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Articles

Magnetic Structure of the Oxygen-Deficient Perovskite YBaCuFeO$_{5+\delta}$

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The magnetic and crystal structures of the oxygen-deficient layered perovskite YBaCuFeO$_{5+\delta}$ have been determined with powder neutron diffraction methods. It crystallizes in the noncentrosymmetric tetragonal space group *P4mm* with $a = 3.8707(2)$ Å and $c = 7.6711(4)$ Å (at room temperature). Structural motifs of corner-sharing severely elongated CuO$_5$ (Cu–O$_{eq}$ = 1.936(2) Å, Cu–O$_{ax}$ = 2.35(9) Å) and slightly squashed FeO$_5$ (Fe–O$_{eq}$ = 2.03(3) Å, Fe–O$_{ax}$ = 1.82(9) Å) square pyramids result in a novel lamellar structure with ordered oxygen defects. Local magnetic moments directed perpendicular to the unique axis (μ perpendicular to c, $\mu = 2.51(15)\ \mu_B$ at room temperature) appear at the Fe^{3+} sites at 442.4(5) K. The magnetic unit cell results by doubling the chemical one along all three crystallographic directions (magnetic propagation vector, $\mathbf{k} = (^1/_2,{}^1/_2,{}^1/_2)$). Despite the long separation between successive FeO$_2$ layers (~7.7 Å), the magnetic behavior can be successfully described by a three-dimensional Heisenberg spin Hamiltonian with a critical exponent $\beta = 0.366(8)$. No evidence of ordering of the Cu sublattice is found on cooling to room temperature.

Introduction

Interest in copper–oxygen chemistry, initiated by the search for new superconducting oxides, has also revealed a wealth of novel perovskites which are structurally and electronically related to the "high-T_c" materials. These systems are invariably characterized by the presence of close-packed perovskite blocks which can stack together in a rich variety of different ways and can accommodate a plethora of oxygen-defect patterns.[1] They share with superconducting copper oxides the common presence of (CuO$_2$)$_\infty$ layers which form part of strongly elongated octahedral[2] CuO$_6$, square pyramidal[3] CuO$_5$, or square planar[4] CuO$_4$ units. The undoped parent materials of high-T_c oxides are further characterized by the presence of antiferromagnetic (AF) long-range order[5] of the Cu^{2+} sublattice which is removed upon doping before the onset of superconductivity. This intimate relationship between the magnetic and (super)conducting properties of the CuO$_2$ layers makes the study of the magnetic properties of these systems particularly important, especially in understanding the role of the strong correlations present. Finally, the conducting properties are also sensitively affected by substitution at the copper sites by both magnetic and nonmagnetic ions.

Fe doping of the superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ first revealed the existence of a novel oxygen-deficient perovskite phase of stoichiometry YBaFeCuO$_{5+\delta}$ with a closely-related lamellar structure.[6] This oxide was found to consist of [CuFeO$_{10}$]$_\infty$ bilayers of corner-sharing CuO$_5$ and FeO$_5$ square pyramids (Figure 1), providing an example of the rare 5-fold square-pyramidal coordination of Fe(III). Y^{3+} layers (coordination number 8) separate the (CuFeO$_{10}$) bilayers and accommodate the oxygen vacancies, while the Ba^{2+} ions (coordination number 12) are located within the bilayer spacing, reminiscent of the YBa$_2$Cu$_3$O$_{7-\delta}$ structure. The crystal structure was determined by powder

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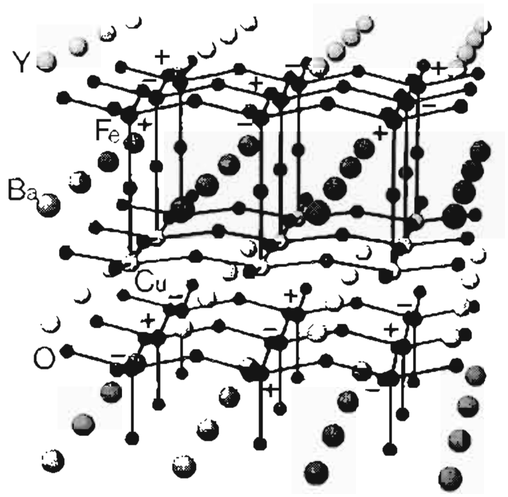

Figure 1. Magnetic and crystal structure of YBaFeCuO$_5$. + and − symbols at the Fe^{3+} sites indicate antiparallel spins lying in the basal plane.

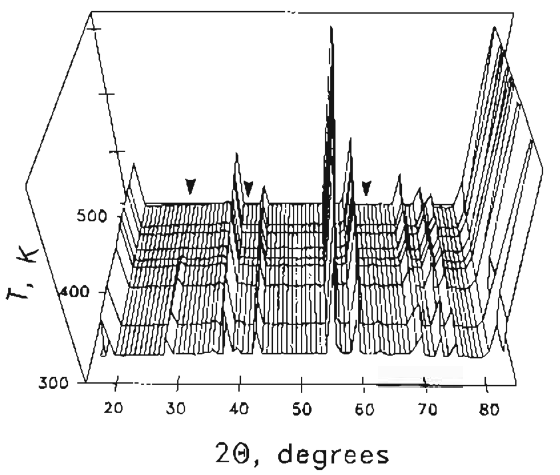

Figure 2. Diffraction profiles of YBaFeCuO$_5$ in the temperature range 300–500 K for 2θ = 17–83° (λ = 2.522 Å), showing the appearance on cooling of additional peaks below T_N = 442 K ascribed to magnetic scattering.

neutron diffraction to be tetragonal (space group *P4mm*) with the Fe^{3+} and Cu^{2+} ions distributed over two symmetry-inequivalent crystal sites. More recent ^{57}Fe Mössbauer results[7,8a,b] revealed an antiferromagnetic ordering transition at T_N = 446 K but are only consistent with the existence of a single unique Fe^{3+} site; this implies that the Fe^{3+} and Cu^{2+} ions are fully ordered, each one occupying a single site in the *P4mm* unit cell (Figure 1). A recent Raman and infrared spectroscopic study[7c] similarly necessitates the adoption of an acentric space group. The structure of YBaCuFeO$_5$ has also been determined by single-crystal X-ray diffraction.[9]

We have been studying[2a,4c,c,5c–j,m,n,10] the structural, magnetic, and transport properties of many parent materials of high-T_c oxides and other closely related systems in an attempt to obtain systematic information about the interrelationship of these properties. The novel structure and the existence of both cation and oxygen vacancy ordering effects in YBaFeCuO$_{5+\delta}$ make it a particularly attractive system to explore. In this paper, we focus on its structural and magnetic properties and report the results of a powder neutron diffraction study of YBaFeCuO$_{5+\delta}$ in the temperature range 300–500 K. Ordered local magnetic moments appear at the Fe^{3+} sites with no evidence of magnetic ordering of the Cu^{2+} sublattice. Rietveld refinements of the magnetic and crystal structures are consistent with complete ordering of the Fe^{3+} and Cu^{2+} ions.

Experimental Section

The YBaFeCuO$_{5+\delta}$ sample was prepared in air by standard solid-state reactions, as reported earlier.[6–8] Phase purity was established by recording X-ray powder diffraction profiles at room temperature on a Siemens D5000 diffractometer. Thermogravimetric analysis, using a Perkin-Elmer TGS-2 apparatus, was employed to determine[8] the excess oxygen present as δ = 0.08. Powder neutron diffraction measurements were performed between 320 and 500 K with the high-intensity medium-resolution D1B diffractometer[11] at the Institut Laue Langevin, Grenoble, France, using neutrons with a mean wavelength of 2.522 Å. Data were recorded for a 2θ range of ~10–90° in steps of 0.2°. A room-temperature run was also recorded with the sample outside the furnace.

Results and Discussion

The details of the YBaFeCuO$_{5+\delta}$ structure (Figure 1) were described in earlier work.[6,8,9] Systematic absences of Bragg reflections are consistent with a number of tetragonal space groups. Among these, space groups *P4/mmm* and *P4mm* lead to distributions of the Fe^{3+} and Cu^{2+} ions consistent with the requirement of the Mössbauer experiments[7,8] of a single Fe^{3+} site. The *P4/mmm* space group represents the situation where Fe^{3+} and Cu^{2+} are statistically distributed in the lattice, while in *P4mm* the two metal ions are fully ordered. The diffraction and spectroscopic evidence have been in favor of the acentric space group *P4mm*. With a standard Rietveld–Hewat profile refinement program, our medium-resolution data at high temperature refine satisfactorily in *P4mm*. The average *R*-factors[12] obtained in the refinements[13] in the temperature range 450–500 K are as follows: R_{wp} = 4.5%, R_p = 3.3%, R_e = 1.1%. On the other hand, the *R*-factors obtained for the *P4/mmm* space group over the same temperature range were as follows: R_{wp} = 4.7%, R_p = 3.5%, R_e = 1.1%.

Inspection of the powder diffraction profiles in the 300–450 K temperature range reveals the presence of seven new peaks of magnetic origin whose intensity smoothly grows with decreasing temperature (Figure 2). They could be readily indexed on the basis of the chemical unit cell as $(h/2, k/2, l/2)$ with h, k, l = odd, implying an enlarged magnetic unit cell ($a_M = 2a$, $c_M = 2c$) and antiferromagnetic ordering of G-type[14] with a magnetic propagation vector $\mathbf{k} = (^1/_2, {}^1/_2, {}^1/_2)$. Rietveld refinements were now performed by taking into account both nuclear and magnetic scattering. We note that, in uniaxial systems, powder diffraction cannot lead to the unambiguous determination of the magnetic moment direction;[15] only the angle between the spin direction and the unique (c) axis can be determined. In the magnetic structure refinements, a number of different magnetic ordering models were investigated. It was immediately apparent that

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[13] The average number of observables used in the Rietveld analyses was 316; 12 nuclear Bragg reflections were included and 16 structural and instrumental variables refined. Attempts to introduce occupancy of the oxygen-defect site at $(^1/_2, {}^1/_2, {}^1/_2)$ to account for the excess oxygen revealed by the TGA measurements did not lead to stable refinements. We attribute this to the limited Q-range over which diffraction data were collected in the present experiment.

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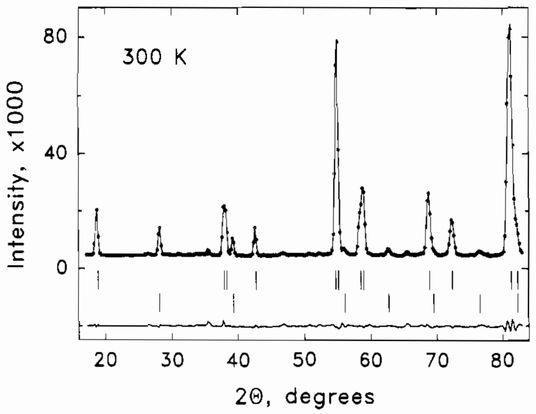

Figure 3. Observed (points), calculated (full curve), and difference profiles for $YBaFeCuO_5$ at 300 K. The positions of the nuclear (top) and magnetic (bottom) Bragg peaks are marked.

Table 1. Final Structural and Magnetic Parameters Derived from the Rietveld Refinements of $YBaFeCuO_{5+\delta}$ at Room Temperature (Nuclear Space Group *P4mm*, Magnetic Propagation Vector **k** = $(^1/_2, {}^1/_2, {}^1/_2)$)[a]

atom	site	x/a	y/b	z/c	$\mu_\perp$ (μ_B)	$\mu_\parallel$ (μ_B)
Y	1a	0	0	0.499(3)		
Ba	1a	0	0	0.006(5)		
Fe	1b	$^1/_2$	$^1/_2$	0.718(2)	2.51(15)	0
Cu	1b	$^1/_2$	$^1/_2$	0.262(2)	0	0
O(1)	1b	$^1/_2$	$^1/_2$	−0.045(6)		
O(2)	2c	$^1/_2$	0	0.266(5)		
O(3)	2c	$^1/_2$	0	0.637(5)		

[a] Lattice constants: $a = 3.8707(2)$ Å, $c = 7.6711(4)$ Å. R-factors: $R_{wp} = 3.7\%$; $R_p = 2.7\%$; $R_{mag} = 9.8\%$; $R_e = 1.1\%$.

Table 2. Selected Bond Distances (Å) and Angles (deg) in $YBaCuFeO_{5+\delta}$ at Room Temperature

Cu–O_{eq}	1.936(2)	O_{eq}–Cu–O_{eq}	90.0(1)
Cu–O_{ax}	2.35(9)	O_{eq}–Cu–O_{ax}	91(2)
Fe–O_{eq}	2.03(3)	O_{eq}–Fe–O_{eq}	85(2)
Fe–O_{ax}	1.82(9)	O_{eq}–Fe–O_{ax}	107(3)

refinement with the disordered model of the *P4/mmm* space group always gave very poor results ($R_{mag} = 15.9\%$ at room temperature). We consider this as additional strong evidence for the correctness of a fully ordered structural arrangement of the Fe^{3+} and Cu^{2+} ions. Our preliminary exploratory refinements allowed a magnetic moment only on the Fe^{3+} ions with its direction being monitored during refinement. We found that the best agreement between the model and the experimental data was achieved when the Fe^{3+} moment was perpendicular to the c axis. We then allowed a magnetic moment associated with the Cu^{2+} sublattice to be also included in the refinement. However, at all temperatures below the ordering transition, this refined to a value essentially equal to zero ($\mu_\perp = 0.03(8)$ μ_B), thus leading to the conclusion that Cu^{2+} magnetic ordering is not present in the temperature range investigated and the magnetic scattering observed wholly arises from AF order of the Fe^{3+} sublattice ($R_{mag} = 9.8\%$).

The results of the Rietveld refinement at 300 K (Figure 3) (with the sample outside the furnace environment) are summarized in Table 1 with selected bond distances and angles collected in Table 2. The magnetic moment associated with the Fe^{3+} sublattice is $\mu = 2.51$ ● 0.15 μ_B and lies parallel to the ab basal plane. Profile refinements were also performed on the data collected for the sample inside the furnace between 320 and 450 K. The average R-factors obtained in these refinements were as follows: $R_{wp} = 4.3\%$, $R_p = 3.1\%$, $R_e = 1.1\%$. The evolution of the lattice constants and of the Cu–O and Fe–O bond lengths with temperature is shown in Figures 4 and 5. Some problems have existed in the earlier structural literature[6–9] about the exact sites of the Fe^{3+} and Cu^{2+} ions. While it is difficult to distinguish between Fe and Cu with X-ray diffraction,[8,9] the neutron scattering lengths for Fe (0.954×10^{-12} cm) and Cu (0.772×10^{-12} cm) are sufficiently different to allow facile identification. In the present work, there was a substantial difference in the fit quality depending on whether a Cu^{2+} or an Fe^{3+} ion was at the center of the severely elongated square pyramid. The observed distorted coordination environment of CuO_5 with Cu–O_{eq} = 1.936(2) Å and Cu–O_{ax} = 2.35(9) Å is in excellent agreement with what is expected for a Jahn–Teller d^9 ion and found in other related cuprates, e.g. in $YBa_2Cu_3O_7$[3d] Cu–O_{eq} = 1.945(1) Å and Cu–O_{ax} = 2.298(6) Å, while in $La_{1.2}Tb_{0.8}CuO_4$[16] Cu–O_{eq} = 1.9348(6) Å and Cu–O_{ax} = 2.333(19) Å. Moreover, within experimental error, the Cu ion lies essentially on the plane (0.03(8) Å) formed by the four equatorial oxygens. On the other hand, the FeO_5 square pyramid is somewhat squashed with the Fe–O_{ax} bond distance (1.82(9) Å) shorter than the Fe–O_{eq} distances (2.03(3) Å) and the Fe^{3+} ion lying 0.62(9) Å above the basal plane of the pyramid. Such a coordination environment has been encountered before in other iron oxides in which Fe^{3+} is five-coordinate, e.g. in $Pb_4Fe_3O_8Cl$[17] Fe–O_{eq} = 2.01 Å and Fe–O_{ax} = 1.93 Å.

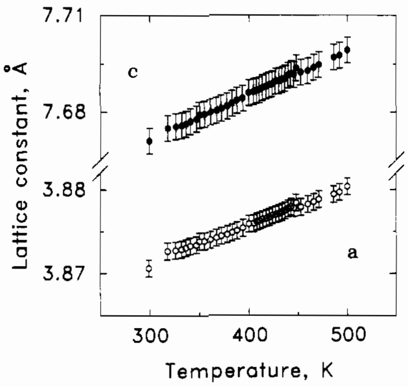

Figure 4. Dimensions (a and c) of the tetragonal unit cell of $YBaFeCuO_5$ plotted as a function of temperature.

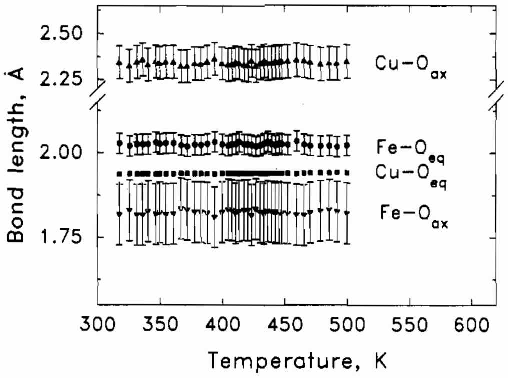

Figure 5. Variation of the Cu–O and Fe–O bond distances with temperature.

The temperature evolution of the Fe^{3+} magnetic moment (Figure 6) is characteristic of a continuous transition. A critical exponent analysis was performed by fitting the magnetic moment to the equation $\mu(T) = (\mu(0))(1 - T/T_N)^\beta$. This gave $T_N = 442.4 \pm 0.5$ K for the Néel temperature, $\mu(0) = 3.78 \pm 0.05$ μ_B for the zero K extrapolated value of the Fe^{3+} magnetic moment, and $\beta = 0.366 \pm 0.008$ for the critical exponent. The observed Néel temperature is in excellent agreement with the value of 446 K, reported earlier from Mössbauer measurements.[6–8] Moreover, our results favor a three-dimensional (3D) Heisenberg spin Hamiltonian (Heisenberg model, $\beta = 0.365$). The strong superexchange interactions between the Fe^{3+} ions and the bridging equatorial O^{2-} ions are principally responsible for the AF order

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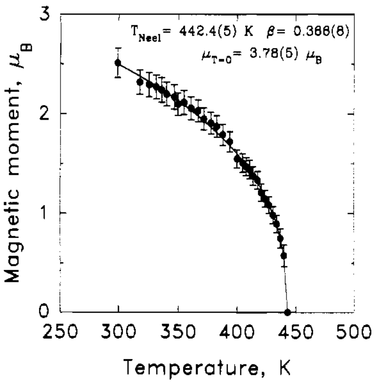

Figure 6. Temperature dependence of the Fe magnetic moment in $YBaFeCuO_5$. The solid line represents a fit to the expression for critical behavior: $\mu(T) = (\mu(0))(1 - T/T_N)^{\beta}$, with $T_N = 442.4(5)$ K, $\mu(0) = 3.78(5)\ \mu_B$, and $\beta = 0.366(8)$.

exhibited by the present system. The interlayer exchange interactions are however crucial in inducing the 3D LRO by coupling the essentially 2D AF Fe^{3+} sublattices. Even though successive FeO_2 layers are separated by ~7.7 Å, the interlayer interactions are considerably enhanced by the presence of the bridging apical oxygen and the CuO_2 layers. It is perhaps surprising that no induced magnetic moment resulting through the polarization of the Cu sublattice by the ordered Fe^{3+} moments was observed in the temperature regime of the present experiment. Small magnetic moments may be missed in a powder experiment and may require single-crystal measurements to be revealed. However, as the temperature is lowered further, unusual critical field behavior associated with the Cu sublattice may be observed.

The Fe^{3+} magnetic moments extracted from the refinements are noticeably reduced from the value expected for a high-spin $S = {}^5/_2$ Fe^{3+} ion ($\mu = 5.9\ \mu_B$). Such an effect may arise from a combination of various factors,[18] including strong covalency of the short Fe–O bonds, zero-point quantum fluctuation effects associated with low dimensionality, and partial oxidation of iron associated with the presence of excess oxygen ($\delta > 0$). However, an alternative explanation may be that the ground state is better described as a quartet with three unpaired electrons ($S = {}^3/_2$, $\mu = 3.9\ \mu_B$). While such a ground state is excluded by ligand field theory for octahedral and tetrahedral coordinations, it is known to exist for square-pyramidal configurations.[19] For instance, a squashed square-pyramidal coordination and a magnetic moment of 3.9 μ_B are encountered for Fe^{III} in the complexes $Fe^{III}X(S_2CNR_2)_2$ (X = halogen, R = alkyl group).

Conclusion

In conclusion, we have shown that antiferromagnetically ordered local magnetic moments lying parallel to the basal plane appear at 442 K at the Fe^{3+} sites of $YBaCuFeO_{5+\delta}$, a novel oxygen-deficient layered perovskite, related to the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$. The Cu^{2+} and Fe^{3+} ions are fully ordered in $YBaCuFeO_{5+\delta}$, occupying distinct sites and adopting differing coordination environments: the CuO_5 units are severely elongated, while the FeO_5 ones are squashed square pyramids. No evidence for magnetic ordering of the Cu moments is found in the temperature range 300–500 K, but coupling between the Fe and Cu sublattices is expected to be strong and should manifest itself through a polarization-induced moment at the Cu sites on further cooling.

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