Microwave studies of high-temperature superconductors

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Intense microwave signals in weak magnetic fields have been detected and studied in superconducting ceramics and single crystals over the frequency range 1–38 GHz. Some new anisotropic ESR signals, which appear at temperatures below 40 K, have also been detected and studied. The intensity, width, and g-factor of these new signals all increase with decreasing temperature.

Microwave methods rank among the most informative for studying the nature of excitations in solids. These methods are extremely promising for identifying the mechanism for the high-temperature superconductivity discovered by Bednorz and Müller.[1] In this letter we report microwave studies of $Y_1Ba_2Cu_3O_x$ ceramics and single crystals and also some other ceramics [$Eu_1Ba_2Cu_3O_x$, $Sm_1Ba_2Cu_3O_x$, $Y_1Ba_2Cu_2O_x$, $Y_{1.85}Ba_{0.15}CuO_x$, and $Gd_{1.85}Ba_{0.15}CuO_x$ ($x = 6.5 + \delta$)] over the frequency range 1–38 GHz and the temperature range[2] 4–300 K. A high-temperature superconductivity was not observed in the last two of these ceramics. The samples were prepared by solid-phase synthesis at 950 °C. In synthesizing the pressed polycrystalline samples we started from the nitrates of copper, barium, yttrium, etc., in the appropriate stoichiometric proportions. The corresponding single-crystal samples, 50–100 μm thick with transverse dimensions ~ 2 mm^2, were prepared from mixtures of the oxides by a technique similar to that described in Ref. 3. Standard 10- and 35-GHz-range ESR spectrometers were used. We also used a nonresonator microwave spectrometer developed especially for this purpose. This spectrometer made it possible to carry out microwave studies with a continuous frequency tuning up to 38 GHz. The magnetic field in the spectrometer was produced by Helmholtz coils.

In all of the test samples which exhibited a high-temperature superconductivity, an intense signal appeared in low magnetic fields at temperatures close to the critical temperature ($T_c \approx 93$ K). A similar low-field signal had been observed in Ref. 2 and, independently, in Refs. 4–7, but not until the present experiments had this signal been observed in single crystals and studied over the wide frequency range 1–38 GHz. In the ceramics and single crystals in which the high-temperature superconductivity was observed (except $Eu_1Ba_2Cu_3O_x$), new, anisotropic ESR signals appeared at temperatures well below T_c. The amplitude, width, and g-factor of these new signals increased sharply with decreasing temperature. Figure 1a shows a low-field signal detected at various temperatures on a standard ESR spectrometer (9.3 GHz). We see that as the temperature is lowered, the maximum of the slow-field signal shifts up the magnetic-field scale, and the lines broaden. The shift of the lines results from a more effective capture of magnetic flux at low temperatures. The capture of magnetic flux can be seen most vividly in Fig. 1b, which shows a typical signal recorded in the nonresonator

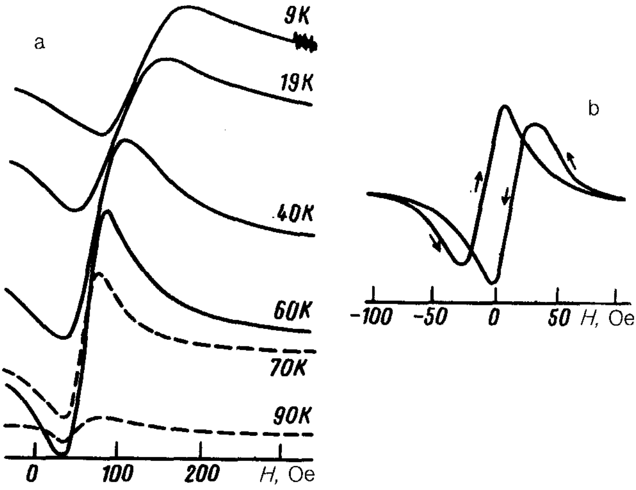

FIG. 1. a—Temperature dependence of the low-field signal. The fluctuations in the signal at $T = 9$ K are shown schematically. The frequency is 9.3 GHz; b—low-field signal at 77 K and a frequency of 26 GHz. The arrows show the direction in which the field H is varied (the ceramic $Y_1Ba_2Cu_3O_x$).

spectrometer at one of the frequencies (26 GHz) at 77 K. The use of the Helmholtz coils made it possible to change the direction of the magnetic field in a symmetric way. The magnitude of the hysteresis corresponds to the magnitude of the captured flux. A low-field signal was observed in all these ceramics and single crystals in which a high-temperature superconductivity was detected. The phase of the low-field signal was opposite that of the ESR lines. We found no changes in the intensity of the low-field single at any frequency up to highest studied, 38 GHz.

Figure 2 shows the new ESR signals detected in $Y_1Ba_2Cu_3O_x$ single crystals in the orientation $\mathbf{H}\perp c$ (solid lines) and $\mathbf{H}\| c$ (dashed lines). We see that new lines appear in place of the ESR signal of Cu^{2+}—which is observed at high temperatures—when the temperature is reduced below 30 K. The inset shows the increase in the intensity (I) and the width (ΔH) of the ESR signal with decreasing T; i.e., the integral intensity of the signal increases sharply in a narrow temperature interval. We see that the ESR signals are anisotropic (at $T = 5$ K we have $g_\perp = 2.27$ and $g_\| = 2.18$; at $T = 20$ K we have $g_\perp = 2.15$ and $g_\| = 2.13$). Figure 2 shows the amplified low-field signal for two orientations at $T = 6.5$ K.

The ESR spectra shown in Fig. 2 were not observed in the samples in which we did not find a high-temperature superconductivity.

Before we take a theoretical look at the problem, let us list the basic properties of the low-field signal: The signal is observed both in ceramics and single crystals in the superconducting state; it exists over a broad frequency interval and does not have a boundary anywhere up to 38 GHz; its integral intensity increases, and the line broadens, with decreasing temperature; the phase of the low-field signal is proportional to the phase of the ESR signals. The high intensity of the low-field signal, which made this signal detectable in small samples by a nonresonant method, and also the fact that the phase of the signals is opposite that of the ESR lines could be attributed to an effect of the electric component of the microwave field (**E**).

Let us examine a possible mechanism for the formation of this low-field signal.

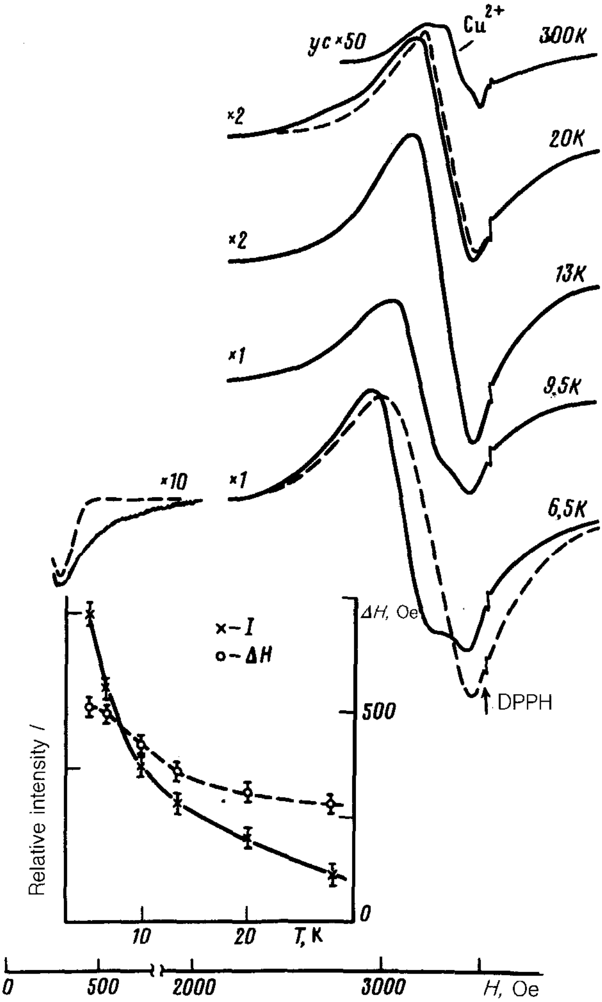

FIG. 2. ESR spectra of $Y_1Ba_2Cu_3O_x$ single crystals at a frequency of 9.3 GHz. Solid lines—The orientation H⊥c; dashed lines—H‖c. The low-field signal is shown for $T = 6.5$ K. The narrow signal is that of DPPH. The inset shows the temperature (T) dependence of the intensity and width of the lines for the case H⊥c.

Specifically, we consider hole pairs which are subject to spatial fluctuations in the composition of the superconductor and irregularities in its structure. As a result, a random multiwell potential is formed for the hole pairs. At the minima of this potential, the energies of the pairs are not the same; they are instead characterized by a distribution with a width $\langle(\Delta U)^2\rangle^{1/2}$, where ΔU is the difference between the energies of the pair in neighboring minima of the multiwell potential. Here the stage is set for the internal Josephson effect, in which hole pairs would tunnel through the barriers between the minima of this potential. A tunneling would become possible when a hole absorbed or emitted a quantum of microwave radiation, $h\nu = \Delta U$. The probability for transitions under the influence of the field component **E** exceeds the probability for transitions under the influence of the magnetic component. The absorption of the **E** component is a consequence of an effective modulation of the energy gap between the states of the pairs in different wells of the random potential. It leads to the possibility of a Josephson tunneling. This situation essentially corresponds to a paraelectric resonance of tunneling pairs under conditions corresponding to the internal Josephson effect. The scattering in the values of ΔU over the sample leads to the existence of a resonance of this sort over a wide frequency range; from the experimental results we find $\langle (\Delta U)^2 \rangle^{1/2} > 1\ \mathrm{cm}^{-1}$. The magnitude of the imaginary part of the electric susceptibility χ'' of a Josephson junction in the resistive model and thus the intensity of the low-field signal are determined by the expression $\chi'' \sim (RI_c)^2 \tanh(\Delta U/2kT) \times \delta(h\nu - \Delta U)$, where I_c is the maximum dissipationless current across the junction, and R is the resistance of the junction in its normal state. The intensification of the low-field signal with decreasing $T < T_c$ is explained in terms of an increase in the number of hole pairs which are participating in the high-temperature superconductivity, a contribution of a temperature factor $\tanh(\Delta U/2kT)$, and also a possible increase in the tunneling matrix elements. This paraelectric resonance of hole pairs can be crossed by the external magnetic field $\mathbf{H}$ because of the magnetic-field dependence of the maximum dissipationless tunnel current through the junction. If the distributions of the potential barriers at the Josephson junctions have different characteristics, we find a resultant functional dependence $\chi''(\mathbf{H})$ in the form of a bell-shaped curve with a maximum at $\mathbf{H} = 0$ and slowly decaying wings. The capture of magnetic flux in the superconducting state causes a shift of the maximum of the low-field signal away from the point $\mathbf{H} = 0$. Finally, the circumstance that the low-field signal is also seen in single crystals suggests that this potential results primarily from spatial fluctuations of the composition of the superconductor, specifically, fluctuations in the concentration of oxygen ions.

The observed ESR spectrum in the superconducting phase, with an intensity which increases with decreasing T, may be due to localized electron states of ferromagnetic O^--Cu^{2+} pairs. As T is reduced, the population of the triplet ground state of the pair—which is active in ESR—would increase. The broadening, on the other hand, of both the ESR signal and the low-field signal with decreasing T might be due to an effect of a superstructure of intermediate-state vortices, whose amplitude increases with decreasing T.

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