Electronic properties of the system $YBa_2Cu_3O_{7-\delta}$

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As a result of measuring the electrical resistance (ESR) and the magnetic susceptibility of the system $YBa_2Cu_3O_{7-\delta}$ with $0.15 \leqslant \delta \leqslant 0.5$, it has been established that this is a heterogeneous system comprised of metallic regions and antiferromagnetically ordered dielectric regions.

Brewer *et al.*[1] have shown that the system $YBa_2Cu_3O_{7-\delta}$ with $0.6 \leqslant \delta \leqslant 1$ is an antiferromagnet with the Néel temperature T_N which decreases with increasing oxygen concentration. In this letter we report the results of a study of the evolution of the properties of an yttrium-barium ceramic as the oxygen deficiency is varied in the range $0.15 \leqslant \delta \leqslant 0.5$.

The polycrystalline samples with a low oxygen deficiency were synthesized from the oxides of the starting elements, using the standard procedure. The lattice constants of the $YBa_2Cu_3O_{7-\delta}$ samples were: $a = 3.812$ Å, $b = 3.874$ Å, and $c = 11.635$ Å. To create a large oxygen deficiency, we heated the samples at a temperature of 900 °C for 3 h at a low oxygen pressure (~ 5 torr) and then we cooled them rapidly to room temperature. As a result of following this procedure, we obtained samples with a

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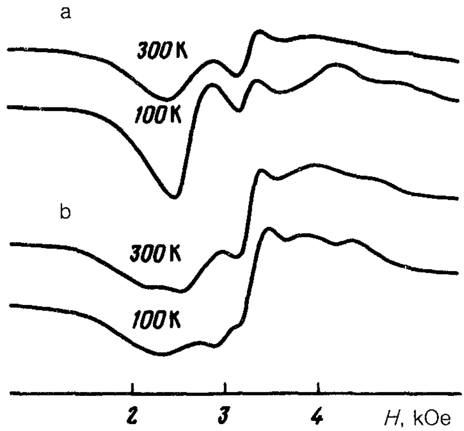

FIG. 1. ESR spectra of the $Y_{0.99}Gd_{0.01}Ba_2Cu_3O_{7-\delta}$ samples. *a*—$\delta = 0.15$; *b*—$\delta = 0.5$.

tetragonal structure with the lattice constants $a = 3.84$ Å and $c = 11.73$ Å. The relative change in the lattice constant c was similar for the samples containing gadolinium. From the correlation of the lattice constants with the oxygen concentration of the samples studied by Kwok *et al.*[2] we can assume that $\delta \approx 0.15$ in the first case and $\delta \approx 0.5$ in the second. To analyze the ESR, we introduced gadolinium into the samples, which replaced yttrium either partially or completely.

Figure 1 shows the ESR spectra of the $Y_{0.99}Gd_{0.01}Ba_2Cu_3O_{7-\delta}$ samples with $\delta = 0.15$ and 0.5 at a frequency $\nu = 9200$ MHz. The observable fine structure of the spectrum is typical of powdered samples which contain a few Gd^{3+} ions. As the temperature is raised, the ESR spectrum changes identically in both samples: The relative amplitude of the central line with $g \approx 2.00$ increases with increasing temperature, while the intensity of the lateral components decreases. Such a transformation of the ESR spectrum usually occurs in metals because of the increase in the Korringa relaxation of the localized moments, which is linearly dependent on the temperature. [3]

The $GdBa_2Cu_3O_{7-\delta}$ samples exhibit a single ESR line from Gd^{3+} ions. The fine structure is contracted by the exchange interactions between the gadolinium spins.[4] Figure 2 shows the results of measurements of the ESR linewidth ΔH. At $T \geqslant 50$ K the increase in ΔH with temperature in both samples is characteristic of metallic samples.

The measurements of the electrical resistance of these samples have shown that at $\delta = 0.15$ the temperature evolution of ρ is of a "metallic" nature and in samples with $\delta = 0.5$ it is of a "semiconductor" nature. Such behavior of ρ can be reconciled with the metallic nature of ESR if it is assumed that the samples with $\delta = 0.15$ and 0.5 constitute a heterogeneous system consisting of a metallic component and a dielectric component, with a percolation in the former case and none in the latter. Such a possibility is also suggested by the law governing the change in the electrical resistance $\rho(T) \propto \exp(A/T^{1/2})$ in a sample with $\delta = 0.5$, which is usually observed in granular systems. More definite conclusions can be drawn on the basis of an analysis of the shape of the ESR line of $GdBa_2Cu_3O_{7-\delta}$ samples with different oxygen deficiencies. The recorded signal is found to be comprised of two lines with approximately equal *g*-

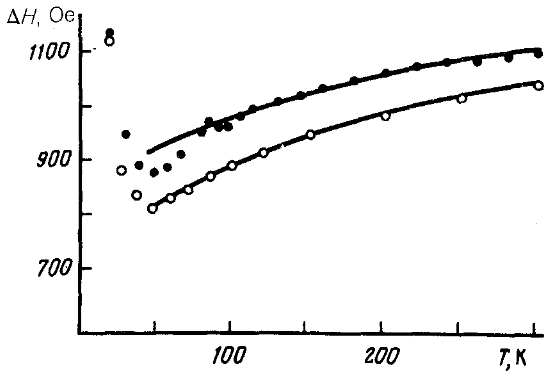

FIG. 2. Temperature dependence of the linewidth of Gd^{3+} in $GdBa_2Cu_3O_{7-\delta}$ samples. ●—$\delta = 0.15$; ○—$\delta = 0.5$. Solid lines—results obtained by simulating the spectra.

factors ($g \approx 1.99$) but with different widths. The width of one of the lines depends linearly on the temperature in accordance with $\Delta H = a + bT$, where $a = 580$ Oe and $b = 0.9$ Oe/K, while the width of the other line, essentially independent of the temperature, is equal to 1000 Oe. We assume that these signals come from respectively the metallic and dielectric regions. A pronounced nonlinearity in the temperature behavior of ΔH (Fig. 2) is the result of a superposition of these two signals. In a sample with $\delta = 0.5$ the contributions from the dielectric and metallic regions to ESR are the same. The absence of a dispersion in the ESR signal means that the metallic inclusions in this sample are much smaller in size than the depth of the skin layer. As a result, the amount of metal the sample contains is estimated to be 50%. In a sample with $\delta = 0.15$ the integrated intensity of the ESR signal is one-third lower, and the dispersion signal is necessary to describe the lineshape. This means that the fraction of the metallic phase increases but its contribution is strongly suppressed by the skin effect. Since the ratio of the contributions of the dielectric and metallic regions to the spectrum is 7:3, the fraction of metal by volume, with $\delta = 0.15$, is estimated to be 80%.

Since the "dielectric" component of the ESR signal in the $GdBa_2Cu_3O_{7-\delta}$ samples ($\Delta H = 1000$ Oe) is much wider than the residual linewidth ($a = 580$ Oe) from the metallic regions, we conclude that magnetism is present in the nearest neighborhood of the Gd^{3+} ions in the dielectric regions. To determine the magnetic state of this heterogeneous system, we have measured the magnetic susceptibility χ of the $YBa_2Cu_3O_{7-\delta}$ samples without any special admixtures of the paramagnetic Gd^{3+} ions and we have also measured the integrated intensity of the ESR signal which is attributable in these samples, as in those in Ref. 4, to the localized moments of Cu^{2+}. The latter quantity determines the contribution of these localized moments to the magnetic susceptibility χ^{ESR}. The results of these measurements are shown in Fig. 3. The difference $\Delta\chi = \chi - \chi^{ESR}$, which depends only slightly on the temperature, increases with increasing fraction of the dielectric component of the sample. With $\delta = 0.15$, $\Delta\chi = 0.9 \times 10^{-6}$ cm^3/g and with $\delta = 0.5$, it is equal to 2×10^{-6} cm^3/g. We can conclude, therefore, that $\Delta\chi$ is determined primarily by the dielectric components which are in the Mott–Hubbard antiferromagnetic state with $\chi_{af} \propto C/T_N$. Knowing the relative fraction of the dielectric at different values of δ, we estimate the Néel

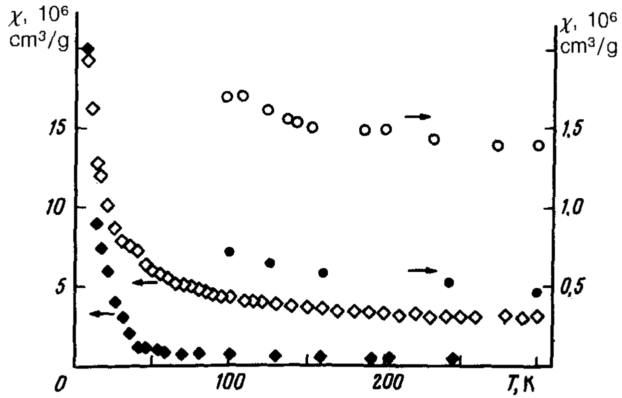

FIG. 3. Temperature dependence of the total magnetic susceptibility χ(○ and ◇) and of the susceptibility χ^{ESR} of the localized moments of Cu^{2+} in the Cu 1 position (● and ◆) in the samples with $\delta = 0.15$ and 0.5, respectively.

temperature of these regions to be $T_N \approx 300$ K. We detected no traces of diamagnetism in $Yba_2Cu_3O_{6.5}$ down to $T = 1.5$ K. If the coherence length of the superconducting samples is assumed to be[5] $\xi = 10$–20 Å, the minimum size of the metallic inclusions, which apparently have the shape of a plate, should be not much greater than 30 Å.

On the basis of the arguments presented above we can assume that $YBa_2Cu_3O_{7-\delta}$ with $\delta \neq 0$ is an inhomogeneous system consisting of metallic and dielectric regions. With an increase in the oxygen deficiency to $\delta = 0.5$, the metallic regions ~30 Å thick become surrounded by well insulating dielectric regions. As to whether superconductivity and antiferromagnetism coexist (see, e.g., Ref. 1) in yttrium ceramics or whether they are spatially separated in them can thus be answered in favor of spatial separation.

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