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Magnetic and structural properties of Fe in single crystals of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$

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Magnetization and lattice-constant measurements were done on four single crystals of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ with Fe concentrations of $x=0.06$, 0.09, 0.15, and 0.24 to determine the structural and normal-state properties. Measurements of magnetization as a function of temperature were done in a temperature range between 90 and 300 K and analyzed using a Curie-Weiss law with a temperature-independent background. The effective magnetic moment obtained corresponds to a low spin state of Fe^{3+} with a magnitude of $2.18\mu_B$. Magnetic anisotropy between the *ab* plane and the *c* direction is only present for the concentration of $x=0.06$ and is attributed to the various oxygen environments surrounding the iron. For concentrations larger than $x=0.06$, the moment on Fe is isotropic and Curie-Weiss fits predict uniform antiferromagnetic ordering. Structural measurements exhibit an orthorhombic-tetragonal transition at an Fe concentration of $x=0.15$, similar to that observed in the polycrystalline material.

INTRODUCTION

Chemical substitution of magnetic ions into $YBa_2Cu_3O_{7-\delta}$ has the potential to reveal many interesting superconducting properties. Surprisingly, substitution of magnetic rare-earth ions at the Y site produces little effect on T_c, despite the large moments of the solute ions.[1-3] This absence of an effect has been attributed to the relative isolation of the Y site from the Cu—O bond system which contains the metallic and superconducting electrons. In contrast, substitution on the Cu sites has a strong effect on superconductivity,[4-6] driving T_c down at various rates.[7-10] Substitution of a magnetic ion offers new possibilities for studying the impurity-environment interaction through magnetic measurements.

Fe substitution produces several interesting effects on the superconductivity and structure. It drives the system toward a tetragonal structure without severely depressing T_c. Because Fe substitutes primarily at the chain Cu site, it allows the role of the chain [Cu(1)] and plane [Cu(2)] copper's to be probed separately. Finally, Fe maintains a moment in $YBa_2Cu_3O_{7-\delta}$, allowing its local environment and valence state to be easily studied.

There has been controversy concerning the substitution of Fe. Various geometries, valences, and occupancy sites have been inferred from Mössbauer spectroscopy and neutron-diffraction measurements.[11-14] Early Mössbauer spectroscopy measurements suggested Fe valences of +2, +3, and +4. More recently, with support from other measurements (extended x-ray-absorption fine structure[15] and x-ray-absorption near-edge structure[16,17]), it is believed that the Fe substitutes as Fe^{3+} in $YBa_2Cu_3O_{7-\delta}$. The value of the magnetic moment for a d^5 ion has two possible values: the low-spin quantum state (t_{2g}^5) equal to $2.2\mu_B$ and the high-spin quantum state ($e_g^2t_{2g}^3$), $5.9\mu_B$. The magnetic moment determined by Mössbauer spectroscopy and susceptibility measurements in polycrystalline studies varies from $2.5\mu_B$ to $4.9\mu_B$.[11,4,18,19]

These intermediate values of the moment could come about in several ways. The measured moment could be an average for Fe substituted in both the Cu(1) and Cu(2) sites with different electronic configurations and a different moment for each. However, Eibschutz, Lines, and Tarascon[20] provided evidence that substitution was mainly in the Cu(1) site. Other studies have shown that only at concentrations of Fe larger than $x=0.23$ does substitution occur at the Cu(2) sites.[21] Another possibility is that Fe at the Cu(1) site finds itself in several different oxygen environments, depending on the number and placement of neighboring oxygen vacancies. Evidence exists for combinations of various geometries (octahedral, capped trigonal, tetrahedra, pyramidal) in polycrystalline materials.[20,22,23] An unusual possibility has been suggested by Dunlap *et al.*[13] who found that Fe may be displaced from its Cu (0,0,0) crystallographic site to a (*y*,*y*,0) site to form a pseudotetrahedral coordination. This displacement in the [110] direction has also been observed with proton-induced x-ray emission (PIXE).[23] Such an environment would affect the Fe moment. Finally, there is the possibility of Fe-atom clustering in a chain, where Fe atoms substitute preferentially with Fe neighbors, again affecting their moment. Electron microscopy has shown that the Fe-doped materials have tweed microstructure and associated diffuse streaks along the [110] direction. The diffuse streaks have been attributed to microdomains of the orthorhombic phase containing small areas of the tetragonal phase associated with Fe impurities. Bordet *et al.*[22] attributed the streaks to linear chain clusters of Fe along the [110] direction separated by orthorhombic domains. This microdomain structure varies with Fe concentration and preparation method.

The questions of the Fe valence, the oxygen environment surrounding the Fe sites, and the magnetic moment on Fe are all related. Therefore, studies of the moment on Fe can give insights into these and other unsettled issues. In this paper we report detailed studies of the anisotropy and concentration dependence of the moment on Fe in high-quality single crystals of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$. These experiments show that there is surprisingly little anisotropy of the Fe moment despite the apparent asymmetry of the Cu chain sites, suggesting that Fe has higher oxygen coordination than Cu. From the concentration dependence of the moment, we are able to determine both the moment on Fe and the moment on Cu. The Fe moment is found to be consistent with the low-spin state of Fe^{3+}. The paramagnetic Curie temperature derived from our magnetization measurements implies antiferromagnetic ordering for concentrations of Fe above $x=0.06$. These results are interpreted with a model based on oxygens shared by neighboring Fe impurities, which explains the structural orthorhombic-tetragonal transition, the nearly isotropic moment on Fe, and antiferromagnetic order at high Fe concentrations.

EXPERIMENT

The Fe-doped single crystals of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ were grown by a self-flux method described elsewhere,[24] yielding plates of average dimensions $0.05\times2.0\times4.0$ mm^3. Several crystals of Fe concentrations of $x=0.06$, 0.09, 0.15, and 0.24 were produced. The largest crystals for each concentration were chosen for the experiments. A fragment of each of these crystals was broken off for structural measurements, and the remainder of the crystal was used for magnetic measurements.

The single crystals were characterized by structural determination of their lattice parameters using x-ray single-crystal diffraction measurements on an Enraf-Nonius CAD4 $4/\omega-2\theta$ automated diffractometer.

The superconducting transition temperatures were measured with a noncommercial low-field superconducting quantum interference device (SQUID) magnetometer. This SQUID magnetometer is designed to operate at fields of 100 G or less at temperatures ranging from 4.2 K to room temperature. The unique features of this magnetometer are its fast field and temperature-sweep capabilities. Reproducible temperatures sweeps over a 30-K range are performed in an hour. The magnetic-flux exclusion is determined by cooling the material in zero field to a temperature well below T_c, applying a field of 0.1–10.0 G and recording the magnetization as the temperature is slowly increased. As the temperature increases, there is a large decrease in the diamagnetic signal corresponding to the transition to the normal site. The normal-state magnetic properties were measured on a commercial Quantum Design SQUID magnetometer operating in the field range 0–5.5 T and temperatures ranging from 4.2 K to room temperature.

RESULTS

Four single crystals of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$ with similar morphology and values of $x=0.06$, 0.09, 0.15, and 0.24 were measured by x-ray diffraction. The lattice constants were determined by the least-squares refinement of $(\sin\theta/\lambda)^2$ values for 25 reflections $\theta>20°$. These were found to be similar in value to those reported by powder and neutron data[25] (Table I). The oxygen stoichiometries were determined to be between 6.8 and 7.0 by comparing the values of the lattice constants and transition temperatures to that of Fe-doped oxygen-deficient polycrystals.[25] For a given Fe concentration, the c lattice parameter is the most sensitive to oxygen concentration. The measured c-axis lattice parameter from x-ray diffraction on the single crystals was compared against neutron-diffraction measurements of the c lattice parameter as a function of oxygen concentration to infer the oxygen content. A second estimate of the oxygen content was made by comparing the measurement of T_c of the single crystal to the smooth variation of T_c as a function of oxygen content in the same set of polycrystalline samples. These two estimates of $7-\delta$ agree within 3%. The a-b lattice constants for these single crystals changed as a function of Fe concentration exhibiting an apparent orthorhombic-tetragonal transition at about $x=0.15$ (Fig. 1).

The superconducting transition temperatures determined from dc magnetization were sharp (Fig. 2). The transition widths ranged from 1 to 5 K. The transition temperature of the $x=0.15$ sample does not scale with the other concentrations as a result of the difference in oxygen stoichiometry. The superconducting transition was measured on several crystals of each Fe concentration and found to be highly reproducible, indicating that the crystals are homogeneous and that there is no significant sample dependence.

Measurements of the temperature dependence of the magnetization were done on single crystals for all Fe concentrations in the $\mathbf{H}\|c$ and $\mathbf{H}\perp c$ directions at a field of 0.8 T. Figure 3 shows the inverse molar susceptibility as a function of temperature. Although the data roughly fol-

TABLE I. Lattice constants, Fe concentration, transition temperature, and inferred oxygen content for the single crystals of $YBa_2Cu_{3-x}Fe_xO_{7-\delta}$. No oxygen content for the $x=0.24$ crystal was determined because there is no polycrystalline reference data for this concentration.

Oxygen content $(7-\delta)$	T_c (K)	x	a (Å)	b (Å)	c (Å)
6.85	85	0.06	3.821(3)	3.889(1)	11.724(5)
6.83	60	0.09	3.830(2)	3.875(1)	11.734(6)
7.02	76	0.15	3.846(4)	3.855(4)	11.709(7)
	49	0.24	3.854(1)	3.858(2)	11.718(4)

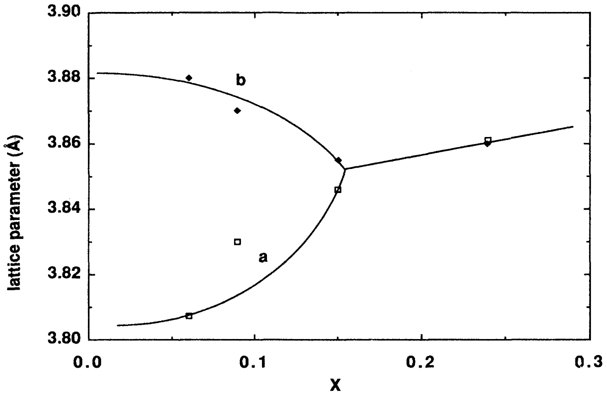

FIG. 1. a-b lattice parameters as a function of Fe concentration showing an orthorhombic-tetragonal transition.

low a Curie-Weiss law, a slight curvature in Fig. 3 implies the presence of a temperature-independent background. To account for this background, the data were fit to the expression

$$\chi=\frac{\partial M}{\partial H}=\frac{Np_{\text{eff}}^2\mu_B^2}{3k_B(T-\Theta_P)}+\chi_0\ , \tag{1}$$

where M is the magnetization per mole, N is the number of magnetic ions per mole, Θ_P the paramagnetic Curie temperature, p_{eff} is the effective magnetic moment in units of μ_B, and χ_0 represents a temperature-independent background susceptibility. The data in Fig. 3 were fit to Eq. (1) by an iterative technique to determine the value of the fitting parameters p_{eff}^2, Θ_P, and χ_0, as shown in Table II.

The moments p_{eff}^2 determined from the fits include the moments on Fe and Cu. The Cu moment is further divided between the chain Cu and plane Cu. Although the free-ion moments of Cu^{3+} and Cu^{2+} are $3.2\mu_B$ and $1.9\mu_B$, respectively, the moments measured in $YBa_2Cu_3O_{7-\delta}$ are invariably much smaller, ranging from 0 to 0.55 μ_B/Cu atom.[4] In addition, their values are sample dependent, suggesting that impurities may be responsible for a large part of the measured moment. For this analysis it is assumed that there is no moment on the Cu plane sites in pure $YBa_2Cu_3O_{7-\delta}$. Furthermore since Fe substitutes on the chain sites, we will not consider the possibility that a moment appears on the Cu plane site due to Fe substitution. However, we do allow for the possibility of a moment on the chain Cu ions, due to the presence of Fe. A similar effect has been proposed for the $La_{2-x}Sr_xCuO_4$ system doped with Zn.[26] Then we may divide the total measured moment according to

$$Np_{\text{eff}}^2=N_{\text{Cu}}p_{\text{Cu}}^2+N_{\text{Fe}}p_{\text{Fe}}^2\ , \tag{2}$$

where the subscript Cu refers to the chain sites only. The number of Cu and Fe ions depends on x according to $Nx=N_{\text{Fe}}$ and $N(1-x)=N_{\text{Cu}}$, leading to

$$p_{\text{eff}}^2=p_{\text{Cu}}^2+x(p_{\text{Fe}}^2-p_{\text{Cu}}^2)\ , \tag{3}$$

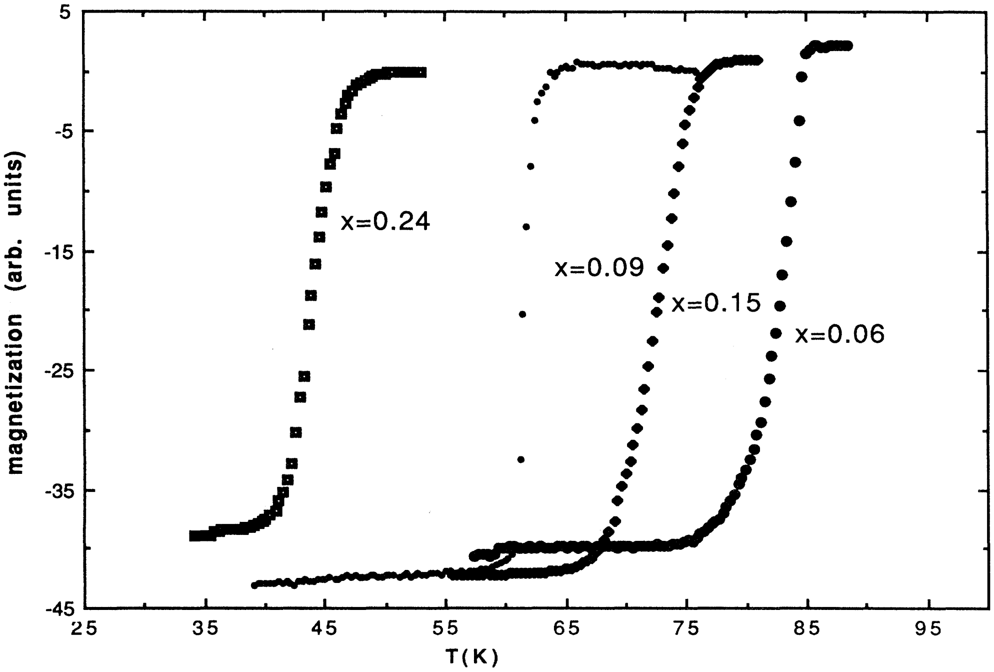

FIG. 2. Superconducting transitions for single crystals of various Fe concentrations measured by dc magnetization in a field of 10 G.

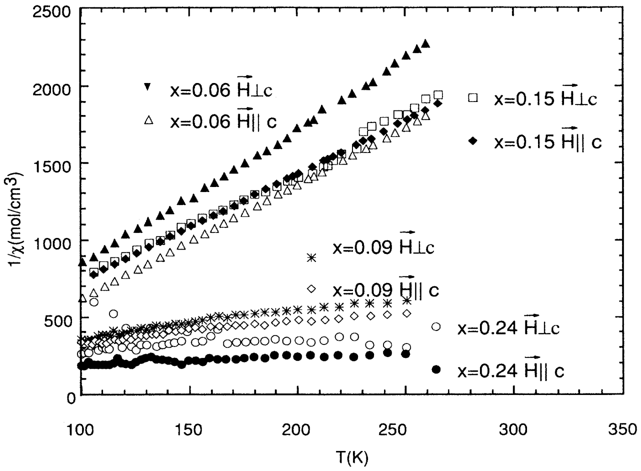

FIG. 3. Inverse susceptibility for single crystals of various Fe concentrations as a function of temperature.

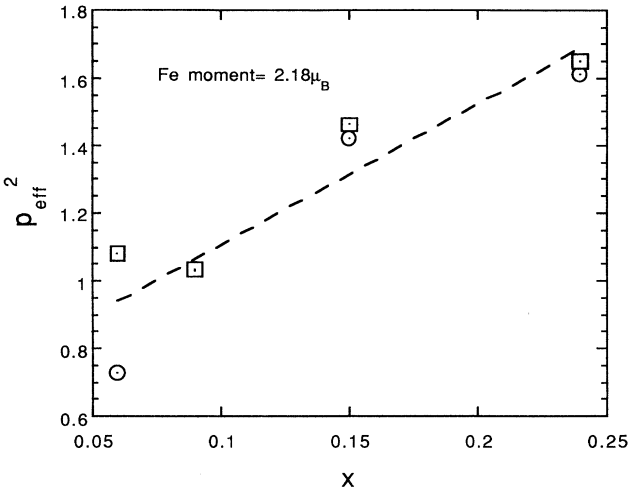

FIG. 4. Total effective moment as a function of Fe concentration for the magnetic field in the *a-b* plane and in the *c* direction.

where N is the total number of chain Cu sites/mol. The moments on the Cu and Fe ions due to Fe doping can be determined using a linear fit of the data in Table II to the Fe concentration using Eq. (3). The intercept gives the moment on the Cu, and the slope gives the difference between the Cu and Fe moments. Figure 4 shows the total moment as a function of Fe concentration and associated linear fit. The Cu moment is $0.84\mu_B$ and the Fe moment is $2.18\mu_B$. If we had allowed an induced moment on the Cu(2) sites as well as the Cu(1) sites due to the presence of Fe, Eq. (3) would have become

$$p_{\text{eff}}^2 = 3p_{\text{Cu}}^2 + x(p_{\text{Fe}}^2 - p_{\text{Cu}}^2) \; . \tag{4}$$

Then the moment on Cu would have been $0.48\mu_B$ and the moment on Fe $2.13\mu_B$. The experiment cannot distinguish the difference between the two cases. However, the results for the moment on the Fe are nearly insensitive to the distinction. The Fe moment compares favorably with that determined by Mössbauer spectroscopy on a polycrystalline sample for which $x=0.15$. The Mössbauer spectra[27] indicate three different Fe environments, probably due to different oxygen configurations, with an average moment of $2.02\mu_B$.

The paramagnetic Curie temperatures obtained are tabulated in Table II. The negative values indicate that within the structure, Fe ions interact antiferromagnetically. Our fits suggest antiferromagnetic order at temperatures between 15 and 28 K, depending on Fe concentration. This agrees well with the antiferromagnetic ordering[14] observed in polycrystalline samples, 9 K for $x=0.15$ and 14 K for $x=0.30$.

DISCUSSION

The results are interpreted in terms of a model for the Fe moment and oxygen coordination in which the presence of neighboring Fe ions becomes increasingly more important at high concentrations. For an isolated Fe impurity, we infer an anisotropy in both the moment p_{eff} and the paramagnetic Curie temperature Θ_p from the $x=0.06$ sample. This anisotropy implies that the six oxygen sites surrounding an Fe are not fully occupied. This conclusion is consistent with the observation of multiple spectra in Mössbauer experiments of the Fe ion.[8,11,14] The splitting of the paramagnetic Curie temperature into a positive and a negative value for the two directions is often observed when single-ion crystal-field effects are important.

At higher concentrations there is evidence from electron microscopy,[28] neutron and electron diffraction,[18] and the Meissner effect[14] that the Fe ions tend to cluster, perhaps in distinctive [110]-type chains. The presence of a neighboring Fe alters the oxygen environment of the

TABLE II. Fitting parameters for the single-crystal magnetization measurements; $C = Np_{\text{eff}}^2\mu_B^2/3k_B$.

H⊥*c*					**H‖*c***					
x	C^{ab} (cm³ K/mol)	χ_0 (cm³/mol)	Θ_P (K)	p_{eff}^2	C^c (cm³ K/mol)	χ_0 (cm³/mol)	Θ_P (K)	p_{eff}^2	x	$p_{\text{eff}}^c/p_{\text{eff}}^{ab}$
0.06	0.0908	0.1×10^{-6}	−21	0.727	0.1350	0.1×10^{-6}	15.4	1.080	0.06	1.48
0.09	0.1287	1.6×10^{-6}	−25	1.030	0.1292	2.0×10^{-6}	−25	1.034	0.09	1.00
0.15	0.1736	1.2×10^{-6}	−27.4	1.420	0.1825	1.8×10^{-6}	−28	1.462	0.15	1.02
0.24	0.2017	4.5×10^{-6}	−14.8	1.610	0.2063	4.0×10^{-6}	−15	1.650	0.24	1.02

site as the Fe ions share oxygens. This increases the net coordination of Fe and tends to reduce the anisotropy that would be expected for an isolated Fe. We see this effect as strong reductions in the effective moment anisotropy and in the splitting of the paramagnetic Curie temperature for the $\mathbf{H}\|c$ and $\mathbf{H}\perp c$ directions for the $x=0.09$, 0.15, and 0.24 samples. Within experimental error the anisotropy in both quantities goes to zero for the high-concentration samples. The isotropy of the effective moment could arise from two models: the filling of all six nearest-neighbor oxygen sites surrounding the Fe or the displacement of the Fe from the octahedral Cu site to a tetrahedral site as suggested by Dunlap, Peng, and Kimball.[14] Since the bond lengths of the chain Cu—O bonds for the three directions of undoped $YBa_2Cu_3O_{7-\delta}$ are unequal, a small magnetic anisotropy might be expected even if all six oxygen sites are occupied. However, this effect is expected to be small compared to the effect of the presence or absence of a neighboring oxygen. In addition, our structural data show that the bond lengths of the oxygens to the chain Cu site tend to equalize as the Fe concentration increases.[29] Because of high thermal parameters and low occupational factors for the oxygen and Fe sites in the structural refinement, it is not possible to quantify this effect. However, the trend in the bond lengths as function of Fe content is clear. An alternative model has the Fe impurity slightly displaced from the Cu site in the [110] direction. The Fe then occupies a tetrahedral position with four neighboring oxygens. Such a geometry is highly symmetric as in the sixfold octahedral coordination and would be expected to produce little anisotropy in the Fe moment. Mössbauer data[14] showing more than one type of site and estimates of the oxygen coordination lower than five are consistent with the tetrahedral symmetry.[17] In any case we interpret the nearly isotropic moment that we observed at high Fe concentrations as a consequence of the highly symmetric oxygen coordination of the Fe. This high symmetry would be consistent with either an octahedral coordination with the Fe on the Cu site or a tetrahedral coordination with the Fe slightly displaced from the Cu site.

Evidence of increasing Fe-Fe exchange interactions with x is provided by the shift of the paramagnetic Curie temperatures to uniformly negative values for the high-concentration samples. These negative values are consistent with antiferromagnetic ordering expected if clustering increases the exchange interactions between the Fe ions. The values of $-\Theta_P$ range from 15 to 28 K, very close to the observed antiferromagnetic ordering temperature[14,30] for polycrystalline samples with $x=0.15$ (9 K) and 0.30 (14 K). Although the increasing Fe-Fe exchange interactions are consistent with a clustering model, our data alone cannot distinguish between clustering and a random distribution, where the average Fe-Fe distance would decrease smoothly with x.

The presence of Fe dopant has a strong effect on the direction of the chains in the structure. Since an Fe tends to fill the neighboring O(5) sites, the chain direction is equally likely to extend in any of the four directions from an Fe site. Thus an Fe site often will coincide with a 90° change in the chain direction. This 90° change is not the same as a twin boundary because it occurs in only one Cu-O layer and is uncorrelated with directional changes in neighboring layers. As the Fe concentration increases, these directional changes are more closely spaced and the difference between the a and b directions is lost if the structure is averaged over a large enough area. These closely spaced interchanges between a and b appear in the diffraction results as an apparent tetragonal structure, even though locally the structure may be orthorhombic. In our data the orthorhombic-tetragonal transition occurs at about $x=0.15$, corresponding to an Fe-Fe separation of 2.5 unit cells if the Fe ions are randomly distributed. A mixing of the a and b directions on this scale would appear tetragonal to x rays.

In conclusion, our magnetic measurements show that the Fe in $YBa_2Cu_3O_{7-\delta}$ has an effective moment of $2.18\mu_B$, as expected for a low-spin state of Fe^{3+}. The moment is uniform as a function of Fe concentration. The presence of anisotropy in the low-concentration crystals of Fe indicate that there are various geometries possible for the oxygen environment of an isolated Fe. At higher Fe concentration, the presence of Fe-O-Fe linkages increases the oxygen coordination of Fe and reduces the local anisotropy, whether the Fe occupies the octahedral Cu site itself or is slightly displaced to a tetrahedral site. The reduced Fe-Fe distances are also seen in the negative paramagnetic Curie temperatures, which suggests antiferromagnetic order at low temperatures. Such ordering is likely for the strongly interacting Fe ions in a cluster. The orthorhombic-tetragonal transition is observed as a function of concentration and may be due only to the effect of the microstructure surrounding the Fe in the system.

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[1] J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, Phys. Rev. B **36**, 226 (1987).

[2] D. W. Murphy, S. Sunshine, R. B. van Dover, R. J. Cava, B. Batlogg, S. M. Zahurak, and L. F. Schnemeyer, Phys. Rev. Lett. **58**, 1888 (1987).

[3] Z. Fisk, J. D. Thompson, E. Zirngiebl, J. L. Smith, and S. Cheong, Solid State Commun. **62**, 743 (1987).

[4] G. Xiao, F. H. Strietz, A. Garvin, Y. W. Du, and C. L. Chien,

Phys. Rev. B **35**, 8782 (1987).

[5] Y. Maeno, T. Nojima, Y. Aoki, M. Kato, K. Hoshino, A. Minami, and T. Fujita, Jpn. J. Appl. Phys. **26**, L774 (1987).

[6] Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. Aoki, K. Hoshino, A. Minami, and T. Fujita, Nature **328**, 512 (1987).

[7] Y. Maeno, M. Kato, Y. Aoki, and T. Fujita, Jpn. J. Appl. Phys. **12**, L1982 (1987).

[8] M. Eibschutz, M. E. Lines, J. M. Tarascon, and P. Barboux, Phys. Rev. B **38**, 2896 (1988).

[9] C. Chaillout, M. A. Alario-Farnco, J. J. Capponi, J. Chenavas, J. L. Hodeau, and M. Marezio, Phys. Rev. B **36**, 7118 (1987).

[10] Z. Zhou, M. Randsepp, Q. A. Pankhurst, A. H. Morrish, Y. L. Luo, and I. Muartense, Phys. Rev. B **36**, 7230 (1987).

[11] M. Takano and Y. Takeda, Jpn. J. Appl. Phys. **26**, L1862 (1987).

[12] C. Blue, K. Elgard, I. Zitkovsky, P. Boolchaud, D. McDaniel, W. C. H. Joiner, J. Oostens, and W. Huff, Phys. Rev. B **37**, 5905 (1988).

[13] B. D. Dunlap, J. D. Jorgensen, C. Segre, A. E. Dwight, J. Matykiewicz, H. Lee, W. Peng, and C. W. Kimball, Physica C **158**, 397 (1989).

[14] B. D. Dunlap, W. Peng, and C. W. Kimball, Physica C **169**, 23 (1990).

[15] A. Koizumi, H. Maeda, N. Bamba, H. Maruyama, E. Takayama-Muromachi, J. Shi, K. Shimizi, M. Mino, and H. Yamazaki, Jpn. J. Appl. Phys. **28**, L203 (1989).

[16] E. Alp, S. M. Mini, M. Rananthan, J. C. Campuzano, G. Jennings, G. Goodman, B. W. Veal, J. Z. Liu, and G. K. Shenoy, Bull. Am. Phys. Soc. **21**, 6 (1989).

[17] C. Y. Yang, A. R. Moodenbaugh, Y. L Wang, Youwen, Xu, S. M. Heald, D. O. Welch, M. Suenaga, D. A. Fisher, and J. E. Penner-Hahn, Phys. Rev. B **42**, 2231 (1990); C. Y. Yang, S. M. Heald, J. M. Tranquerda, Youwen Xu, Y. L. Wang, A. R. Moodenbaugh, D. O. Welch, and M. Suenaga *ibid.* **39**, 6681 (1989).

[18] A. Junod, A. Bezinge, D. Eckert, T. Graf, and J. Muller, Physica C **152**, 485 (1988).

[19] Z. Hiroi, M. Takano, Y. Takeda, R. Kanno, and Y. Bando, Jpn. J. Appl. Phys. **27**, L580 (1988).

[20] M. Eibschutz, M. E. Lines, and J. M. Tarascon, Phys. Rev. B **38**, 8858 (1988).

[21] S. Katsuyama, Y. Ueda, and K. Kosuge, Physica C **165**, 404 (1990).

[22] P. Bordet, J. H. Hodeau, P. Strobel, M. Marezio, and A. Santoro, Solid State Commun. **66**, 435 (1988).

[23] L. T. Romano, D. N. Jamieson, C. Chen, J. T. Czermuszka, G. W. Grime, and F. Watt (unpublished).

[24] D. L. Kaiser, F. Holtzberg, M. F. Chisholm, and T. K. Worthington, J. Cryst. Growth **85**, 593 (1987).

[25] B. W. Veal and J. D. Jorgensen (private communication); L. Nuñez, B. Veal, G. W. Crabtree, W. H. Kwok, H. Claus, A. P. Paulikas and J. W. Downey, Bull. Am. Phys. Soc. **22**, 4 (1989).

[26] Gang Xiao, M. Z. Cieplak, and C. L. Chien, Phys. Rev. B **42**, 420 (1990).

[27] R. Gomez, S. Aburto, M. L. Marquina, and M. Jimenez, Phys. Rev. B **36**, 7226 (1987).

[28] Youwen Xu, M. Suenaga, J. Tafto, R. L. Sabatini, A. R. Moodenbaugh, and P. Zolliker, Phys. Rev. B **39**, 6667 (1989).

[29] B. D. Dunlap, W. Peung, and C. W. Kimball, Physica C **169**, 23 (1990); (private communication).

[30] L. Nuñez, Ph.D. dissertation, Northern Illinois University, DeKalb, IL, 1990.