Magnetic resonance and relaxation in $GdBa_2Cu_3O_x$ single crystals below T_c

A. G. Badalyan, P. G. Baranov, V. I. Aleksandrov,[1] M. A. Borik,[1]
and V. V. Osiko[1]
A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad; [1]
Institute of General Physics, Academy of Sciences of the USSR, Moscow

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Intense magnetic-resonance signals have been observed below T_c in crystals with a certain oxygen concentration. The conditions under which these signals are observed have been studied. Relaxation effects accompanying the rotation of the crystals in a magnetic field have also been studied.

Electron spin resonance is widely used to study the high-temperature superconductors. There have been studies of nonresonant microwave absorption in magnetic fields[1,2] and the ESR of Cu^{2+} ions in nonsuperconducting phases in ceramics.[3] In the present letter we report a study of $GdBa_2Cu_3O_x$ single crystals with various oxygen concentrations by the method of microwave spectroscopy. Crystals containing oxygen in concentrations $x \geqslant 6.5$ were high-temperature superconductors with critical temperatures of 50 K ($x \approx 6.5$) and 90 K ($x > 6.5$). The crystals with an oxygen concentration $x \approx 6.2$ were nonsuperconducting. The crystals with $x \geqslant 6.5$ have an orthorhombic symmetry.

The crystals were grown from nonstoichiometric melts containing an excess of the copper and barium oxides by the method of direct rf melting in a cold container, followed by a heat treatment of blocks obtained by melting at 700–900 °C in air.[4] The typical dimensions of the crystals were $3 \times 3 \times 0.05$ mm. The composition and quality of the crystals were monitored by x-ray spectral analysis and x-ray structural analysis. We used a 3-cm-range ESR spectrometer. The sample temperature could be held anywhere in the range 3.5–300 K.

For some of the samples with $T_c = 90$ K we observed a magnetic resonance at temperatures below 50 K. The magnetic-resonance line has a width ΔH of 600–700 Oe and a g-factor of 2.2. It intensifies with decreasing temperature.

The observed signal is characterized by a high intensity for very small sample dimensions in the 9-GHz microwave range. According to our estimates, the concentration of magnetic-resonance centers in the sample should be on the order of 10^{21} cm^{-1}. Such a high concentration could not be explained on the basis of uncontrollable impurities in the initial materials. In other words, the magnetic-resonance signal must be associated with ions of the host lattice, probably copper or oxygen. The width of the line is apparently determined primarily by spin-spin couplings.

It was established that the magnetic-resonance signal appears in crystals which are deficient in oxygen. A magnetic resonance is observed in all the crystals with $T_c = 50$ K. In this case we observe a temperature dependence of not only the line intensity but also the width. In crystals with $T_c = 90$ K the dependence of the linewidth is masked by the pronounced magnetic flux creep. For the nonsuperconducting crystals ($x \approx 6.3$) we do not observe a magnetic-resonance signal. The magnetic resonance disappears from the crystals with $T_c = 90$ K after they are subjected to an additional saturation with oxygen. The magnetic resonance is thus observed only when the crystal is in the superconducting state, and only if the oxygen concentration in the crystal does not exceed a certain limit.

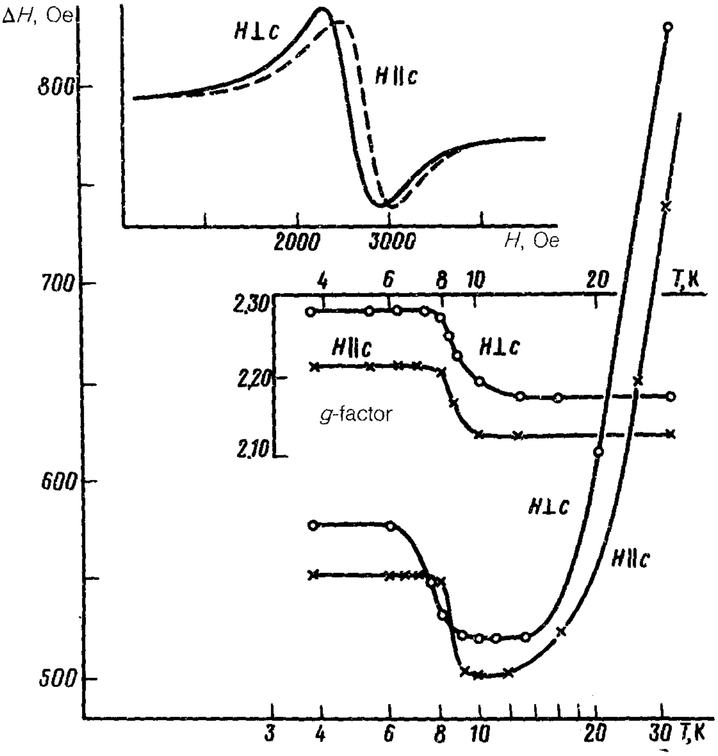

FIG. 1. Magnetic-resonance spectrum of a $GaBa_2Cu_3O_x$ single crystal. a—$T_c = 50$ K, $\nu = 9$ GHz, $T = 13$ K; b—temperature dependence of the linewidth ΔH; c—that of the g-factor.

Figure 1a shows the magnetic-resonance signal for a crystal with $T_c = 50$ K. Figure 1b and c, shows the temperature dependence of the linewidth ΔH and that of the g-factor. We see that the lines become narrower as the temperature is lowered from 30 K to 13 K; the linewidth remains essentially constant over the interval 13–9 K and then increases abruptly at $8 < T < 9$ K. The g-factors, which are essentially constant above 9 K, change abruptly as the temperature is lowered. This jump may be a consequence of magnetic ordering. Note that anomalies have been observed in studies of the muon resonance[5] and of the nuclear spin-lattice relaxation[6] in this temperature range in superconducting samples deficient in oxygen. We should also stress the anisotropy of the magnetic resonance. It can be seen from the angular dependence of an individual magnetic-resonance line that the center is oriented along the c axis.

Figure 2a shows the temperature dependence of the integral intensity of the magnetic-resonance signals for samples with $T_c = 50$ and 90 K. As the temperature is lowered, the signal intensity increases in the same way for the samples with different

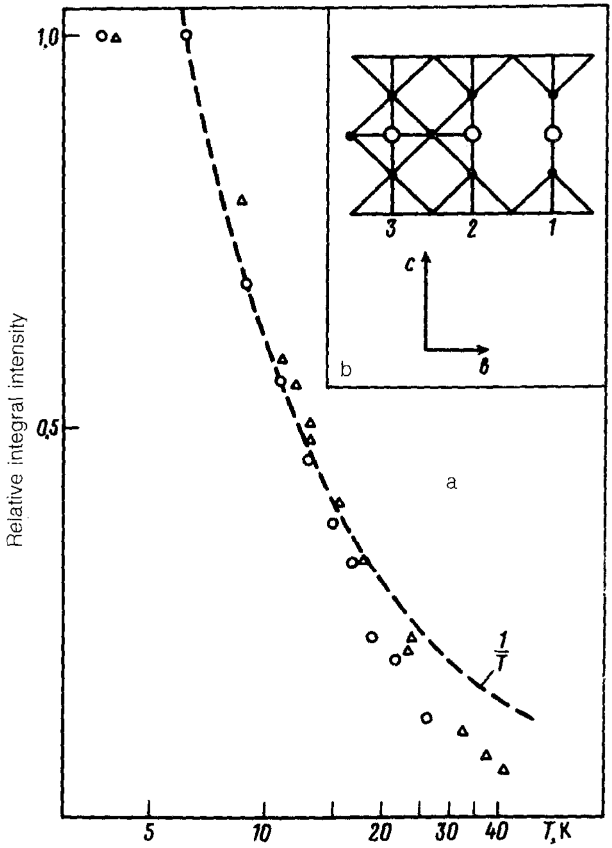

FIG. 2. a: Temperature dependence of the integral intensity of the magnetic resonance for single crystals with (circles) $T_c = 50$ K and (triangles) $T_c = 90$ K. b: Diagram of the yttrium high-temperature superconductor. Large open circles—Cu I; filled circles—O^{2-}; 1,2—$6 < x \leqslant 6.5$; 3—$6.5 < x < 7$.

values of T_c. Above 15 K the intensity of the magnetic resonance increases more rapidly than it would according to the Boltzmann factor, which is shown in this figure as a plot of $1/T$. Below 6 K, the magnetic-resonance signal reaches saturation.

Figure 2b shows a structural diagram of the yttrium high-temperature superconductors. The large open circles represent the copper ions Cu I, while the filled circles represent oxygen ions which are bound directly to the copper ions. Cases 1 and 2 correspond to oxygen concentrations $6<x\leqslant 6.5$, and case 3 to $6.5<x<7$. We believe that the magnetic resonance is observed in crystals having a structure of type 2. These can be crystals having either $T_c = 50$ K or $T_c = 90$ K, for which the bonds are not completely saturated with oxygen. An important point is that the magnetic resonance is observed only if the crystal is in a superconducting state. The magnetic resonance is apparently associated with electrons which localize at a defect before they manage to pair off, and it is not observed when all of the electrons capable of pairing off have done so.

In the crystals with $T_c = 90$ K, the shape of the magnetic-resonance line is distorted below T_c by a magnetic flux creep. For crystals with $T_c = 50$ K this creep is considerably weaker, and essentially no effects of a distortion of the lineshape upon a variation of the magnetic field are observed. We did observe that when the sample was rotated rapidly in a static magnetic field, with a magnitude no lower than the resonant

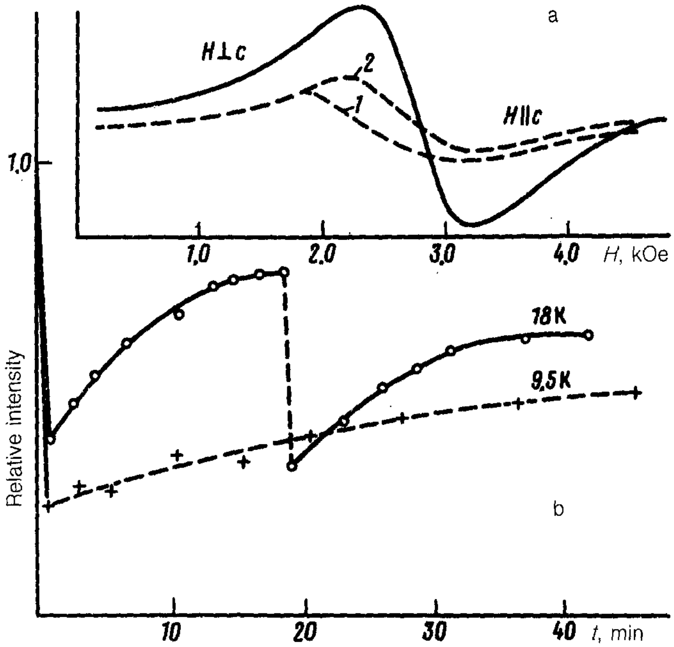

FIG. 3. a—Magnetic resonance spectra of a $GdBa_2Cu_3O_x$ single crystal with $T_c = 90$ K; b—relaxation of the magnetic-resonance signal after the crystal is rotated through 360° in a 5-kOe magnetic field at two temperatures. Two rotations are shown for 18 K.

value, there was a significant decrease in the amplitude of the magnetic-resonance signal, and its shape was distorted. Figure 3 shows a magnetic-resonance signal recorded at 18 K in the orientation **H**⊥**c**, for a sample which was cooled in this orientation. After the crystal was rotated 90°, i.e., in the orientation **H**||**c**, we first observed line 1, and then the signal increased. After a few minutes, it acquired shape 2. In the orientation **H**||**c** we observed a pronounced hysteresis when the magnetic field was swept in the opposite direction. Furthermore, the shape and width of the resonance line in the case **H**||**c** depend strongly on the point at which the sweep of the external magnetic field is begun in the case of a sweep in the forward direction: As the point of the beginning of the sweep approaches the resonant value, the signal narrows and shifts up the magnetic-field scale.

Figure 3b illustrates the relaxation of the resonance signal after the crystal is rotated through 360° in 20 s in an external magnetic field of 5 kOe. The crystal was in the **H**⊥**c** orientation in this case. We see that the signal rise depends on the crystal temperature. A rapid and complete restoration or the original resonance signal requires that the crystal be heated to a temperature on the order of $T_c = 90$ K and then recooled. Note that — in contrast with experiments carried out to observe relaxation of the magnetic moment of the basis of measurements of the microwave absorption and the magnetization — in our case the relaxation of the magnetic moment has been observed for the first time through the recording of a magnetic-resonance signal.

In summary, a magnetic resonance is observed in the superconducting phase in the crystals with $T_c = 50$ K; i.e., it is a characteristic of this phase. The magnetic-resonance signal in crystals with $T_c = 90$ K stems from an impurity of the phase with $T_c = 50$ K; the vortical local fields broaden the resonance signal, and the pinning and depinning of these vortex fields give rise to relaxation and hysteresis effects.

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