

## Effects of substitution of O by S and Cu by Fe on superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_7$

I. Felner and I. Nowik

*Racah Institute of Physics, The Hebrew University, Jerusalem, Israel*

Y. Yeshurun

*Department of Physics, Bar-Ilan University, Ramat Gan, Israel*

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The single-phase high- $T_c$  superconductors  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$  and  $\text{YBa}_2\text{Cu}_3(1-y)\text{Fe}_y\text{O}_7$  have been prepared and studied by dc magnetometry.  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{S}$  has a larger unit cell than  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , and yet has the same  $T_c$ ; its phase transition is sharper and displays full Meissner effect. Substitution of Cu by Fe leads to a sharp decrease in  $T_c$ .

The compounds  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $R = \text{Y}$  or a rare-earth metal) have an orthorhombic distorted oxygen-deficient perovskite structure and, as is already well known, exhibit high- $T_c$  superconductivity.<sup>1</sup> The fact that even when  $R$  is Gd the superconducting transition temperature is similar to that of  $R = \text{Y}$  indicates that the rare-earth site is not much involved in the superconductivity process. Substitution in the Ba site (25% Sr) also does not affect  $T_c$ .<sup>2</sup> Here we report studies of the effect of substitution in the oxygen site (sulfur) and in the copper site (iron). In both cases the superconductivity features are strongly affected; by iron for the worse, by sulfur for the better. Substitution of Cu by trivalent iron ions sharply decreases  $T_c$  monotonically with iron concentration. On the other hand, substitution of oxygen by sulfur ( $\text{YBa}_2\text{Cu}_3\text{O}_6\text{S}$ ) does not change  $T_c$ , but the phase transition is much sharper and the Meissner effect is almost complete. The fact that  $T_c$  is not affected by substitution of oxygen is consistent with reported observations about the lack of an oxygen isotope effect in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .<sup>3</sup>

Since the details of sample preparation strongly affect the properties, the procedure of our sample preparation is outlined here.

Single-phase  $\text{YBa}_2\text{Cu}_3\text{O}_7$  was prepared by mixing  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$ , grinding it, and heating it at  $950^\circ\text{C}$  in air for one day. The mixture was then cooled to ambient temperature, pressed into pellets, sintered in flowing  $\text{O}_2$  for 16 h at  $800^\circ\text{C}$ , and cooled slowly to  $200^\circ\text{C}$  in  $\text{O}_2$  before removal from the furnace. The iron- and sulfur-containing compounds were prepared in the same manner.  $\text{Fe}_2\text{O}_3$  and  $\text{CuS}$  were used as starting materials. Samples were examined by x-ray powder diffraction. The diffraction patterns for all compounds investigated show that the observed lines could be indexed with the orthorhombic unit cell and that the lattice parameters for the "pure"  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are  $a = 3.822 \text{ \AA}$ ,  $b = 3.891 \text{ \AA}$ , and  $c = 11.67 \text{ \AA}$ , which are in fair agreement with published data.<sup>4</sup> The iron-doped samples have practically the same lattice constants. On the other hand, in  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{S}$  we definitely see an expansion in the lattice constants which are  $a = 3.855 \text{ \AA}$ ,  $b = 3.919 \text{ \AA}$ , and  $c = 11.75 \text{ \AA}$ , which indicates that the bigger sulfur atoms really substitute for oxygen. The compound  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{S}$  was examined by a

scanning electron microscope; its composition was found to be uniform from grain to grain. There were no detectable additional phases in this sample and the chemical composition of the system was confirmed to be  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{S}$ .

Together with the orthorhombic phase, which is associated with the superconducting state at 90 K, a high-temperature (above  $600^\circ\text{C}$ ) tetragonal phase was also reported.<sup>3</sup> We obtained this tetragonal phase by rapid quenching the sample from  $800^\circ\text{C}$  to liquid nitrogen. It was found to be nonsuperconducting down to 4.2 K.

The dc susceptibility ( $M/H$ ) measurements were carried out by a 155 Princeton Applied Research vibrating sample magnetometer and by a SQUID magnetometer in various magnetic fields  $4 \text{ Oe} < H < 40 \text{ kOe}$  as a function of temperature in the range 4.2–170 K. There is a difference of about 2 K between the values of  $T_c$  measured in these two magnetometers. The magnetization was measured by two different procedures. (a) The sample was zero-field cooled (ZFC) to 4.2 K, a field  $H$  was applied, and the magnetization of the shielding branch was measured as a function of temperature. (b) The sample was field cooled (FC) from above  $T_c$  in a field  $H$  and the Meissner branch was measured.

Figure 1 displays FC susceptibility measurements obtained for  $\text{YBa}_2\text{Cu}_3(1-y)\text{Fe}_y\text{O}_7$ . One observes a strong shift of  $T_c$  to lower temperatures as  $y$  increases (inset in Fig. 1). This means that the Cu ions, unlike the rare-earth ions, are strongly involved in the superconducting process. Mössbauer studies were carried out on the  $y = 1\%$  and  $10\%$  iron-doped compounds at different temperatures. Generally speaking, the spectra of the two samples are quite the same at the same temperatures, and consist of two quadrupole doublets in the ratio 2:1 according to the distribution of copper into two crystallographic sites.<sup>4</sup> An additional weak subspectrum corresponding to iron in an additional site or in the tetragonal phase is also present. The detailed analysis of the Mössbauer studies will be published elsewhere.

The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$  compounds  $x = (0,1)$  were prepared at the same time under the same conditions and studied by magnetic-susceptibility measurements. Qualitatively, the two samples exhibit similar magnetic proper-

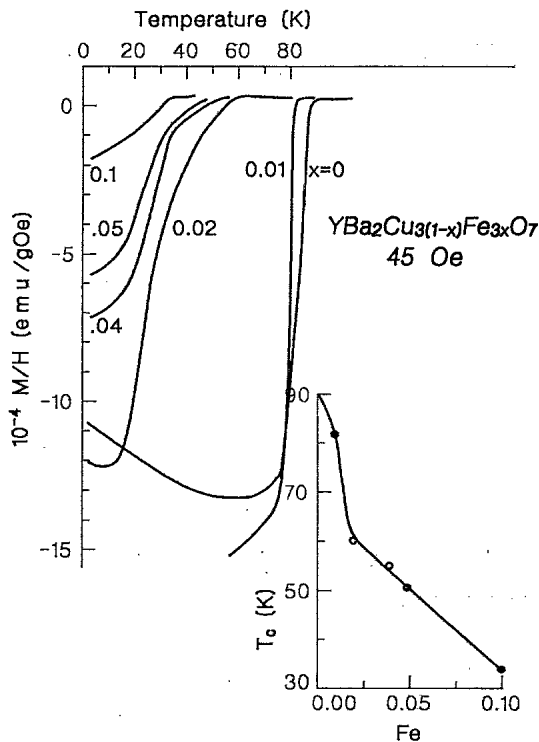


FIG. 1. Magnetic dc susceptibility curves for "pure"  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and iron substituted compounds, measured by Princeton Applied Research vibrating-sample magnetometer.

ties above and below  $T_c$ . The most exciting fact is that sulfur does not affect  $T_c$ , which is 90 K for  $x=0,1$ . It should be added that we also substituted the oxygen with chlorine, and  $T_c$  for  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{Cl}$  is 72 K.

In Fig. 2 we represent the Meissner branch for the lowest field ( $H \approx 4$  Oe). It is clear that for  $x=1$  the tran-

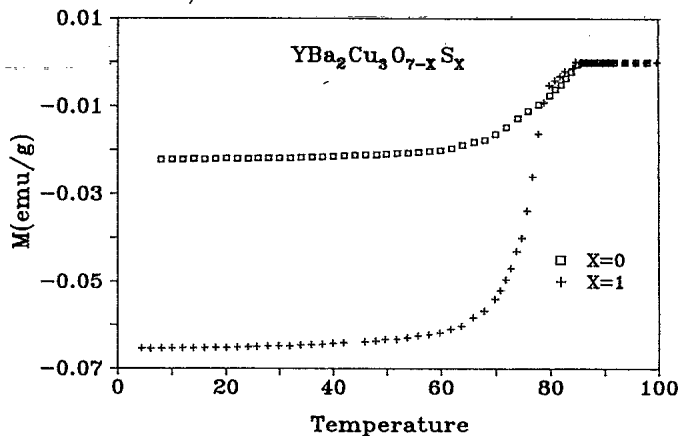


FIG. 2. Magnetic susceptibility vs temperature curves at  $H=4$  Oe for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$ , where  $x=0$  and 1, measured by SQUID magnetometer.

sition is sharper and our low-temperature diamagnetic susceptibility value is close to the full  $(-1/4\pi)$  Meissner effect, when demagnetization and porosity corrections are applied. The magnitude of this Meissner effect is one of the largest reported and indicates that the superconductivity in this system is a bulk property.

The paramagnetic susceptibility above  $T_c$  is composed of a Curie-like contribution and of an enhanced temperature-independent (Pauli) contribution.  $\chi = \chi_0 + C/T$ , where  $\chi_0 = 9.4 \times 10^{-5}$  and  $46.6 \times 10^{-5}$  emu/mole and  $C = 0.32$  and  $0.12$  emu/mole for  $x=0$  and 1, respectively.

For the quenched sample no superconducting transition is obtained down to 4.2 K, and the paramagnetic susceptibility in the range 4.2–100 K yields a Curie constant of 0.4 emu/mole, in fair agreement with  $C$  for  $x=0$ . This  $C$

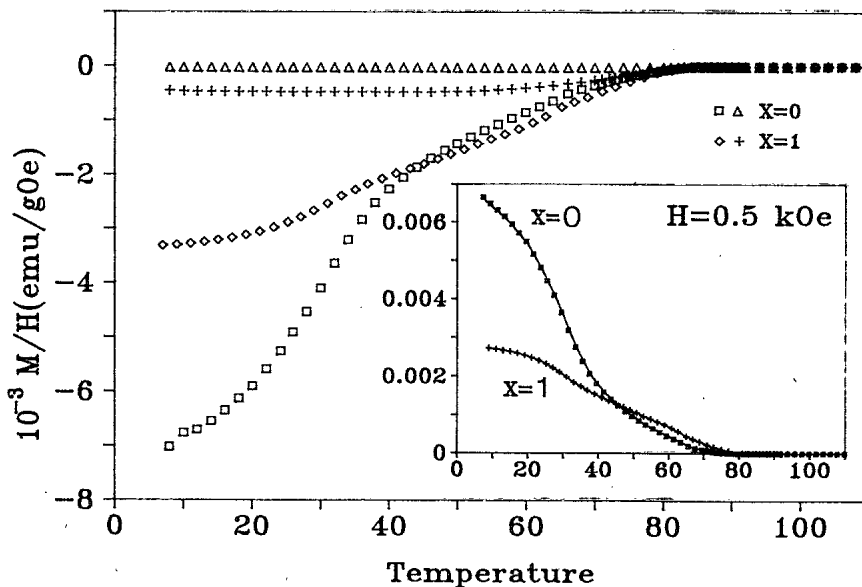


FIG. 3. Susceptibility vs temperature curves for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$  ( $x=0,1$ ) at 500 Oe showing diamagnetic shielding (lower curves ZFC) and Meissner effect (upper curves FC). In the inset the difference between FC and ZFC is shown.

value shows that the amount of the paramagnetic copper ions, in both quenched and slowly cooled materials, corresponds to  $1.7\mu_B$  per formula unit which means that only one third of the localized divalent copper ions is paramagnetic. The unanswered question is whether the magnetic ions are all located in one crystallographic minority site, or are distributed at random over the two equivalent positions in the copper majority site.

In Fig. 3 we exhibit the ZFC and FC branches for  $x=0$  and  $x=1$  in an applied field of 500 Oe. The shielding (ZFC branch) is better for the  $x=0$  sample, but the FC branch is lower for  $x=1$ , which means that in this compound the Meissner effect is higher. The amount of irreversibility defined as the difference between the FC and ZFC branches is shown in the inset. For  $x=0$  the difference is higher at low temperatures and becomes smaller at high temperatures close to  $T_c$ . We measured the critical fields  $H_{c2}$  close to  $T_c$  and found that  $H_{c2}(x=1, T) > H_{c2}(x=0, T)$ . This implies that at this temperature range the density of fluxons is smaller for  $x=0$ . Indeed, the shielding effect for  $x=0$  is small near  $T_c$ . On the other hand, at low temperatures one observes in Fig. 3 that the opposite occurs. The shielding effect for  $x=0$  is quite below the curve of  $x=1$ . Our highest applied field is limited to 50 kOe and  $H_{c2}$  at low temperatures is well above this field and so the question of the higher shielding effect for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at low temperatures remains unsolved. It should be added that the higher Meissner branch for  $x=0$  is consistent with the high Curie term observed at elevated temperatures.

Figure 4 serves to demonstrate the effect of the paramagneticlike background which characterizes all the high- $T_c$  superconductors.<sup>5</sup>

The measured magnetization below  $T_c$  is composed of diamagnetic and paramagnetic contributions. In the high-field regime, actually above  $H_{c1}$ , the diamagnetic signal decreases with the field and therefore the paramagnetic contribution dominates the magnetic behavior, especially in the low-temperature regime, where the  $C/T$  term is more significant. For  $H=20$  kOe the effect is most dramatic for  $x=0$ , where the measured signal is positive for all temperatures below  $T_c$ .

The observations reported in the present paper lead to

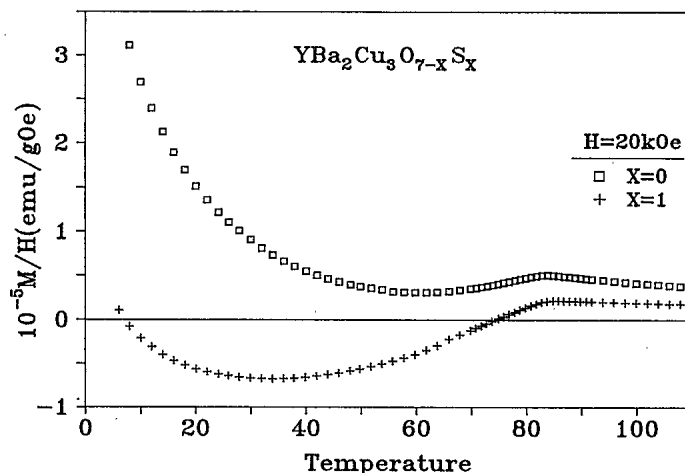


FIG. 4. Magnetic-susceptibility curves of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$  ( $x=0,1$ ) at 20 kOe showing the dominance of the superconducting diamagnetism over paramagnetism in the  $x=1$  sample and vice versa in the  $x=0$  sample.

the following conclusions: (1) The superconducting temperature in the high- $T_c$   $\text{YBa}_2\text{Cu}_3\text{O}_7$  decreases when copper is substituted by iron. (2) No significant effect on  $T_c$  occurs when the oxygen is substituted with sulfur. This result, which is in agreement with the lack of isotope effect,<sup>3</sup> sheds more doubts on the possibility that the BCS<sup>6</sup> phonon mechanism is appropriate for explaining the high- $T_c$  superconductors. (3) The system with the sulfur exhibits a larger Meissner effect and a larger critical field,  $H_{c2}$ . (4) Glassy features appear below  $T_c$  which are quite different for the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{S}$  compounds. (5) The amount of paramagnetic copper ions is about one third in both orthorhombic and tetragonal (quenched) structures. (6) The high-field (20 kOe) magnetic-susceptibility measurements show that in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  the paramagnetism overcomes the superconducting diamagnetism contribution, whereas in  $\text{YBa}_2\text{Cu}_3\text{O}_6\text{S}$  the diamagnetism still dominates, proving once again that the addition of sulfur improves the superconducting characteristics of the system.

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