PHYSICAL REVIEW B VOLUME 36, NUMBER 7 1 SEPTEMBER 1987

Quasiparticle excitations in the superconducting state observed in light scattering

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(Received 22 May 1987)

In light scattering experiments on superconducting Y-Ba-Cu-O ceramic oxides we observe an unexpectedly intense Stokes-shifted spectrum from about 100 cm^{-1} ($\approx$13 meV) to 4000 cm^{-1} ($\approx$0.5 eV). We propose that this is due to light scattered from energy-density fluctuations of quasiparticle states excited above the superconducting ground state. The temperature dependence of the scattering intensity shows strong hysteresis, not observed in other experiments on the oxide superconductors.

Inelastic scattering of light from a solid-state plasma can provide important information about the excitation spectrum of the carriers in the medium. Both single-particle and collective excitations (plasmons) in semiconductors have been extensively studied by light scattering.[1-4] The large cross section for single-particle light scattering in semiconductors is due to energy-density fluctuations from the nonparabolicity of the conduction band. Charge-density fluctuations are too effectively screened to be observed. Light scattering from metals, on the other hand, is limited to collective excitations with no mechanism for nonscreened fluctuations to scatter light.

We have previously found in Raman scattering experiments[5] that light penetrates the surface of the ceramic superconductors both above and below T_c and this led us to believe that we should observe light scattering from elementary excitations in the superconducting ceramics. The shape of the spectrum should provide direct information about excitations in the superconducting state. Before the discovery of Bednorz and Müller[6] of possible high-temperature superconductivity and the recent report of possible room-temperature superconductors,[7] the gap in the light scattering was too close to the laser line ($\sim$24 cm^{-1}) to be observed even for T_c's in the 20-K region, and the superconducting materials were far too good metals for light scattering to be feasible.

In this paper we present light scattering spectra from the Y-Ba-Cu-O superconductor both above and below the superconducting transition. The ceramic samples used in our experiments were obtained in the usual way with a sharp (2 K) superconducting drop in resistivity.

The spectra were measured in a backscattering geometry with 488- and 514.5-nm laser excitation, dispersed in a Spex Triplemate spectrograph and detected with a microchannel plate intensified cooled photo-diode array detector. The sample was mounted in a standard optical cryostat in vacuum (10^{-8} bar) in good thermal contact with its support. To minimize laser heating, the spectra were recorded with always less than 5 mW incident on the sample. Many spectra were recorded each time from different points on the surface and at different excitation wavelengths in order to check the variation of intensities across the sample. The surface of the sample was optically polished before each experiment. From micrographs of the polished surface we observe that the material is polycrystalline with very few inclusions, similar to that observed previously in La-Sr-Cu-O,[5,8] with typical crystallite size $\sim$5 μm across. With a laser spot size $\sim$40 μm, the intensity of the spectra depended somewhat on the position on the sample, due to superconducting domains in the polycrystalline sample. We obtained much more consistent results when the spectra were recorded with laser defocused with excitation over a larger area (0.5×1 mm^2) in order to average over the domains.

The general shape of the spectra do not change much with temperature as shown in Fig. 1. The intensity of scattering is strongly temperature dependent, however (Fig. 2). The room-temperature spectrum shows a set of phonons[8] but no significant broad features. On cooling, a broad spectrum appears, whose intensity gradually starts to increase around 120 K with a maximum at T_c ($\sim$90 K). Below 90 K the intensity of the broad feature falls off again. Upon heating, the intensity shows significant hys-

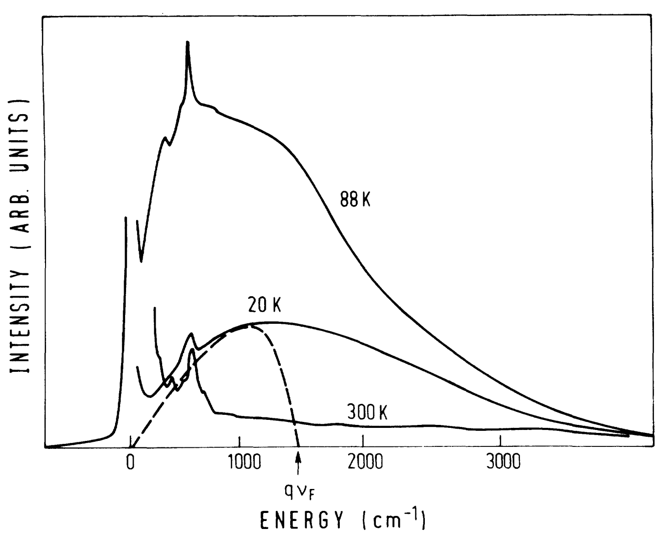

FIG. 1. Excitation spectra of Y-Ba-Cu-O at 300, 88, and 20 K. The dashed line is the calculated single-particle spectrum for a degenerate Fermi-Dirac gas at $T=0$, assuming a weakly nonparabolic band. The intensity of the calculated curve has been normalized to the 20-K spectrum.

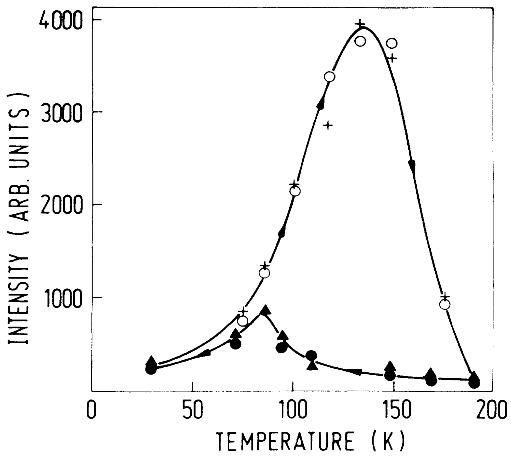

FIG. 2. Scattering intensity as a function of temperature. The solid lines are as a guide to the eye only and do not represent any theoretical model. The lower curve represents the intensity on cooling; the upper curve represents the intensity on heating. The circles represent incident and scattered light in crossed polarizations, while the triangles and pluses are spectra taken with parallel polarizations.

teresis: The maximum is shifted to 150 K, and the spectrum remains visible up to 190 K. The spectrum is unpolarized. Repeated temperature cycling of the same sample and other samples shows consistent hysteresis. In energy, the maximum intensity is at $\sim 1000\ \mathrm{cm}^{-1}$ and extends to about $4000\ \mathrm{cm}^{-1}$, but importantly, the shape of the feature above $1000\ \mathrm{cm}^{-1}$ does not change significantly with temperature.

Before proceeding further we exclude a few possibilities for the cause of the observed spectrum. (a) We have examined the spectra from superconducting $La_{1.85}Sr_{0.15}CuO_4$ to check that the effect is not due to some spurious surface adsorption effect. The spectra were not investigated in detail, but we were satisfied that, upon cooling, the intensity maximum in the scattering was at T_c (38 K), tying in the effect with superconductivity in the ceramic oxides. (b) Spectra at different excitation energies (488 and 514.5 nm) show that the spectra are indeed due to light scattering and not on an absolute energy scale, such as due to luminescence, for example. (c) The absence of anti-Stokes scattering even at low energies shows that all possible phonon contributions (e.g., from local modes or multiphonon Raman scattering) can be excluded.

As a result we conclude that the observed spectrum is due to light scattering from excitations from the superconducting ground state. As such, to our knowledge this is the first observation of quasiparticle light scattering from a superconductor. Our analysis requires only that the observed excitations have an energy gap above the ground state. Normal Y-Ba-Cu-O is metallic with no gap and cannot give rise to the scattering.

In substantiating our proposal, we will first draw an analogy to the treatment of Wolff[3] applied to semiconductors. For light scattering experiments in semiconductors, as well as in our case, the wave vector q transferred to the plasma is much smaller than the characteristic plasma wave vector $\mathbf{q}_p$; charge-density fluctuations are heavily screened to light. Extending the theory to a nonparabolic conduction band introduces the concept of energy-density fluctuations which do not carry charge and are not screened; the cross section of single-particle excitations is enhanced by a factor $(q/q_p)^2$, and these are then more readily observable in light scattering. A requirement for this is the existence of nonparabolic energy band in the material, to provide a mechanism for nonscreened energy fluctuations to be observed in light scattering.

The superconducting state in the ceramic oxides has been found to contain paired states,[9] and the existence of a gap has been observed in infrared absorption measurements. In the superconductor we therefore have a nonparabolic energy band for quasiparticle excitations with a minimum at $\mathbf{k}_F$ and a mechanism to provide energy-density fluctuations with an enhanced cross section for light scattering.

Assuming that the only possible excitations involve the ones with an energy gap above the ground state, light is scattered by fluctuations in the energy of the quasiparticle excitations above the gap. On excitation, each quasiparticle carries momentum $\mathbf{k}_F \pm \mathbf{q}$, where $\mathbf{q}$ is the momentum transferred by the photon and $\mathbf{k}_F$ is the Fermi momentum.

A simple excitation spectrum of quasiparticle states for $(q/k_F) \to 0$ is given by

$$e(\mathbf{k}) = [\Delta^2 + \mathcal{E}^2(\mathbf{k})]^{1/2} , \qquad (1)$$

where $\mathcal{E}(\mathbf{k}) = E(\mathbf{k}) - E_F$ is the kinetic energy of an excited particle measured above the Fermi level E_F. For small q, we are exciting close to the Fermi surface and the "dispersion" relation for quasiparticle excitation has a minimum at $\mathbf{k}_F$. Invoking an expansion for electronlike excitations close to $\mathbf{k}_F$, we write

$$\mathcal{E}(\mathbf{k}) \approx (\hbar^2/m^*) k_F [k - k_F] , \qquad (2)$$

with $k = k_F \pm q$. A similar expression applies for holelike excitations at $-\mathbf{k}$. From (2) we find that at $T=0$, the maximum excitation energy of a quasiparticle is given by qv_F. With increasing $\mathbf{q}$, the band becomes rapidly nonparabolic. The light scattering spectrum from resulting energy-density fluctuations has been worked out for both the Fermi-Dirac and the Maxwell-Boltzmann distribution.[4] The dashed curve in Fig. 1 represents the single-particle spectrum for the case of a degenerate Fermi-Dirac distribution at $T=0$ with a constant value of $v_F \approx 0.5 \times 10^6\ \mathrm{m\,s^{-1}}$.

We can only expect agreement with this simple model for small energy transfer, i.e., in the low-energy region of our spectra. The relation (1) becomes rapidly nonparabolic for larger excitation energies, and the expansion (2) no longer applies, nor does the treatment of light scattering by a weakly nonparabolic band. Our calculation does not take into account the finite temperature in the distribution, which would have the effect of rounding the cutoff at qv_F. A similar alteration of the single-particle excitation spectrum would be caused by taking into account nonconstant v_F. The velocity at the Fermi surface v_F varies significantly with $\mathbf{k}$ and is maximum at the nesting wave vector[10] in the Brillouin zone. The theory also does not include multiple quasi-electron-hole pair excitations which would appear as a broad spectrum superimposed on the single-particle spectrum.

The theoretical analysis we have used in discussing the obtained spectra is only a qualitative approximation to substantiate our claim that we are observing quasiparticle excitations. We have indicated the essential requirements of a more precise theoretical treatment at nonzero temperatures with real Fermi surfaces. The spectra contain a wealth of information about quasiparticle excitations and can be used to determine their velocity distributions in nonequilibrium situations.

The hysteresis observed with temperature in our excitation spectra clearly indicate that remnants of the superconducting state exist in the ceramic oxides above the nominal superconducting temperature, and it is clearly a new requirement to be explained by a successful theory of high-temperature superconductivity. It is interesting to speculate on the shape of the hysteresis curve. The inflection of the curve at T_c seems to indicate the onset of a different mechanism by which light is scattered in the superconducting phase, which on heating persists to temperatures nearly twice the nominal T_c. Developing our argument further, we find that since the observed excitations are from a "superconducting" ground state, regions of our sample are in this state up to 200 K. We are not surprised, therefore, that superconductivity has been reported recently at much higher temperatures in the same material.[7]

In conclusion, the measurement of the quasiparticle excitation spectrum in the Y-Ba-Cu-O superconducting ceramics opens a number of questions relating to the mechanism of superconductivity, but also gives us information about the velocity distribution of excited quasiparticles. Detailed information is available from the spectra, providing a more adequate theory is applied to the light scattering spectra.

We wish to thank I. Batistić, M. Prester, and K. Biljaković for useful discussions on this subject and S. Bernik for help in preparation of the samples.

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