

Magnetic order and superconductivity in $R\text{Ba}_2\text{Cu}_3\text{O}_z$

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(Received 10 May 1988)

Mössbauer studies ^{57}Fe in $R\text{Ba}_{2-y}\text{K}_y(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$, with $R=\text{Y}$ and Pr , $y=0$ and 0.5 , $x=0.01$, 0.05 , and 0.1 , and z between 5.9 and 7.1 , have been performed. A minority of the iron ions enter the $\text{Cu}(2)$ site and reveal its magnetic order. For $R=\text{Y}$, $y=0$, and $x=0.1$, T_N equals 280 and 415 K for $z=6.5$ and 6.1 , respectively. The magnetic moments lie in the basal plane. In tetragonal, oxygen-rich $\text{PrBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{6.9}$, $T_N=325$ K; in superconducting $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{7.1}$ there is no magnetic order. In nonsuperconducting $\text{YBa}_{1.5}\text{K}_{0.5}(\text{Cu}_{0.95}\text{Fe}_{0.05})_3\text{O}_{6.1}$ two distinctly inequivalent magnetic iron sites are observed, corresponding to iron in the $\text{Cu}(2)$ site with different Ba-K neighbors. Moments of iron ions that have three Ba and one K as first-nearest neighbors have a different temperature dependence and T_N ($T_N=450$ K) from those with four Ba neighbors, where $T_N=415$ K, showing that the antiferromagnetic exchange in the $\text{Cu}(2)$ planes is strongly affected by the replacement of Ba^{2+} by K^+ , probably by repelling oxygen from the $\text{Cu}(2)$ plane. In superconducting $\text{YBa}_{1.5}\text{K}_{0.5}(\text{Cu}_{0.95}\text{Fe}_{0.05})_3\text{O}_{6.5}$ the iron site with $T_N=450$ K remains magnetic. The implications of these findings on the valencies of the Cu ions are discussed.

I. INTRODUCTION

From the first days of the discovery of the high- T_c superconductors there were suspicions that the Cu sublattices might be magnetic. The recent discovery¹ that, indeed, the $\text{Cu}(2)$ site in tetragonal nonsuperconducting $\text{YBa}_2\text{Cu}_3\text{O}_6$ is antiferromagnetically ordered confirmed our similar suspicions, aroused by many Mössbauer spectra accumulated to date. We report here Mössbauer studies of ^{57}Fe in $R\text{Ba}_{2-y}\text{K}_y(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$, with $R=\text{Y}$ or Pr , $y=0.0$ and 0.5 , $x=0.01$, 0.05 , and 0.1 , and $z=5.9$ to 7.1 at temperatures between 4.1 and 480 K. These studies show that the fraction of iron ions that enter the $\text{Cu}(2)$ site order magnetically in some of the compounds, with different ordering temperatures. In $\text{YBa}_2\text{Cu}_3\text{O}_z$, the iron spectra reveal magnetic order for $z \leq 6.5$. There is magnetic order in the $\text{Cu}(2)$ site in tetragonal nonsuperconducting $\text{PrBa}_2\text{Cu}_3\text{O}_{6.9}$, with $T_N=325$ K. There is no magnetic order in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$. In $\text{YBa}_{1.5}\text{K}_{0.5}\text{Cu}_3\text{O}_z$ magnetic order in the $\text{Cu}(2)$ site exists up to 450 K. Two inequivalent magnetic $\text{Cu}(2)$ sites are observed. They are explained in terms of their different local environment, according to the number of K neighbors. The results indicate that the Ba-K ions play either an active or passive (rejecting oxygen) role in the magnetic exchange within the $\text{Cu}(2)$ planes. Iron ions in the $\text{Cu}(1)$ site are not ordered magnetically in either the superconducting or the quenched nonsuperconducting sample. The magnetic hyperfine structure observed in the Fe ions replacing $\text{Cu}(1)$ in the nonsuperconducting samples with both $x=0.01$ and $x=0.1$ as well as in the superconducting samples with $x=0.1$, are all due to long paramagnetic spin-relaxation times. The lower the superconducting transition temperature, the longer the spin-relaxation times.

Previous Mössbauer studies of ^{57}Fe in $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$ (Refs. 2-4) have been analyzed in terms of

several Fe inequivalent sites and yield the iron and oxygen concentration dependencies. It was claimed² that the iron is magnetically ordered at 12 K even in the superconducting samples.

II. EXPERIMENTAL DETAILS

The samples were prepared by conventional methods.⁵ Four kinds of preparations of the $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$ were employed. When slow cooling from 850°C in an oxygen atmosphere was applied, fully oxygenated superconducting samples were obtained. Based on the oxygen content measured in iron-free samples, we assumed $z=6.9$ for the samples with $x=0.01$. In samples with $x=0.1$, the value of z was found to be 7.1 by neutron-diffraction measurements.⁶ When the samples were quenched from 800°C , the tetragonal phase was obtained and according to independent oxygen content estimates (based on weight loss) $z=6.1$ in these samples. For the samples quenched from 600°C , which are tetragonal and not superconducting for $x=0.1$, we estimate $z=6.5$,⁷ and for samples that were cooled in a vacuum furnace, we estimate $z=5.9$.⁸ The $\text{PrBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$ samples were cooled slowly and fully oxygenated; we estimate that $z=6.9$. For the $\text{YBa}_{1.5}\text{K}_{0.5}(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$ samples, which were cooled slowly, we used iodometric analysis, which measures the total amount of Cu and the concentration of Cu^{3+} , and allows us to calculate the total amount of oxygen.⁹ According to this chemical analysis, $z=6.5$ in the superconducting samples; we estimate $z=6.1$ in the samples quenched from 800°C . In the fully oxygenated as well as in the quenched samples, the absolute z values are uncertain by as much as 0.1 . All samples were analyzed by x-ray-diffraction measurements and their lattice parameters were obtained. These studies showed that all samples were of single phase.

III. RESULTS AND DISCUSSION

We discuss in detail four families of compounds.

A. $\text{YBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_z$ with $z=5.9$ to 6.9

In all these compounds, the iron replaces mostly the Cu(1) ions,¹⁰ and no well-defined magnetic subspectrum is found in most of these compounds at any temperature above 4.1 K. The spectra obtained at 90 K and above are all composed of six quadrupole doublets, corresponding to six inequivalent iron sites, due to different oxygen neighbor configurations in the Cu(1) site.¹⁰ The relative sizes of the quadrupole splittings in the six sites agree with point-charge calculations for Fe^{3+} .¹⁰ At 4.1 K, the spectra for $z \leq 6.5$ show a complicated structure. These spectra may be due to spin-glass-like order of the iron in the Cu(1) site, but could more reasonably be interpreted as due to paramagnetic slow spin relaxation. Some of the spectra obtained at 4.1 K with different z values were shown in Fig. 2 of Ref. 3. In the spectra we obtained with $z=5.9$ samples, a weak, but well-defined, magnetic sextet is observed up to 400 K (Fig. 1). In these samples, a larger percentage of the iron enters the Cu(2) site, and thus yields the sextet as explained below.

B. $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_z$ with $z=6.1, 6.5,$ and 7.1

In the samples with $z \leq 6.5$, which are not superconducting, we observe a well-defined magnetic sextet, which accounts for about 25% of the spectral area. We attribute this spectrum to iron, which now also replaces copper in the Cu(2) site and orders antiferromagnetically.¹ All iron ions in the Cu(2) site are equivalent in terms of oxygen environment and yield a well-defined magnetic spectrum. At 4.1 K, the magnetic hyperfine field is 514 kOe and the

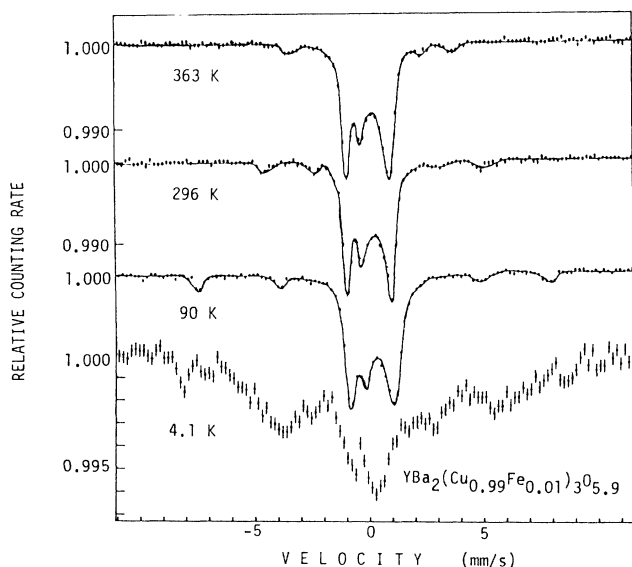


FIG. 1. Mössbauer spectra of ^{57}Fe in $\text{YBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{5.9}$ at several temperatures.

quadrupole interaction is $eqQ/4 = -0.17$ mm/s. The same values are obtained for all other samples discussed in this paper. As the temperature is raised, the magnetic splitting decreases and the Néel temperature in each of the compounds can be obtained. The Néel temperature depends on the oxygen content, increasing as z decreases. No magnetic sextet is observed in superconducting $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{7.1}$. Figures 2, 3, and 4 show the spectra obtained in $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$ with $z=6.1, 6.5,$ and 7.1 at various temperatures. The well-defined magnetic subspectrum is clearly seen and the change of the size of the hyperfine field can easily be followed. A Néel temperature of 415 K is obtained for $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{6.1}$. In $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{6.5}$ similar spectra are observed, yet the magnetic ordering temperature in this compound is $T_N = 280$ K. The electric field gradient at the Cu(2) site according to point charge calculations is positive and points along the c axis. The measured negative effective quadrupole interaction proves that the magnetic moments lie in the basal plane.¹ No magnetic subspectrum can be seen in the $\text{YBa}_2(\text{Cu}_x\text{Fe}_{1-x})_3\text{O}_{7.1}$ samples. Figure 5 shows the hyperfine fields as function of temperature in the different samples. The lines were extrapolated to give an estimate of the ordering temperatures. The fact that the ordering temperature of Fe in $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{6.1}$ agrees so well with the neutron-diffraction results¹ proves that we are indeed measuring

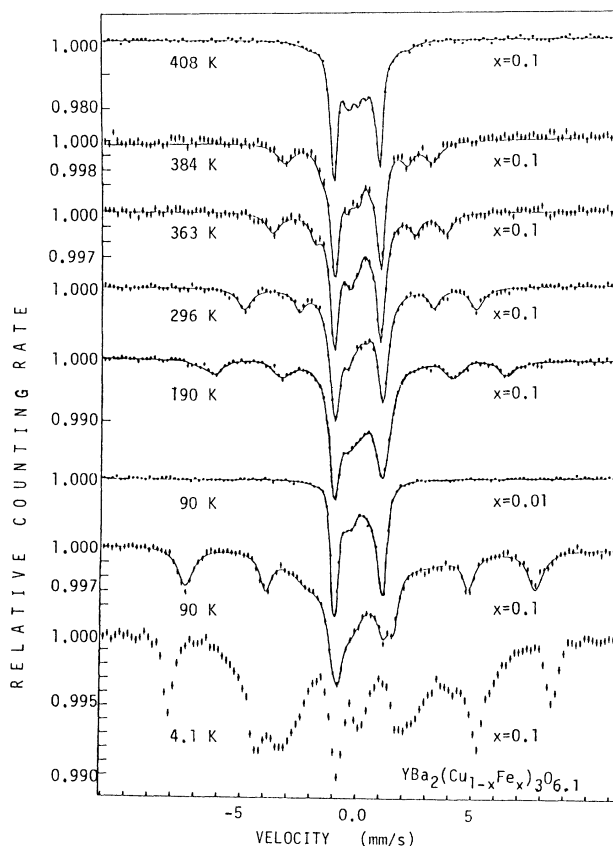


FIG. 2. Mössbauer spectra of ^{57}Fe in $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{6.1}$ at several temperatures. Note that $x=0.1$ in all spectra, except at 90 K, where the spectrum with $x=0.01$ is also shown.

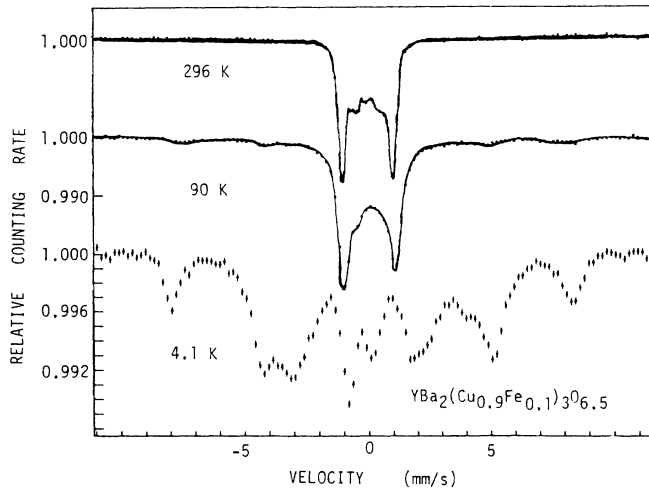


FIG. 3. Mössbauer spectra of ^{57}Fe in $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{6.5}$ at several temperatures.

through the iron the magnetic ordering of copper in the Cu(2) site, and that this ordering is not affected by the presence or concentration of the iron impurity. All spectra at 4.1 K show, besides the well-defined sextet, a complicated central subspectrum, similar to those observed in the $\text{YBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{6.1}$ samples, which are attributed to magnetic spin-glass-like order of the iron in the Cu(1) site or to long spin-relaxation-time phenomena.

The nonsuperconducting samples with $z = 6.1$ and 6.5 in which the magnetic site is seen, differ from the metallic superconducting sample with $z = 7.1$ in several respects: (1) They are semiconductors with different electronic properties and band structure, (2) they are deficient in their oxygen concentration, and (3) they have a tetragonal structure. In order to decide whether all these conditions are essential for magnetic order, or whether any one of them is sufficient, we measured the following two systems:

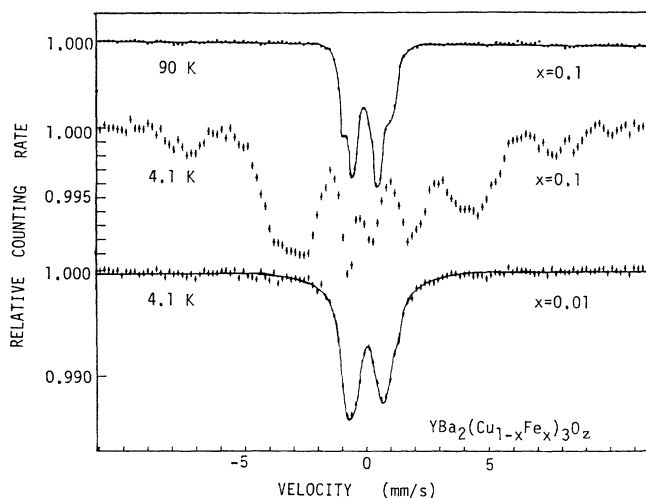


FIG. 4. Mössbauer spectra of ^{57}Fe in $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$ (with $z = 6.9$ for $x = 0.01$ and $z = 7.1$ for $x = 0.1$) at 4.1 and 90 K.

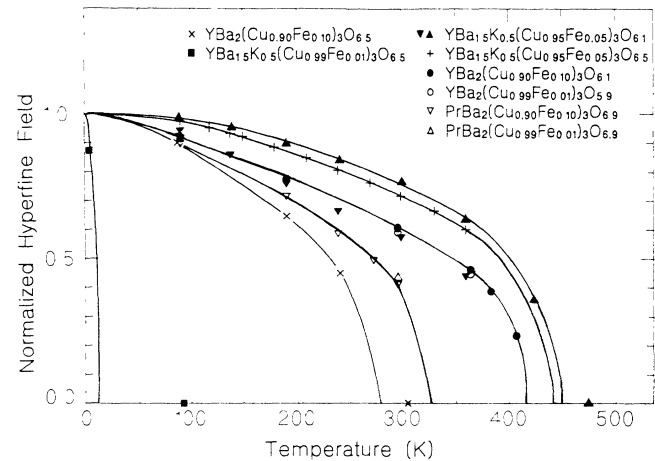


FIG. 5. Temperature dependence of the magnetic hyperfine field acting on ^{57}Fe nuclei in the Cu(2) site in $R\text{Ba}_{2-y}(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$.

$\text{PrBa}_2\text{Cu}_3\text{O}_{6.9}$, although fully oxygenated, is well known not to be a superconductor. On the other hand, the low-oxygen content $\text{YBa}_{1.5}\text{K}_{0.5}\text{Cu}_3\text{O}_{6.5}$ is superconducting with $T_c = 88$ K.¹¹

C. $\text{PrBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{6.9}$ with $x = 0.01$ and $x = 0.1$

These tetragonal compounds, with $a = b = 3.900$ Å and $c = 11.66$ Å for $x = 0.01$ and $a = b = 3.927$ Å, $c = 11.69$ Å for $x = 0.10$, are rich in oxygen yet not superconducting. In these compounds, a well-defined magnetic subspectrum is seen even for $x = 0.01$ (Fig. 6). It thus seems that in these compounds a larger fraction of the Fe ions enter the Cu(2) site. The Néel temperature of the iron ions in the Cu(2) site is 325 K for both $x = 0.1$ and 0.01 (Figs. 5 and 6), proving again that T_N does not depend on iron concentration. Thus, though this compound is rich in oxygen, like the orthorhombic superconducting compounds, it is nevertheless nonsuperconducting, and tetragonal, and its magnetic behavior resembles that of oxygen-poor, tetragonal, nonsuperconducting compounds. This shows that the number of oxygen ions alone cannot account for the disappearance of the magnetic interactions in the Cu(2) site.

D. $\text{YBa}_{1.5}\text{K}_{0.5}(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$, $x = 0.01, 0.05$, and $z = 6.1$ and 6.5

These compounds exhibit superconductivity for $z = 6.5$, with $T_c = 88$ K for $x = 0.01$ and $T_c = 60$ K for $x = 0.05$. The magnetization curves are shown in Fig. 7. The structure is orthorhombic for $x = 0.01$ and $z = 6.5$, and tetragonal for all other samples. The Mössbauer spectra at different temperatures obtained in samples with $x = 0.05$ are shown in Figs. 8 and 9. One observes magnetic subspectra both in the samples with $z = 6.5$ (which are superconducting) and in those with $z = 6.1$ (which are not). In the latter, two magnetic sites are clearly observed. One of these sites follows the magnetic behavior of $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{6.1}$ with $T_N = 415$ K, the other shows a higher T_N

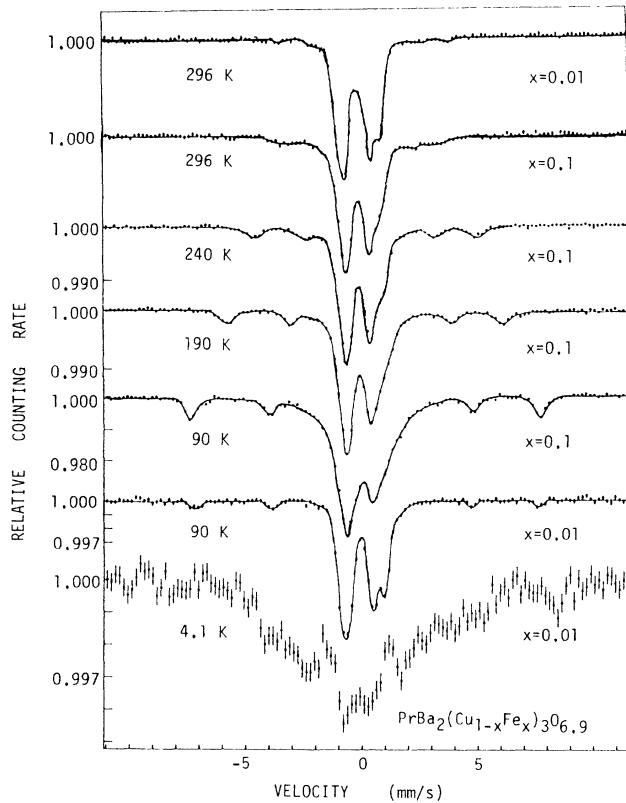


FIG. 6. Mössbauer spectra of ^{57}Fe in $\text{PrBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{6.9}$ with $x=0.01$ and 0.1 , at several temperatures.

of 450 K (Fig. 5). The relative intensity of the magnetic subspectra is higher in samples containing K than in samples that do not contain potassium. Since we attribute the magnetic subspectra to iron in the Cu(2) site, this would imply that K attracts iron into this site. It is reasonable that K^+ , which replaces Ba^{2+} , prefers to have as its neighbor Fe^{3+} instead of Cu^{2+} . In the sample with $z=6.5$, which is superconducting with $T_c=60$ K, only one magnetic site with $T_N=450$ K is observed. It thus seems that, in this compound, superconductivity and magnetic order in the Cu(2) site coexist. A reasonable explanation

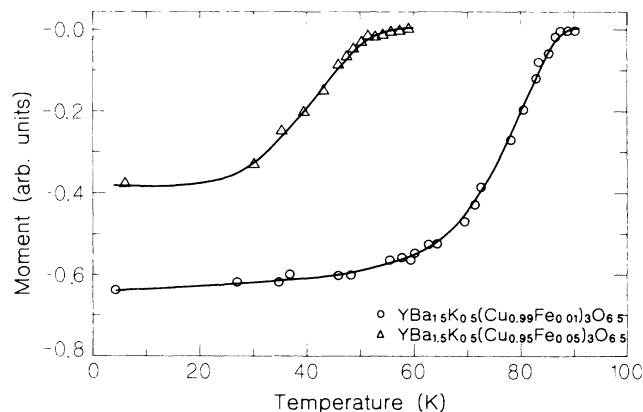


FIG. 7. The magnetic susceptibility of $\text{YBa}_{1.5}\text{K}_{0.5}(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$.

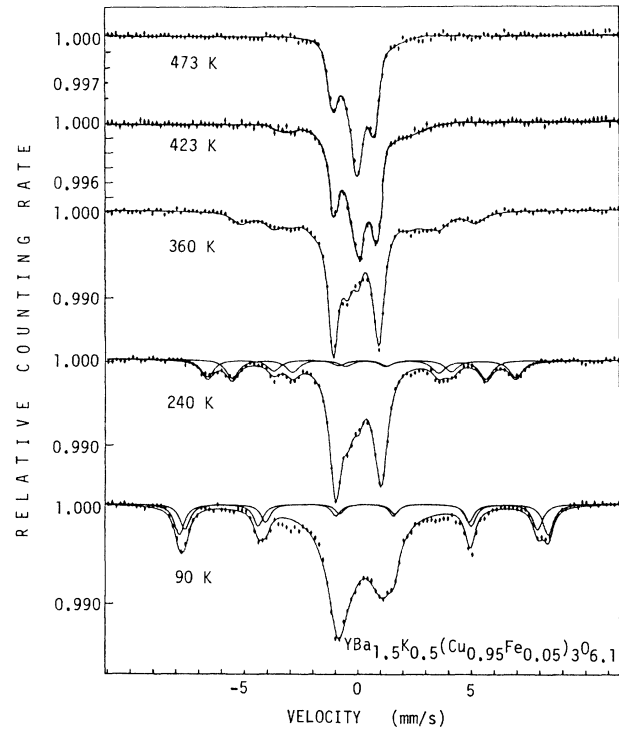


FIG. 8. Mössbauer spectra of ^{57}Fe in $\text{YBa}_{1.5}\text{K}_{0.5}(\text{Cu}_{0.95}\text{Fe}_{0.05})_3\text{O}_{6.1}$, at several temperatures.

for the appearance of the two different magnetic sites in the $z=6.1$ samples, with different T_N and different quadrupole interactions, is to assume that the Fe ions in the different magnetic sites differ in their local environments. The samples with K contain less oxygen.¹¹ In order to

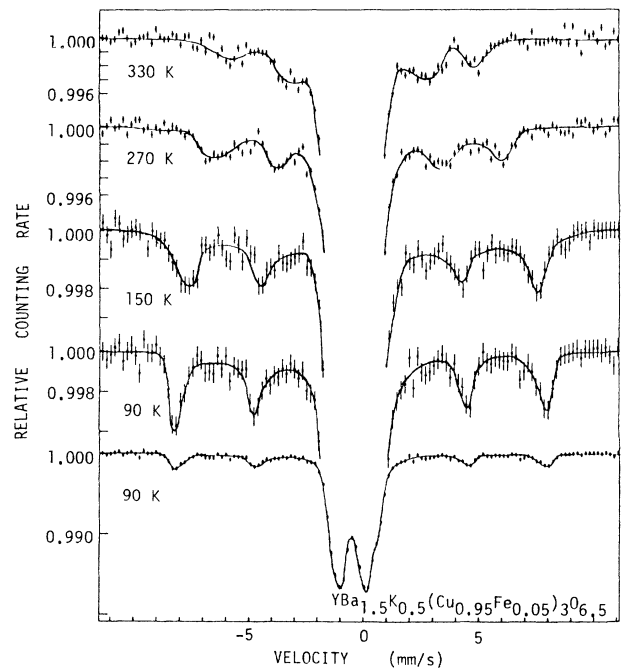


FIG. 9. Mössbauer spectra on an expanded scale of ^{57}Fe in $\text{YBa}_{1.5}\text{K}_{0.5}(\text{Cu}_{0.95}\text{Fe}_{0.05})_3\text{O}_{6.5}$ at several temperatures. The spectrum at 90 K is shown in normal and expanded scale.

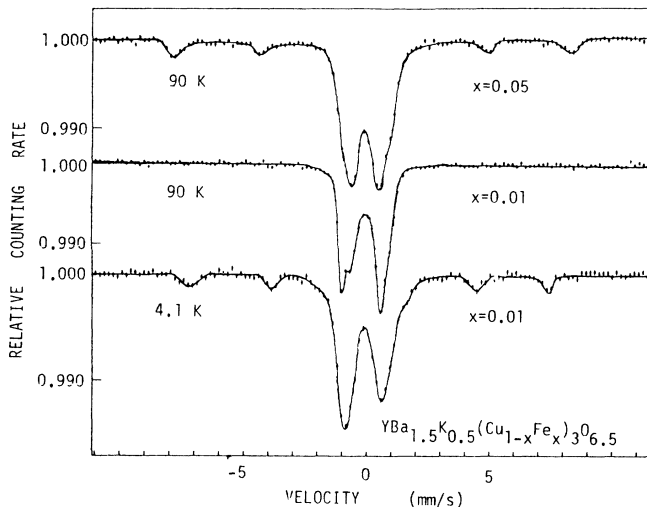


FIG. 10. Mössbauer spectra of ^{57}Fe in $\text{YBa}_{1.5}\text{K}_{0.5}(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{6.5}$. Note that the spectra with $x=0.01$ show a magnetic subspectrum at 4.1 K, but not at 90 K.

compensate for the lower valence of K, oxygen may be expelled from the Cu(2) plane and/or change the valence of Cu(2) near it. Those iron ions which have no oxygen vacancy and have regular Cu(2) as neighbors show the same magnetic behavior as those in $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{6.1}$ with $T_N=415$ K, losing their magnetic interactions (in the compounds with and without K) as more oxygen is added in the Cu(1) chains. Yet oxygen is not added to the Cu(2) plane, so that those iron ions with less oxygen near them show different magnetic behavior. As the iron probes the magnetic behavior only of the Cu(2) ions, only those Cu(2) ions that lack oxygen near them remain magnetic even in the superconducting samples, with $T_N=450$ K. Thus, in the samples with K and $z=6.1$, there are two magnetic sublattices.

In the samples with $x=0.01$, Fe enters the Cu(2) site only where oxygen is lacking in the neighborhood and thus stays magnetic in the superconducting state (Fig. 10). Here we find $T_N=15$ K, whereas $T_c=88$ K. Recent data show that the magnetic transition temperature is very sensitive to the oxygen content (z) of the sample.¹² There is a sharp transition region where the Néel temperature changes drastically with z : $dT_N/dz = -4000$ K. The low T_N is therefore probably due to a slightly higher oxygen content in this sample.

IV. CONCLUSIONS

The magnetic ordering temperatures found here are independent of the iron content and for $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{6.1}$, T_N is identical to that found in $\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$,¹ which does not contain any iron. This proves that iron serves here only as a probe for the magnetic properties of Cu in the Cu(2) site.

The results show that K attracts iron into the Cu(2) site and also that at very low oxygen content ($z=5.9$), prepared by slow cooling in a vacuum furnace, a relatively larger percentage of the iron enters the Cu(2) site.

The relative values of the quadrupole splittings for iron with different numbers of oxygen neighbors in the Cu(1) site are consistent with point-charge calculations,¹⁰ according to which the electric field gradient in the Cu(2) site should be positive and point along the c axis. The measured negative effective quadrupole interaction indicates, therefore, that the magnetic moments lie in the basal plane.¹ All Fe ions in the Cu(1) site have similar isomer shifts. The isomer shift of Fe in the Cu(2) site is greater, pointing to a smaller electron density at the Fe nuclei in this site.

The collected evidence indicates that superconductivity and Cu(2) antiferromagnetism in the $R\text{Ba}_2\text{Cu}_3\text{O}_z$ compounds do not generally coexist. Magnetic order is enhanced with decreasing oxygen content in the sample. Nevertheless magnetic order appears in oxygen-rich $\text{PrBa}_2\text{Cu}_3\text{O}_{6.9}$. Superconductivity is enhanced with increasing oxygen concentration, but $\text{PrBa}_2\text{Cu}_3\text{O}_{6.9}$ is again a counter example. Only in $\text{YBa}_{1.5}\text{K}_{0.5}(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_z$ do we find coexistence of a magnetic sublattice with superconductivity. Even in this case one may claim that the compounds contain phases with different amounts of oxygen and/or potassium.

It seems that all these results can be explained by the valence of Cu mainly in the Cu(2) site. In order for magnetic order to appear, Cu in the Cu(2) site has to be predominantly divalent. In order for superconductivity to appear, Cu in the Cu(2) site has to be of a different valence, probably mixed divalent-trivalent. The valence of Cu in the Cu(2) site may depend either on the oxygen content or on the valence of its neighbors in the R or the Ba site. Thus, when Pr replaces Y^{3+} , the higher valence of Pr has the same effect as the lower oxygen content in the $R=Y$ compounds and keeps the Cu predominantly as Cu^{2+} , so that the magnetic subspectrum appears. When K^+ partly replaces Ba^{2+} , superconductivity occurs even with lower oxygen content; thus K^+ has the same effect as high oxygen content and though $z=6.5$, the Cu is not predominantly divalent, as it is with this oxygen content in the absence of K. The magnetic site, which exists even in the superconducting sample, may come from regions which have (due to the immediate neighborhood of K^+) an even lower oxygen concentration, and in these regions Cu is predominantly divalent and magnetic. It seems reasonable that the valence of the ions in the R and Ba sites influences the valence of the Cu(2) ions more than that of the Cu(1) ions, which are much farther from them. On the other hand, it is more reasonable that the oxygen content has a greater influence on the valency of Cu(1). The picture that emerges therefore is as follows.

In order to preserve charge neutrality in a sample of $\text{YBa}_2\text{Cu}_3\text{O}_6$, Cu(1) has to be predominantly monovalent, and Cu(2) predominantly divalent. In this case, Cu(2) is magnetic as observed. As more oxygen is added, both Cu(1) and Cu(2) become of mixed valencies. Adding oxygen mainly changes the valence of Cu(1) due to the proximity of Cu(1) to these oxygens—but it also changes somewhat the valence of Cu(2), which becomes of mixed divalent-trivalent valence and thus, in the samples with $z \geq 6.5$, which are superconducting, it loses its magnetic moment. If Y is replaced by Pr, since Pr is not purely

trivalent (but rather mixed trivalent-tetravalent)¹³ it keeps the Cu in Cu(2) more divalent, and, therefore, it is magnetic even for high oxygen content. K^+ on the other hand, when it replaces Ba^{2+} , makes Cu(2) more trivalent even for lower oxygen content. It thus seems that for superconductivity to occur, Cu ions both in the Cu(1) and Cu(2) site have to have mixed valencies, while for magnetic order to appear, Cu(2) has to predominantly be divalent. This picture is consistent with extended x-ray-absorption fine-structure spectroscopy results,¹⁴ which

leads to the conclusion that both Cu(1) and Cu(2) atoms have a local oxygen coordination which favors a mixed divalent-trivalent character.

ACKNOWLEDGMENT

This research was supported in part by a grant from the U.S.-Israel Binational Science Foundation (BSF), Jerusalem, Israel.

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- ¹J. M. Tranquada, D. E. Cox, W. Kunmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S. K. Sinha, M. S. Alvarez, A. J. Jacobson, and D. C. Johnston, *Phys. Rev. Lett.* **60**, 156 (1988); J. Rossat-Mignod, P. Burlet, M. J. G. M. Jurgens, J. Y. Henry, and C. Vettier, *Physica C* **152**, 19 (1988).
- ²A. Pankhurst, A. H. Morrish, M. Raudsepp, and X. Z. Zhou, *J. Phys. C* **21**, L7 (1988).
- ³E. Baggio-Saitovitch, I. Souza Azevedo, R. B. Scorzelli, H. Saitovitch, S. F. da Cunha, A. P. Guimaraes, P. R. Silva, and A. Y. Takeuchi, *Phys. Rev. B* **37**, 7967 (1988).
- ⁴Chuck Blue, Khaled Elgaid, Ivan Zitkovsky, P. Boolchand, Darl McDaniel, W. C. H. Joiner, Jean Oostens, and Warren Huff, *Phys. Rev. B* **37**, 5905 (1988).
- ⁵I. Felner, I. Nowik, and Y. Yeshurun, *Phys. Rev. B* **36**, 3923 (1987).
- ⁶P. Bordet, J. H. Hodeau, P. Strobel, M. Marezio, and A. Santoro, *Solid State Commun.* (to be published).
- ⁷J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki, and A. P. Paulikas, *Phys. Rev. B* **36**, 5731 (1987).
- ⁸I. Felner and B. Barbara, *Solid State Commun.* **66**, 205 (1988).
- ⁹D. C. Harris, M. H. Hills, and T. A. Hewston, *J. Chem. Educ.* **64**, 847 (1987).
- ¹⁰E. R. Bauminger, M. Kowitt, I. Felner, and I. Nowik, *Solid State Commun.* **65**, 123 (1988).
- ¹¹I. Felner, M. Kowitt, Y. Lehavi, L. Ben-Dor, Y. Wolfus, and I. Nowik, in *Proceedings of the International Conference on High- T_c Superconductors: Materials and Mechanisms of Superconductivity, Interlaken, Switzerland*, edited by J. Müller and J. L. Olsen [*Physica C* **153-155**, 898 (1988)].
- ¹²J. H. Brewer *et al.*, *Phys. Rev. Lett.* **60**, 1073 (1988).
- ¹³I. Felner, M. Kowitt, Y. Lehavi, D. Edery, L. Ben-Dor, Y. Wolfus, and I. Nowik, *Mod. Phys. Lett. B* **2**, 713 (1988).
- ¹⁴G. M. Antonini, C. Calandra, F. Corni, F. C. Matocotta, and M. Sacchi, *Europhys. Lett.* **4**, 851 (1987).