

Measurement of Local Magnetic Fields in the CuO_2 Planes of $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ Superconductors

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A fully oxygenated $\text{Cu}(1)\text{Ba}_2\text{YCu}(2)_2\text{O}_{7-\delta}$ sample having 0.167 at % of the Cu atoms replaced by enriched ^{57}Fe was synthesized. As confirmed by ^{57}Fe Mössbauer spectroscopy $\sim 16\%$ of the Fe atoms entered the superconducting $\text{Cu}(2)\text{O}_2$ planes. Mössbauer spectra recorded at various temperatures between 77 and 373 K exhibited the presence of a weak magnetic hyperfine interaction in the Fe atoms entering the CuO_2 planes. The nonzero internal field obtained from the Mössbauer data increased following a Brillouin-type behavior, from the estimated Néel-like temperature of ~ 400 K down to 96 K where it reached ~ 1.5 T. Upon further cooling below T_c the internal field decreased fast down to ~ 0.4 T at 77 K. The presence of the internal field is believed to be related to magnetic correlations among the CuO_2 -plane atoms, i.e., to reflect local antiferromagnetic coupling between the Cu atoms.

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The first layered copper oxides exhibiting high- T_c superconductivity were discovered already 20 years ago [1]. Despite intense research efforts, the theoretical understanding of the phenomenon is still not fully developed. However, several recent experiments indicate that the basic interactions behind the formation of Cooper pairs are magnetic; see, e.g., Ref. [2] for a recent review. There are many experimental difficulties connected with observation of possible magnetic interactions. As the phases do not exhibit long-range commensurate magnetic ordering, ordinary diffraction methods do not reveal much; instead, one needs suitable local probes. Nuclear magnetic and quadrupolar resonances have been employed as well as Mössbauer spectroscopy. The former methods have problems connected with resolution due to various line-broadening effects, whereas the latter requires doping of the CuO_2 planes with suitable Mössbauer isotopes. In the late 1980s and early 1990s several Mössbauer studies using the ^{57}Fe resonance on iron-doped samples were carried out [3–6]. Although a wealth of information on the interesting crystal chemistry of high- T_c copper oxides was obtained, very little was learned on superconductivity itself. This was partially because in the prototype $\text{Cu}(1)\text{Ba}_2\text{YCu}(2)_2\text{O}_{7-\delta}$ high- T_c superconductor most of the Fe doping goes into the $\text{Cu}(1)\text{O}$ chains instead of the superconducting $\text{Cu}(2)\text{O}_2$ planes. On the other hand, the antiferromagnetic (AF) ordering of the $\text{Cu}(2)\text{O}_2$ planes in reduced $\text{Cu}(1)\text{Ba}_2\text{YCu}(2)_2\text{O}_{6.2}$ can be observed in ^{57}Fe Mössbauer spectra, proving that at least some Fe atoms enter the more interesting $\text{Cu}(2)$ sites [3]. Other early studies also proved that although the distribution of Fe between the plane and chain sites of Cu is not equal, a chemical substitution in the $\text{Cu}(2)\text{O}_2$ planes does indeed occur [5].

In this Letter we report the observation of magnetic hyperfine fields at the ^{57}Fe nuclei originating from a local AF ordering of the $\text{Cu}(2)\text{O}_2$ -plane atoms in fully oxygenated $\text{Cu}(1)\text{Ba}_2\text{YCu}(2)_2\text{O}_{7-\delta}$ with small amounts of the Cu atoms replaced by ^{57}Fe . The temperature dependence of the local magnetism on either side of the superconductivity transition temperature was investigated. In order to ensure a large distance between the substituted Fe atoms in the planes, only 0.167 at % of the Cu atoms were replaced by enriched ^{57}Fe . The fully oxygenated sample was synthesized using an ordinary solid-state reaction scheme. In brief, stoichiometric quantities of high-purity (99.99%) Y_2O_3 , BaCO_3 , CuO , and $^{57}\text{Fe}_2\text{O}_3$ (95% enriched, Gamma Lab. Co.) were mixed in an agate mortar and calcined in air for 24 h at 900 °C. The powder was re-ground, pelletized, and sintered twice in air for 24 h at 940 °C. Oxygen loading in an O_2 gas flow was performed at 400 °C for 24 h and at 350 °C for 48 h in powder form.

Mössbauer absorbers were prepared by spreading ~ 50 mg of the sample material mixed with epoxy resin on a thin Al foil having a diameter of ~ 20 mm. The Mössbauer spectra were recorded at various temperatures between 77 and 373 K (four of which were below the T_c of 93 K) in transmission geometry using a Cyclotron Co. $^{57}\text{Co}:\text{Rh}$ (25 mCi February 2004) source. A maximum Doppler velocity of 3.0 mm/s was used. A second source mounted on the same Mössbauer transducer was used to continuously monitor the velocity scale using a standard α -Fe absorber. The spectra were fitted using four spectral components. Three of them were simple symmetric quadrupole doublets, with the quadrupole coupling constants (eQV_{zz}), isomer shifts (s), and component intensities (P) as fit parameters. One common linewidth (Γ) was used for all four spectral components. A small deviation from the

Lorentzian line shapes was taken care of by assuming a slight distribution of the eQV_{zz} values. A Gaussian distribution was used and the width $eQ\Delta V_{zz}$ of the distribution was included as a global fit parameter for the paramagnetic components. The fourth spectral components exhibited the presence of magnetic hyperfine interactions. Therefore, the combined electric and magnetic Hamiltonian was employed for that particular component. The magnetic Hamiltonian is due to nuclear Zeeman splitting and is given by [7]

$$\mathcal{H}_M = -\frac{\hat{I}_z}{I} \mu B, \quad (1)$$

where \hat{I}_z is the magnetic nuclear spin operator, I the spin of the nucleus ($\frac{3}{2}$ and $\frac{1}{2}$ in the excited and ground states, respectively), μ the magnetic moment of the nucleus, and B the internal field at the nucleus. The electric Hamiltonian is due to the electric quadrupole interaction [7]:

$$\mathcal{H}_Q = -\frac{eQV_{zz}}{4I(2I-1)} \left[3\hat{I}_z^2 - \hat{I}^2 + \frac{\eta}{2}(\hat{I}_+^2 + \hat{I}_-^2) \right], \quad (2)$$

where \hat{I} , \hat{I}_\pm are nuclear spin, raising and lowering operators, and η the asymmetry parameter of the local electric field gradient (EFG), defined as

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}},$$

with V_{xx} , V_{yy} , V_{zz} being principal components of the EFG, chosen so that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, i.e., $0 \leq \eta \leq 1$. In case the spatial directions of V_{zz} and B coincide, the combined Hamiltonian is a simple sum of Eqs. (1) and (2). If this is not the case, either of the Hamiltonians should be reexpressed in the local coordinate system of either magnetic or electric interaction. We used the matrix representation of Ref. [8] and thus the angles α and β , specifying the orientation of B in relation to V_{zz} (and V_{xx} , V_{yy}), enter as additional fit parameters, but the distribution $eQ\Delta V_{zz}$ was not included. Among the fit parameters of combined interaction, α , β , η , eQV_{zz} , and B , the span of the line splitting and general line shape are to a high extent determined by three parameters: eQV_{zz} , B , and β . Note that in the paramagnetic case ($B = 0$) the line splitting is essentially due to eQV_{zz} .

The synthesized sample was free from even minute impurities according to x-ray diffraction (Rigaku: RINT2550VK/U diffractometer equipped with a rotating Cu anode). The T_c was 93 K, as determined by the onset of the sharp diamagnetic signal seen in a dc magnetic-susceptibility measurement using a superconducting quantum interference device (Quantum Design: MPMS-XL). In Fig. 1 Mössbauer spectra recorded from the sample at various temperatures are shown. Three spectral components are pure quadrupolar doublets reflecting various oxygen coordination polyhedra of Fe atoms populating the Cu(1)-chain site [5] and are here collectively denoted

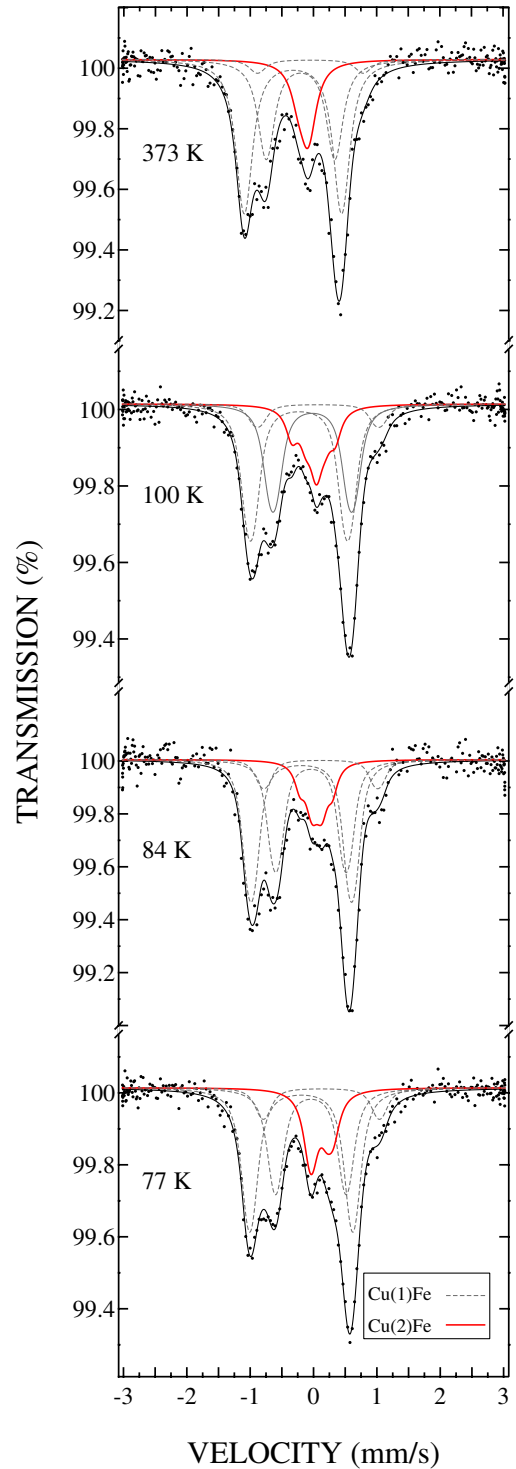


FIG. 1 (color online). ^{57}Fe Mössbauer spectra of the Fe-doped $\text{Cu(1)Ba}_2\text{YCu(2)}_2\text{O}_{7-\delta}$ sample recorded at indicated temperatures. Components used in the fitting are displayed above each spectrum. Components belonging to the Cu(1) are drawn using the same line type and lumped together in the legend.

Cu(1)Fe. The fourth component marked by the thick solid lines covers 16% of the spectral intensity and is the only one which has been assigned to Fe atoms located at the superconducting Cu(2)-plane site [6], and is therefore de-

noted Cu(2)Fe. For a detailed discussion of the site assignment of the Cu(1)Fe components, see, e.g., Ref. [6].

Owing to the reasonably large intensity of component Cu(2)Fe, its peculiar temperature evolution is readily observed: At 77 K, close to 0 mm/s a strong feature is observed for component Cu(2)Fe. Some of the intensity seen at ~ 0 mm/s is redistributed upon increasing the temperature towards 100 K, as the splitting of component Cu(2)Fe increases. Above 100 K the span of the splitting slowly diminishes, resulting in a singletlike resonance line at 373 K. The only way to obtain a good fitting of any of the spectra was by including B and β as fit parameters to component Cu(2)Fe. Attempts to fit the spectra without a magnetic field of ~ 0.5 – 1.5 T did not yield good fittings, except at 373 K where component Cu(2)Fe is almost paramagnetic. The electric parameters of component Cu(2)Fe were practically constant at all temperatures, remaining at $eQV_{zz} \approx -0.4$ mm/s, $\eta \approx 0.6$, and $\alpha \approx 60^\circ$, indicating that the local atomic structure remained intact. Also the component intensities remained constant, despite the change in the shape of component Cu(2)Fe rendering support to the consistency of the fittings.

Generally, in ^{57}Fe Mössbauer spectra nonzero internal fields can be observed whenever a sample is magnetically ordered. The Cu(2)Fe component originates from ordinary trivalent Fe, which most probably resides in the high-spin state, as indicated by studies of this phase and similar perovskite-derived phases [5,9]. The saturation field for high-spin Fe^{3+} is around 50 T; i.e., the observed value is far from saturated. In the paramagnetic state, internal fields can be observed if the temperature is decreased below a critical limit where the atomic spin relaxation times become longer than the Larmor precession time of the nuclear spins. Normally this would require cooling of the sample down to temperatures of a few hundreds of mK. None of the above criteria are fulfilled for the present samples; i.e., one would not expect the presence of nonzero magnetic fields in any of the spectral components.

The normal-state susceptibility for $\text{Cu}(\text{1})\text{Ba}_2\text{YCu}(\text{2})_2\text{O}_{7-\delta}$ does not follow a paramagnetic Curie-Weiss behavior [10,11]. The susceptibility decreases upon lowering the temperature. Although the contribution from the Cu(2) atoms to the susceptibility increases (and that of the Cu(1) atoms decreases) upon decreasing the temperature, it is far from an inverse-temperature relation [12]. As the only atoms with nonzero spins are the various Cu species, the internal field seen for component Cu(2)Fe is an intrinsic effect of the $\text{Cu}(\text{2})\text{O}_2$ planes, as the ^{57}Fe substituents are too far from each other to inflict magnetic ordering. The obvious conclusion is that a strong spin-spin correlation between the Cu atoms will prevent the average field from reaching zero. The anomalous normal-state susceptibility is also a result of this correlation.

In Fig. 2 the internal field B and the angle β between the internal field and the main component V_{zz} of the electric field gradient, as obtained from the computer fittings, are presented. As V_{zz} is parallel to the c axis, β gives directly

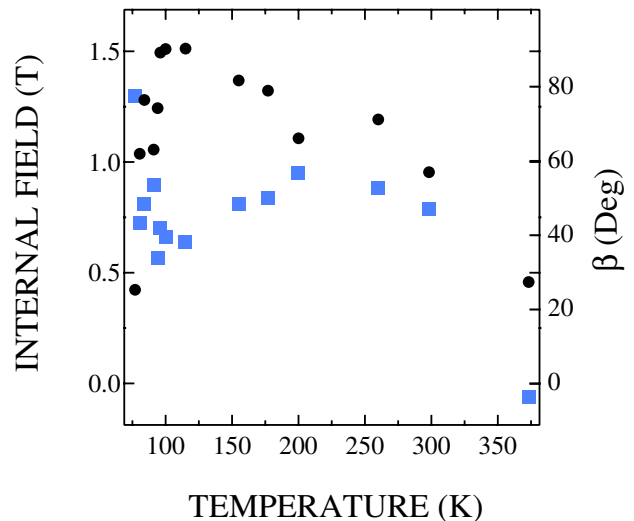


FIG. 2 (color online). Parameters of the magnetic hyperfine interaction obtained from fit parameters of component Cu(2)Fe: internal field (solid circles) and β angle (solid squares).

the angle between the internal field and the c axis. The temperature evolution of the internal field of component Cu(2)Fe upon cooling is interesting, as the maximum value of ~ 1.5 T is reached just above T_c , below which the field decreases strongly. Above T_c the internal field follows a Brillouin-like curve, suggesting a complete disappearance of the internal field at $T \approx 400$ K. This is close to the ~ 410 -K Néel temperature of the AF oxygen-depleted $\text{Cu}(\text{1})\text{Ba}_2\text{YCu}(\text{2})_2\text{O}_{6.2}$ phase [13], indicating that the observed magnetism could be connected to short-range AF order in the ab planes. Thus, the situation is probably as was observed for a slightly reduced Zn-substituted superconducting $\text{Cu}(\text{1})\text{Ba}_2\text{YCu}(\text{2})_2\text{O}_{6.7}$, in which enhanced AF correlations in the $\text{Cu}(\text{2})\text{O}_2$ planes were observed by ^{63}Cu NMR measurements [14]. It was found that every zero-spin Zn atom in the $\text{Cu}(\text{2})\text{O}_2$ planes being surrounded by four Cu atoms picks up the magnetic field from these Cu atoms, the spin directions of which are identical. This local order is in accord with the original AF order of the reduced $\text{Cu}(\text{1})\text{Ba}_2\text{YCu}(\text{2})_2\text{O}_{6.2}$ phase.

Also for the present sample any ^{57}Fe atom in the $\text{Cu}(\text{2})\text{O}_2$ plane is surrounded by a ring of four Cu(2) atoms. The magnetic field observed in the Mössbauer spectra may originate from (i) Fe atoms participating in the local order, i.e., if the electronic spin ($S = 5/2$) of the Fe atom couples antiferromagnetically with the Cu atoms the Fermi contact interaction (FCI) will mediate a nonzero magnetic field to the ^{57}Fe nucleus, or (ii) the transferred hyperfine field from the Cu atoms may directly give rise to the nonzero magnetic field at the ^{57}Fe nucleus. The field mediated by the FCI is antiparallel to the electronic spins of the Fe atom, i.e., parallel to the spin directions of the four nearest Cu atoms. Therefore, contributions to the hyperfine field obtained through either mechanism add constructively. The dipolar field from the Cu(2) atoms could also contribute to

the measured field, but due to the distance of ~ 3.7 Å to the nearest Cu(2) spins ($S = 1/2$) we estimate that it would be less than 0.1 T. Disruption of the local order, e.g., by increasing the temperature, will extinguish all three contributions simultaneously. Hence, the Brillouin-type behavior of Fig. 2 is seen.

However, the angle β remains close to $\sim 45^\circ$, indicating that the observed internal field is strongly canted away from the ab plane at all temperatures (Fig. 2). (At 77 and 373 K the β values differ, most probably because the internal field has decreased too much to enable reliable fitting of the angles.) The canting may suggest the presence of other contributions to the internal field along with the local AF order of the Cu(2) atoms in the ab plane. There could, e.g., be interactions between the Cu(2)O₂ planes, probably ferromagnetic, as there are no oxygen atoms in between to act as superexchange mediators. One may speculate that the situation could be somewhat similar to the valence-mixed phase of BaTbFe₂O₅, in which the strong electron-doping of the Fe atoms causes the occurrence of ferromagnetically coupled intermediate valence-state Fe^{2.5+} pairs sharing an electron through the basal plane of the square-planar oxygen coordination pyramids [15]. The local structures around the rare-earth atoms in BaTbFe₂O₅ and Cu(1)Ba₂YCu(2)₂O_{7- δ} are very similar.

In conclusion, substituting the Cu atoms in the Cu(1)Ba₂YCu(2)₂O_{7- δ} high- T_c superconductor with very small amounts of ⁵⁷Fe enabled detection of small local fields in the Cu(2)O₂ planes using ⁵⁷Fe Mössbauer spectroscopy. As the mean distance between the ⁵⁷Fe atoms in the Cu(2)O₂ planes is larger than several lattice constants, the observed fields reflect properties of the bulk material. The hyperfine fields from the Cu(2) atoms seen by the ⁵⁷Fe nuclei are compatible with a local AF ordering of the Cu(2)O₂-plane atoms, but the presence of an out-of-plane contribution is also seen. The observed fields prevail at temperatures far above and below the superconductivity transition temperature, following roughly a Brillouin-type behavior down to a few degrees above T_c . The onset of superconductivity suppresses the field but does not extinguish it completely even at 77 K. Similar investigations on the temperature dependence of the magnetic fields in various superconducting copper-oxide phases should shed light on local magnetic properties of these phases.

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