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# Electron paramagnetic resonance absorption in high-$T_c$ superconducting $GdBa_2Cu_3O_x$

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Electron paramagnetic resonance absorption has been measured in the Gd-Ba-Cu-O system. These measurements provide experimental evidence which supports the notion that the magnetic rare-earth $Gd^{3+}$ ions are decoupled from the Cu-O network in high-$T_c$ $GdBa_2Cu_3O_x$.

Our main interest in this communication concerns the effects of localized magnetic moments on the properties of the highly anisotropic copper oxide ceramic superconductors.[1] Our motivation is driven by the surprising result that in the *R*-Ba-Cu-O system, with *R* a rare-earth ion such as Gd or Ho, $T_c$ is still comparable to that of the Y-Ba-Cu-O system, even though the rare-earth ions are strongly paramagnetic.[2,3] Electron paramagnetic resonance (EPR) is a powerful tool for probing the magnetic properties of materials, and in this communication we report on the EPR absorption in $GdBa_2Cu_3O_x$.

$GdBa_2Cu_3O_x$ (1:2:3 phase or structure) was prepared by first dissolving stoichiometric amounts of $Gd_2O_3$, $BaCO_3$, and CuO in nitric acid, followed by evaporation to dryness in order to obtain an intimate mixture of starting nitrates. The mixture was then placed in a platinum crucible and heated in air at ~870 °C for about 1 h. During the calcining process the sample was cooled to room temperature several times and ground in a mortar and pestle. The reground calcined product was then pressed into pellets and sintered in a tube furnace at 900 °C under a continuous flow of oxidizing gas for 48 h. The pellets were then cooled slowly to 400 °C and held at this temperature for about 12 h. Finally, the pellets were cooled to room temperature at a rate of 30 °C/h. As with the sintering process, the cooling stages of material processing were also carried out in a flowing oxidizing atmosphere. The samples were examined by x-ray powder diffraction and differential thermal analysis to confirm their structure and establish their composition. Magnetic levitation and resistivity measurements were used to confirm superconductivity in selected samples.

Electron paramagnetic resonance (EPR) measurements at *X*-band (~9 GHz) were obtained with a Varian Century Series *E*-9 spectrometer using 25-kHz magnetic-field modulation. Microwave frequencies were measured with a Hewlett-Packard 5342A automatic microwave frequency counter and the magnetic field was measured with a nuclear-magnetic-resonance gaussmeter. EPR spectra at 77 K were obtained using a quartz insertion dewar. Measurements were made on both powder and pellet samples.

Shown in Fig. 1 are EPR spectra of $GdBa_2Cu_3O_x$ at room temperature and at 77 K. These spectra are typical of both powder and sintered pellet samples. The spectra at both temperatures consist of a broad resonance with a linewidth of ~2000 G. There is a notable difference, however, in the microwave absorption in the vicinity of zero magnetic field in the spectrum measured at 77 K. This low-field nonresonant microwave absorption, as shown in Fig. 2, is characteristic of the superconducting state, and we have observed it in other copper oxide-based superconductors such as $YBa_2Cu_3O_x$ and $LaBa_2Cu_3O_x$. Davidov *et al.*[4] have also observed low-field nonresonant microwave absorption in the intermetallic compounds $Gd_xLa_{1-x}Al_2$ and attributed it to superconducting absorption below the critical field. During the course of our work we obtained a preprint of Blazey *et al.*[5] which also reports similar observations in a variety of high-$T_c$ copper oxide ceramics. These authors relate the nonresonant microwave absorption at low magnetic fields to the behavior of superconducting clusters as described by Ebner and Stroud.[6]

In this communication our primary concern is the broad EPR absorption with zero crossing in the $g \simeq 1.9$ spectral region. We believe that the observed resonance signal is due to $Gd^{3+}$ ions ($4f^7, {}^8S_{7/2}$) in the 1:2:3 phase. Care must be taken in establishing that the observed EPR absorption is from the $GdBa_2Cu_3O_x$ phase rather than from

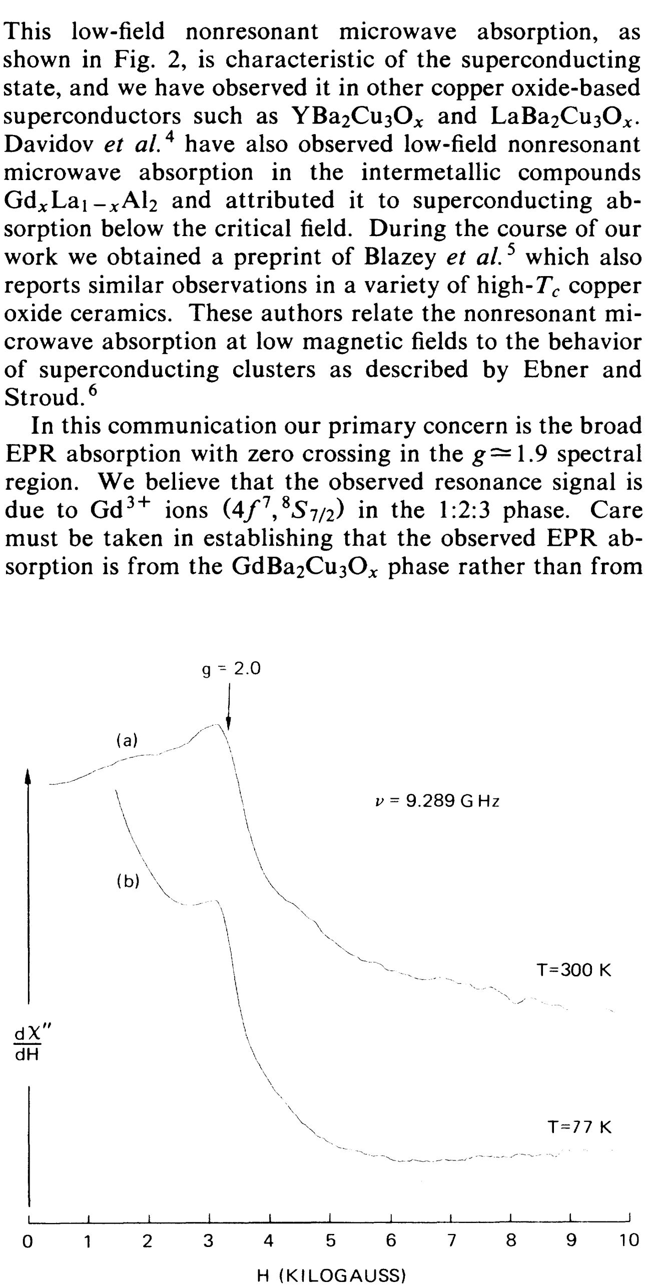

FIG. 1. *X*-band EPR spectra of a sintered pellet of $GdBa_2Cu_3O_x$. (a) 300 K and (b) 77 K.

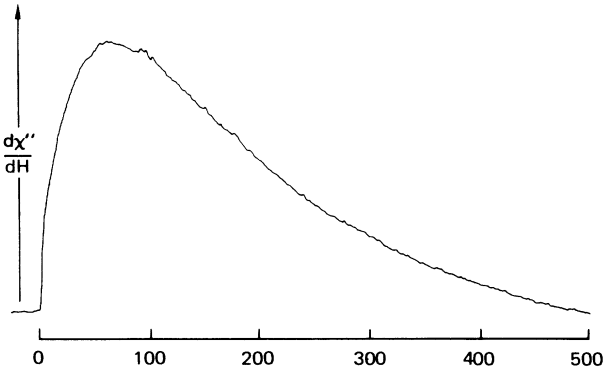

FIG. 2. Low-magnetic-field microwave-absorption spectrum of a sintered pellet of $GdBa_2Cu_3O_x$ at 77 K. The spectrum was obtained by first cooling the sample in zero magnetic field and then sweeping the field from zero to 500 G at a rate of 3.33 G/s.

some unidentified secondary phase. Room-temperature x-ray powder diffraction data established that the Gd-1:2:3 compound was isomorphic with the Y-1:2:3 compound. Furthermore, the absence of lines associated with secondary phases indicated that the material used in our experiments was single phase. The assignment to $Gd^{3+}$ was based on the following observations: (a) The spin-lattice relaxation time is relatively long at room temperature and (b) the $g$ value is approximately two. These paramagnetic resonance features are typical of a $^8S_{7/2}$ (half-filled $4f$ level) ground-state ion in a cubic or even lower symmetry crystalline field.[7] The unusual line shape is due to a combination of several factors, including powder averaging over the highly anisotropic, large multiline fine-structure spectrum,[8] ion-ion interactions such as exchange and magnetic dipolar coupling,[7] and the fact that these materials are metallic.[9]

It is well established that the introduction of a dilute concentration of paramagnetic impurities into a superconductor results in a considerable modification of superconducting behavior.[10-13] In particular, it has been found that magnetic impurities with large spin angular momentum are more effective in reducing $T_c$ than those with large magnetic moments. The origin of these effects is the exchange interaction between the localized spin of the magnetic impurity and the conduction electrons.[10-13] At sufficiently high concentrations of magnetic impurities, Abrikosov and Gor'kov[13] show that superconductivity is completely destroyed.

It is clear that the EPR absorption provides direct experimental evidence for the paramagnetic nature of $Gd^{3+}$ in $GdBa_2Cu_3O_x$. The fact that one observes the localized spin of the $Gd^{3+}$ ions without quenching the superconductivity, suggests that the magnetic $Gd^{3+}$ ions are only weakly coupled to the two-dimensional framework of Cu—O planes which form the molecular network over which electrical transport occurs in both the normal and superconducting states. The fact that magnetic rare-earth ions do not affect superconductivity in high-$T_c$ copper oxide ceramics has also been noted by other workers.[2,3] Theoretical evidence supporting the decoupling of the lanthanide series cations from the superconducting "sublattice" of the 1:2:3 structure is provided by the electronic structure calculations of $YBa_2Cu_3O_x$ by Yu, Massida, Freeman, and Koeling[14] and Herman, Kasowksi, and Hsu.[15] In particular, the calculations by Herman *et al.*[15] indicate that the atomic orbitals of the Y and Ba ions do not hybridize with the occupied Cu and O orbital, but rather serve to define the unoccupied bands. These authors conclude, therefore, that the primary function of the Ba and Y atoms is to serve as electron donors for the O atoms, and thus control and/or regulate the crystal structure through ionic size and electrostatic effects. Since Gd substitutes for Y in the 1:2:3 structure, it is anticipated that the results described above will also apply to $GdBa_2Cu_3O_x$.

In summary, the observation of EPR absorption in $GdBa_2Cu_3O_x$ provides unique experimental evidence indicating that the magnetic rare-earth $Gd^{3+}$ ions are decoupled from the Cu—O network. These results support the view that the electrical transport in both the normal and superconducting state of the 1:2:3 phase is highly anisotropic.

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