,T)$ is calculated using $I_n(\omega,T)=\text{const}\{1+n(\omega,T)\}/\{1+n(\omega,190\ K)\}$, since $I_n(\omega,T)$ is found to be constant at T=190 K [see Fig. 1(a)] and to have a conventional temperature dependence in the normal state described by the Bose-Einstein factor $\{1+n(\omega,T)\}=\{1-\exp(-\hbar\omega/kT)\}^{-1}$ [9]. The temperature dependence of $I_s(\omega,T)/I_n(\omega,T)$ is similar in samples $B1$ and $B2$, where the peak frequencies remain almost constant, but is qualitatively different in sample $B3$. The stronger temperature dependence of the peak frequencies in sample $B3$ is observed at both the xy and the xx polarization [Fig. 3(a)].

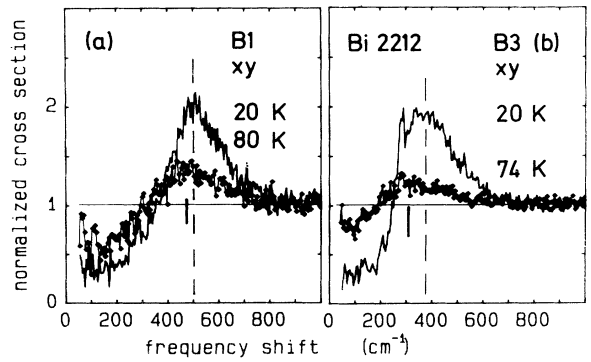

FIG. 2. Temperature dependence of the normalized electronic scattering cross section for (a) sample $B1$ (T_c =86 K) and (b) sample $B3$ (T_c =79 K). The spectra close to T_c are recorded approximately at the same reduced temperature. The peak positions are indicated.

The following discussion of the electronic Raman cross section focuses first on the zero-temperature limit. As basic assumptions of the BCS theory, such as the existence of pairing correlations and the overlap of many pairs, have been verified experimentally, it is tempting to begin the interpretation of the data on this footing. The

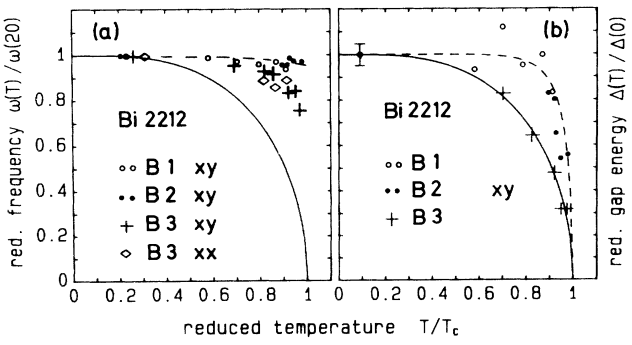

FIG. 3. (a) Reduced peak frequencies of the superconducting electronic spectra as a function of reduced temperature. (b) Reduced gap energies determined via Eq. (1). The point at T/T_c =0.1 is the mean value of the gap energies observed between 50 and 75 K in sample $B1$. The full lines represent the BCS theory; the dashed lines are a guide to the eye.

BCS result for the Raman scattering cross section [10] invokes the existence of a characteristic energy $2\Delta_0(T)$ which can be interpreted as the binding energy of Cooper pairs. The Raman intensity is predicted to vanish well below and to display a maximum near $2\Delta_0$. Indeed, in xy symmetry of sample $B3$ an almost ideal spectrum of a superconductor is found. Such a significant reduction of scattering intensity at low energies has not even been observed in metallic superconductors like Nb_3Sn or V_3Si [11]. At all other symmetries a considerable scattering intensity is found at low frequencies and temperatures [Figs. 1(b) and 1(d)], which must be considered to be intrinsic in view of the vanishingly small cross section at the xy polarization. Therefore, the material appears to have a completely developed clean gap for a certain polarization, while for others only a reduced density of states is compatible with the data at low energies. Finite scattering intensity at low frequencies which does not extrapolate to zero is reminiscent of gapless superconductivity. Several pair-breaking mechanisms have been proposed for metallic [2,3] and oxide [12] superconductors, which may actually lead to a nonzero density of states (DOS) inside the "gap" at $T=0$. It is noted that strong electron-phonon coupling results in an enhanced DOS below Δ only at $T>0$ [13]. In contrast to classical superconductors [11], the scattering cross section increases continuously from low frequencies up to a maximum located at symmetry-dependent shifts between 300 and 500 cm^{-1} (Table I). Unlike other authors [5], we did not find the slope to be linear at any polarization. The spectra of Bi 2:2:1:2 agree almost quantitatively with the spectra of Y 1:2:3 [6] if the polarizations of the light are given in the coordinate system of the Cu-O bonds. However, the scattering intensity $I_s(\omega=0,T=0)$ at the $x'y'$ polarization in Y 1:2:3, corresponding to the xy polarization in Bi 2:2:1:2, is certainly not zero [6].

We did not attempt to compare the experimental data of Bi 2:2:1:2 with the cross section calculated on the basis of a BCS model like in Y 1:2:3 [6] because the origin of the electronic continuum extending to $\omega \gg 2\Delta_0$ is not clear at all [9]. An appropriate treatment has to include actually both pair breaking and continuum scattering. Presently existing theories [10] predict the pair-breaking maximum to be located between approximately 0.9 and 1.2 in units of the characteristic energy $2\Delta_0$. Symmetry-dependent values for $2\Delta_0$ ranging from $3.0kT_c$ to $8.0kT_c$ may therefore be deduced for Bi 2:2:1:2 from the Raman spectra. The large width of the structures can originate from either a broad distribution of gaps [6] or a short lifetime of the excited quasiparticles [10].

We now address the temperature dependence of the electronic structures in the different samples. In crystals with an essentially nonmetallic resistivity characteristic ρ_c (samples $B1$ and $B2$), the maxima hardly change their positions upon heating from $T=20$ K to $T=T_c$, while in sample $B3$ a softening by some 25% occurs [Figs. 2 and 3(a)]. It is generally accepted that oxygen doping creates additional free carriers in the Bi-O layers [14]. At a small hole concentration the superconducting Cu-O double layers are coupled only by Josephson tunneling via the insulating Bi-O layers [7]. If the Bi-O layers become metallic, a really three-dimensional superconductor may be established, since the proximity effect induces pairing of the carriers in the Bi-O layers (cf. Ref. [14]). The normalized cross section at $T>20$ K is almost constant below 200 cm^{-1} (Fig. 2) and can easily be extrapolated to $\omega=0$. According to the raw data, $I_s(\omega=0,T=0)/I_n(0,0)$ is assumed to be zero in $B3$, but finite in $B1$ and $B2$. Since a real gap is found at the xy symmetry in $B3$, it seems reasonable to describe the temperature dependence of $I_s(\omega=0,T)/I_n(0,T)$ within a conventional Fermi-liquid model, yielding

$$\frac{I_s(0,T)}{I_n(0,T)} = \frac{2}{\exp[\Delta(T)/kT]+1}. \quad (1)$$

This identity has been shown explicitly for metallic superconductors with high normal-state conductivity and low T_c [15] and has a direct analog in semiconductors. At elevated temperatures, $0.5<T/T_c<1$, the gap $\Delta(T)$ can be directly determined using Eq. (1) [Fig. 3(b)]. It turns out that $\Delta(T)$ obeys the weak-coupling BCS temperature dependence of the gap, extrapolating, however, to $2\Delta(0)=2.4kT_c$. If there exists indeed a distribution of gaps, 2Δ calculated from Eq. (1) may be smaller than the characteristic value $2\Delta_0$, since the quasiparticle excitation is, of course, determined by the small gaps. It seems worthwhile to analyze the data of samples $B1$ and $B2$ in a similar way assuming, however, a temperature-independent residual scattering intensity at $\omega=0$. Up to $0.9T_c$ the "gap" remains constant at a mean value of $2\Delta(0)=2.7kT_c$. For $0.9<T/T_c<1$, $\Delta(T)$ drops to zero continuously as required by a second-order phase transition [Fig. 3(b)]. The results shown in Figs. 3(a) and 3(b) look somewhat contradictory. However, any broadening of the superconducting structures may result in a discrepancy between the temperature dependence of the peak frequency and that of the order parameter (cf. Ref. [15]).

In conclusion, we have investigated differently doped Bi 2:2:1:2 single crystals by Raman scattering below T_c. Generally, the compound does not have a real and uniform gap. We conjecture that an intrinsic pair-breaking mechanism generates quasiparticles inside the "gap" at certain symmetries even at $T=0$ and $\omega=0$. For oxygen-annealed samples, a clean gap is observed at the xy polarization. The peak frequency of the superconducting spectra is reduced by some 25% near T_c in comparison to the low-temperature value. In samples with a reduced carrier concentration a finite cross section is found at $\omega=0$ even in the xy polarization. The gap is essentially temperature independent, but apparently drops continuously to zero at T_c. The deviation from the conventional temperature dependence of the gap originates obviously in the dimensionality [16], and conventional and unconventional be-

havior may well be observed in samples having only a slightly different T_c. The electronic scattering in Bi 2:2:1:2 and Y 1:2:3 turns out to be similar above [9] and below T_c, if the polarizations are given in the coordinate system of the Cu-O octahedra. Therefore, we believe the electronic scattering to be dominated by carriers in the planes. We speculate that in an idealized compound consisting only of Cu-O planes, the gap would always be clean with the polarizations of the incident and the scattered light perpendicular and at an angle of 45° to the Cu-O bonds. At this symmetry (tetragonal B_{1g}), the normal-state electronic spectra are indicative of a temperature-independent relaxation of the carriers [9]. At all other symmetries gapless superconductivity is believed to be an intrinsic property of the planes. Here, the spectra above T_c are virtually temperature independent [9]. In the framework of linear response theory, this implies that the damping rate of the excited quasiparticles is proportional to the maximum of temperature and energy.

Valuable discussions with O. V. Misochko are gratefully acknowledged. We are indebted to K. Andres and D. Einzel for critically reading the manuscript. The work has been supported by the BMFT.

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