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TWO TYPES OF MEASUREMENTS ON SINGLE CRYSTAL $YBa_2Cu_3O_{7-\delta}$: THE FLUCTUATION CONTRIBUTION TO THE SPECIFIC HEAT AND RAMAN SCATTERING FROM SUPERCONDUCTING GAP EXCITATIONS

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INTRODUCTION

We have made high-quality single crystals of $YBa_2Cu_3O_{7-\delta}$. With one of them, we have measured the contribution of thermodynamic fluctuations to the specific heat near the superconducting transition. With another crystal, we have observed Raman scattering from superconducting gap excitations. The "single crystals" of this material are, of course, heavily twinned.

SAMPLE PREPARATION

To make the crystals, we employed a flux technique similar to the one used in the pioneering work of Schneemeyer et al.[1]. The ingredients were thoroughly mixed and ground, and were loosely poured into a crucible of 10.5% yttria-stabilized zirconia. The material was then heated by stages in air and slowly cooled back to room temperature. The crucible was crushed in a hydraulic press, revealing a broad, flat cavity which had formed in the matrix near the bottom of the crucible. Many crystals broke away from the cavity walls, and were harvested. Others were plucked gently from the cavity wall with tweezers. The crystals typically were 1 or 2 mm on a side and about 0.1 mm thick; a few had about twice that thickness. Laue backscattering x-ray diffraction disclosed that the c axis was perpendicular to the largest faces, and that the lattice constants had the expected values. Optical microscopy with crossed polarizers displayed the twinning which we have mentioned. The crystals were heated and then cooled in flowing oxygen on a wafer of polycrystalline $YBa_2Cu_3O_{7-\delta}$. The processing is described in greater detail elsewhere, and the magnetic transition is displayed there as well.[2] This transition occurs at approximately 90K; it is very sharp and well shaped. We have made crystals by our method successfully eight times.

SPECIFIC HEAT MEASUREMENTS

An ac method was used to determine with high resolution the shape of the specific heat curve in the neighborhood of the superconducting transition temperature T_c.[3] The entire sample, with a mass of about 600 µg, becomes superconducting in a narrow temperature range. The shape of the specific heat curve shows the effect of fluctuations quite clearly: As the temperature is increased from below T_c, the specific heat curve rises above a linear dependence, falls sharply and then gradually approaches a linear behavior above T_c. The rise above a linear dependence below T_c and the rounding of the curve above T_c are clear indications of thermodynamic fluctuations. We fit the fluctuation contribution to the specific heat to the equation

$$C = C_{\pm} \, |t|^{-1/2} \qquad (1)$$

where

$$t = (T - T_c)/T_c \qquad (2)$$

and where the + and − signs in the subscript refer to $T>T_c$ and $T<T_c$, respectively. According to the theory of phase transitions, the ratio of C_+ to C_- is given by

$$C_+/C_- = 2^{-d/2}n, \qquad (3)$$

independent of details such as the spatial anisotropy of the system. In this equation, d is the dimensionality of the system and n is the number of components in the superconducting order parameter. The equation for that ratio is a corrected version of one which can be found in the literature[4].

The shape of the specific heat curve above and below T_c verifies the temperature dependence given in Eq.(1), indicating that the material is behaving as a 3-dimensional system. Putting d=3 in Eq.(3), the experimental value of the indicated ratio yields n:

$$n = 7 \pm 2. \qquad (4)$$

This value rules out the standard Landau-Ginzburg superconducting order parameter, which has 2 components (the real and imaginary parts of a scalar function of position and time). A possible interpretation of the result given in Eq.(4) is that n = 6 and we are dealing with a p-wave order parameter in an orthorhombic environment.

RAMAN EFFECT MEASUREMENTS

We made measurements of Raman scattering in one of our single crystals using polarized light provided by an argon laser. The measurements were made in a near-backscattering geometry, with the incident light polarized perpendicular to the c axis of the crystal. The scattered light was dispersed with a triple-stage monochromator, and a liquid helium cryostat was used for temperature control. A small power density (roughly 10 W/cm^2) was used to minimize laser heating and to prevent boiling of the superfluid helium during the low-temperature (3 K) runs. Data were taken at a series of temperatures up to T_c. Just above T_c we observe strong interband electronic scattering through interference effects, as seen in an asymmetric "Fano" line shape for some of the phonons. This lineshape indicates Auger-like processes, in which a broad continuum interacts with a discrete phonon state, providing a "radiationless" decay channel for the phonon. As the temperature is reduced below T_c, this electronic scattering changes, showing a redistribution of spectral weight caused by the formation of a superconducting energy gap. This gap formation is indicated by alterations in the background scattering, and in both the damping rates and the peak positions of the strongly coupled phonons. By comparing the low-frequency Raman spectra at several temperatures, we conclude that at T = 3 K a spectral weight representing about 25% of the normal-state value still remains below the gap edge. In other words, the gap edge is spread out rather than being the discontinuous rise from zero which is predicted by the BCS theory[5] and is observed in conventional superconductors. Thus, a gapless region of the Fermi surface may be indicated. The good quality of the sample is indicated by the observed sharpness of the Raman lines, and by the absence of any phonon structure in the 470 – 490 cm^{-1} range of the spectrum; it is in this range that a mode is observed in $YBa_2Cu_3O_{7-\delta}$ samples which are poor in oxygen.[6] We observe a softening of a line at 338 cm^{-1}, in agreement with results of Macfarlane et al.[7] We suggest that this softening results from a repulsion of the phonon state by the redistributed continuum to which it is coupled. This indicates that the 2Δ gap is opening at a higher energy, providing a lower limit for the gap parameter of $2\Delta/k_BT_c = 5.2$, where k_B is Boltzmann's constant. This value of $2\Delta/k_BT_c$ is considerably larger than the BCS value of 3.53.

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