Pressure-induced onset of long-range magnetic order in two-dimensional spin-frustrated $CuFeO_2$

W. M. Xu,[1] M. P. Pasternak,[1,2] and R. D. Taylor[2]
[1]*School of Physics and Astronomy, Tel-Aviv University, 69978 Tel-Aviv, Israel*
[2]*MST-10, MS-K764, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
(Received 8 September 2003; published 9 February 2004)

Magnetic properties of two-dimensional spin-frustrated $CuFeO_2$ have been studied up to 19 GPa by means of ^{57}Fe Mössbauer spectroscopy. The partially disordered spin arrangement at ambient pressure in the 11–16 K range, transforms with pressure to a long-range ordered ''5-sublattice'' phase with a distinct T_N, a similar role played by external magnetic field in neutron studies. This phase gradually substitutes for the ''4-sublattice'' magnetic ground state present at ambient pressure, reaching 100% at 19 GPa. Despite the presence of long-range order, this high pressure phase exhibits magnetic relaxation above 20 K attributed to the notwithstanding weak interplanar superexchange interaction. The dramatic twofold increase of T_N at 19 GPa is explained in terms of the unusual increase of the intraplanar direct exchange $J_{\|}$ caused by the anomalous anisotropic compression of $CuFeO_2$ in which c/a increases with pressure.

DOI: 10.1103/PhysRevB.69.052401 PACS number(s): 75.50.Lk, 76.80.+y, 75.50.Ee, 75.30.Gw

INTRODUCTION

Frustration of spin-spin interaction plays an important role in triangular-lattice antiferromagnets. The ground state of a two-dimensional (2D) triangular-lattice is highly degenerate;[1] a macroscopic number of states are possible with exactly the minimum number of parallel spins. In the 2D plane no unit triangle exists with the three spins parallel. However in real cases an additional interaction between planes lifts the degeneracy giving rise to a complex magnetic ordering at finite temperature. Cuprous ferrite ($CuFeO_2$) with the hexagonal α-$NaFeO_2$ or the delafossite type structure is a rather close approximation to a 2D triangular-lattice antiferromagnet. Its lattice structure in the hexagonal[2] description is shown in Fig. 1(a). The structure consists of hexagonal layers of Cu, Fe, and O with a stacking sequence of A–B–C [A(Cu), A(O), B(Fe), C(O), C(Cu), C(O), A(Fe), etc., along the *c* axis to form a layered triangular lattice antiferromagnet, where the triangular lattices of ferromagnetic Fe^{3+} are separated by layers of nonmagnetic Cu^{1+} and O^{2-}. Moreover, the Fe^{3+} ions are not positioned right above each other on the adjacent Fe layer, but above the center of a triangle formed by the Fe^{3+} ions. Thus, from geometrical considerations alone spins are expected to be highly frustrated both between neighboring layers as well as within the layer.

The ambient pressure magnetic properties of $CuFeO_2$ have been extensively investigated.[3–6] Powder neutron diffraction measurements[7,8] led to the discovery of successive magnetic transitions of a partially disordered (PD) phase [see Fig. 1(c)] with $T_{N1}=16$ K to the low temperature, ''4-sublattice'' long-range magnetically ordered phase with $T_{N2}=11$ K [see Fig. 1(b)]. Recent neutron studies with an applied magnetic field[9] established the onset of a long-range order ''5-sublattice'' phase [Fig. 1(d)] evolving from the PD phase. High pressure x-ray diffraction studies by Zhao *et al.*[10] showed that the *delafossite* structure is stable up to at least 10 GPa and that the *a* axis is approximately four times more compressible than the *c* axis.

The main motivation of the present studies was to investigate the effect of pressure on the spin frustration caused by the unusual anisotropy in the delafossite structure. In particular we were interested in the effect of the highly compressible *a* axis on T_N which for 2D systems is predicted[11] to be proportional to the in-planar direct exchange interaction $J_{\|}$. ^{57}Fe Mössbauer spectroscopy, the best method so far for studies of high-pressure magnetic and electronic properties of iron oxides, has been utilized in the present work.

EXPERIMENT

A polycrystalline $CuFeO_3$ sample was synthesized from Cu_2O and Fe_2O_3, the latter enriched to 20% ^{57}Fe. The thoroughly ground mixture was pressed into a disc. The quality of the fired sample was confirmed through Mössbauer spectroscopy (MS) at RT and cryogenic temperatures.

The sample was loaded into a 150×25 μm cavity drilled in a Re gasket which also served as a collimator for the 14.4 keV γ rays. A TAU miniature piston-cylinder diamond anvil cell (DAC)[12] was used with anvils having 300 μm diameter culets. Argon was used as a pressurizing medium and ruby fluorescence served as a manometer. Mössbauer studies were carried out with a 10 mCi ^{57}Co(Rh) point source in the 4–300 K temperature range using a top-loading He cryostat.[13] Typical collection time of a single spectrum was $\sim$24 hours.

RESULTS AND DISCUSSIONS

Mössbauer spectra measured at ambient pressure are shown in Fig. 2. At RT a quadrupole split spectrum is observed with an isomer shift, IS$=0.38$ mm/s and QS $(e^2qQ/2)=0.61$ mm/s, similar to values obtained by Mitsuda *et al.*[7] and Muir *et al.*[14] The onset of the PD phase is detected at $\sim$16 K and the 14 K spectrum is typical of a hyperfine interaction of PD state with a distribution of hyperfine fields. From 11 K down, long-range magnetic order of the ''4-sublattice'' (4SL) phase is detected with remnants of the magnetic-ordered ''5-sublattice'' (5SL) phase. Below 11 K the PD phase is barely detected. The hyperfine fields,

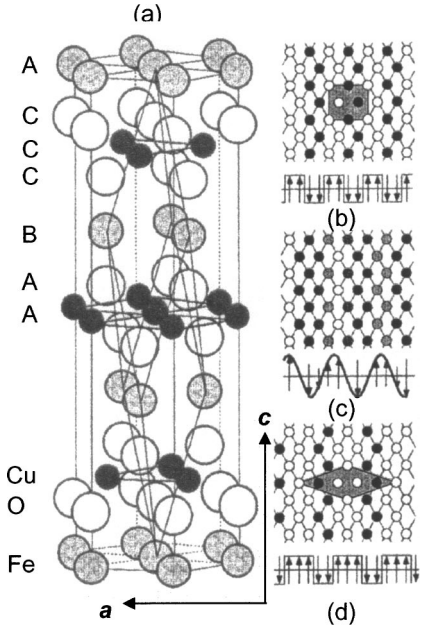

FIG. 1. (a) The crystal structure of $CuFeO_2$ (Ref. 17). The $A-B-C$ stacking of the elemental planes is shown in the figure. With increasing pressure the a axis is considerably more compressed than the c axis, giving rise to the unusual enhancement of T_N (see text). (b) The 4SL, (c) the PD, and (d) the 5SL states in the hexagonal c plane. White and black circles correspond to moments parallel and antiparallel to the out-of-plane c axis (Ref. 9). The spin arrangements along the $\langle 110 \rangle$ axis is indicated in the subfigures.

H_{hf}, of 4SL and 5SL phases first obtained by Mitsuda *et al.*[7] using single crystal absorbers were found to be $H_{\mathrm{hf1}}=51$ T and $H_{\mathrm{hf2}}=48$ T, respectively. The respective T_N values were obtained from neutron magnetic studies[7,8] with oriented crystals and as can be seen fit rather well with the rich details of the Mössbauer spectra.

Spectra recorded at 6 K ($T<T_N$) to 19 GPa showing different spectral components evolving with increasing pressure are presented in Fig. 3. The solid lines through the experimental points are theoretical fits. At ambient pressure and 6 K the Mössbauer spectrum is composed of one sextet with hyperfine field $H_{\mathrm{hf1}}=51$ T, and as mentioned, has been assigned to the 4SL magnetic ground state. The component with its slightly lower hyperfine field H_{hf2} (48 T) is evident (Fig. 3, 0.01 GPa, and Ref. 7). The abundance of the 5SL phase increases with pressure and becomes equal to the 4SL phase at ~12 GPa. At 19 GPa the 4SL phase vanishes leaving only the 5SL phase. The Ising-spin triangular lattice model[7] predicts that the interplane interaction favors the 5 sublattice structure. The lack of the long-range order of this configuration is explained by the weak interplanar interaction. X-ray results[10] show that in spite the unusual c/a increase with pressure, c decreases by about 1% at 10 GPa (and at 19 GPa it should have decreased even further). Thus, the unusual relative stiffness of the c axis in $CuFeO_2$ explains the need of such a high pressure (19 GPa) to attain some degree of 3D character sufficient to accomplish the $4\mathrm{SL}\rightarrow 5\mathrm{SL}$ transformation.

The Mössbauer spectra recorded at 19 GPa at several tem-

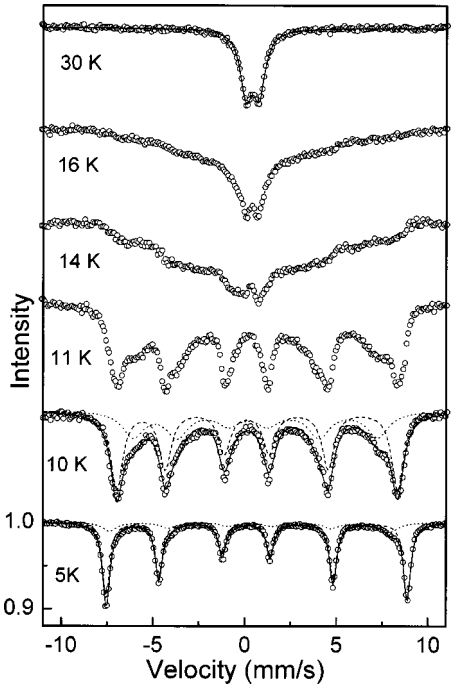

FIG. 2. Mössbauer spectra of $CuFeO_2$ at ambient pressure measured at $T<30$ K. The fits to the experimental points represent the convolution of two magnetic components. The dashed curves correspond to spectra components resulting from the 4SL state and the dotted lines of the 5SL. By lowering the temperature one observes the successive magnetic phase transitions from the PD ($T_{N1}=16$ K) to the mixed long-range ordered 4SL ($T_{N2}=11$ K) and 5SL phase to the practically pure 4SL state at 5 K. The temperature driven transition is gradual (see text). The 11–16 K spectra consist of static and relaxation spectral components. No fitting was tempted in those cases.

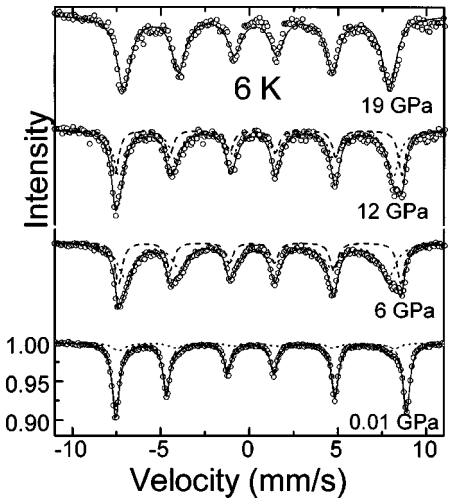

FIG. 3. Mössbauer spectra taken to 19 GPa at 6 K ($T\ll T_N$). The fits to the experimental points represent the convolution of two magnetic components. The dashed curves correspond to spectra components resulting from the 4SL state and the dotted lines of the 5SL. As can be seen the abundance of the 5SL increases with pressure reaching unity by 19 GPa.

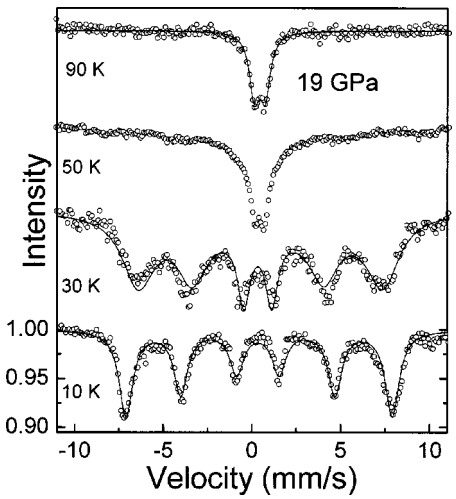

FIG. 4. Mössbauer spectra of $CuFeO_2$ at 19 GPa at different temperatures. $T_N = 36$ K at this pressure. Magnetic relaxation is observed in the 20–36 K region and is attributed to the weak interplanar superexchange interaction.

peratures are shown in Fig. 4. No change is observed in the hyperfine parameters up to 20 K; the spectra can be well fitted with only one static magnetic hyperfine field, consistent with the onset of long-range magnetic order of the 5SL phase. At this pressure T_N reaches ~38 K. Towards T_N, in the 25–35 K range, the spectra are typical of a magnetic relaxation pattern[15] and due to their complexity no efforts were made to fit them. Thus, instead of successive magnetic transitions T_{N1} and T_{N2} are observed at ambient pressure, the $CuFeO_2$ magnetic system in this regime can be described as one with long-range order and a single T_N with a Fe^{3+} magnetic moment typical of the 5SL phase. The origin of the magnetic relaxation in the 25–35 K range in which the *Larmor* precession period is comparable to the lifetime of the 14.4 keV transition in ^{57}Fe is not clear. It may be an indication that at 19 GPa the *c*-axis length or the interlayer Fe–O–Cu–Fe overlap is not sufficient to create a robust superexchange interaction $J_\perp$. The hyperfine field parameters at different pressures are listed in Table I, and as can be seen, the IS and QS hardly change with pressure.

The mechanism behind the large increase in T_N with increasing pressure following the unusual pressure dependence of c/a, viz. $(d(c/a)/dP > 0)$, can be explained on the basis of numerical modeling by Keimer *et al.*[11] who derived an expression for T_N for undoped La_2CuO_4, a universality class of the *xy* model which also applies to triangular-lattice-gas.[16]

$$T_N = 2\pi M_0 J_\square / \ln\{4\alpha_{\text{eff}}/[M_0 \pi^2 \ln(4\alpha_{\text{eff}}/\pi)]\}$$
$$\approx a J_\square / \ln(k\alpha), \quad (1)$$

where $\alpha_{\text{eff}} = z_\square \alpha_{xy} + z_\perp \alpha_\perp$, $z_\parallel$ and $z_\perp$ are the in- and out-of-plane coordination numbers, α_{xy}, $\alpha_\perp \ll 1$. $M_0 = 0.3$; a and k are constants. Thus, with increasing pressure and once frustration is removed (see Fig. 3), T_N increases rapidly because of the Fe–Fe in-plane enhancement of the direct exchange interaction.

TABLE I. The hyperfine interaction parameters of $Cu^{57}FeO_2$, measured at various pressures. Pressures were determined using the ruby fluorescence standard. Errors in the last digit are shown in parentheses. H_{hf1} and H_{hf2} correspond to the 4SL and 5SL phases, respectively.

P (GPa)	0.001	4.0(2)	12(1)	19(1)
IS (mm/s)[a]	0.38(2)	0.39(2)	0.37(2)	0.40(2)
QS (mm/s)	0.62(2)	0.61(2)	0.57(2)	0.57(2)
H_{hf1} $(T \ll T_N)$	50.7(1)	50.7(1)	50.5(1)	
H_{hf2} $(T \ll T_N)$		47.6(2)	48.1(2)	48.1(1)

[a]The IS is with respect to Fe metal at RT.

CONCLUSIONS

By using Mössbauer spectroscopy at various temperatures and pressures, it is shown that as the pressure is increased; the PD phase gradually turns into the long-range ordered 5SL phase. At 19 GPa this becomes the only long-range order antiferromagnetic state of $CuFeO_2$. The role of the applied magnetic field in the neutrons studies by Mitsuda *et al.*[9] in which the PD→5SL also takes place shows the similar equivalence of the pressure variable. Because pressure affects the anisotropy in this particular oxide, relatively high pressures are needed: (i) to produce the PD→5SL transformation, and (ii) to reverse the $CuFeO_3$ magnetic ground state from 4SL to 5SL. The unusual increase in T_N with pressure is attributed to the high compressibility of the *a* axis, and despite the onset of long-range magnetic order, we witness spin-spin relaxation starting at $T \sim 2/3 T_N$. This phenomenon evokes a rather weak interplane superexchange interaction arising from the ever increasing c/a with pressure.

It is noteworthy that both the IS and QS barely change with pressure up to 19 GPa which is consistent with the unchanging x-ray diffraction results measured to 10 GPa. Similarly the unchanging IS and QS above 10 GPa suggest the delafossite structure of $CuFeO_2$ likely persists up to 19 GPa. A lack of a structural phase transition and its abrupt molar volume change suggest that the observed magnetic phase transition is second order. Finally, we note that the Ising-spin triangular lattice model predicts that the interplanar interaction favors the 5SL structure.[7] And indeed upon increasing the pressure we show that indeed the long-range order 5SL structure is stabilized as a consequence of a 2D →3D gradual transformation.

ACKNOWLEDGMENTS

This research was supported in part by BSF Grant No. 98-00003 and the Israeli Science Foundation Grant No. 36/00-3.

[1] P. Fazekas and P. W. Anderson, Philos. Mag. **30**, 423 (1974).
[2] A. Pabst, Am. Mineral. **75**, 105 (1988).
[3] M. Mekata, N. Yaguchi, T. Takagi, T. Sugino, S. Mitsuda, H. Yoshizawa, N. HoSoito, and T. Shinjo, J. Phys. Soc. Jpn. **62**, 4474 (1993).
[4] M. Uhrmacher, R. N. Attili, K. P. Lieb, K. Winzer, and M. Mekata, Phys. Rev. Lett. **76**, 4829 (1996).
[5] S. Mitsuda, N. Kasahara, T. Uno, and M. Mase, J. Phys. Soc. Jpn. **67**, 4026 (1998).
[6] O. A. Petrenko, G. Balakrishnan, M. R. Lees, D. McK. Paul, and A. Hoser, Phys. Rev. B **62**, 8983 (2000).
[7] S. Mitsuda, H. Yosizawa, N. Yaguchi, and M. Mekata, J. Phys. Soc. Jpn. **60**, 1885 (1991).
[8] M. Mekata, N. Yaguchi, T. Takagi, S. Mitsuda, and H. Yoshizawa, J. Magn. Magn. Mater. **104–107**, 823 (1992).
[9] S. Mitsuda, M. Mase, T. Uno, H. Kitawaza, and H. A. Katori, J. Phys. Soc. Jpn. **69**, 3513 (2000).
[10] T. R. Zhao, M. Hasegawa, T. Kondo, T. Yagi, and H. Takei, Mater. Res. Bull. **32**, 151 (1997).
[11] B. Keimer, A. Aharony, A. Auerbach, R. J. Birgenau, A. Cassanho, Y. Endoh, R. W. Erwin, M. A. Kastner, and G. Shirane, Phys. Rev. B **45**, 7430 (1992).
[12] G. Yu. Machavariani, M. P. Pasternak, G. R. Hearne, and G. Kh. Rozenberg, Rev. Sci. Instrum. **69**, 1423 (1998).
[13] G. R. Hearne, M. P. Pasternak, and R. D. Taylor, Rev. Sci. Instrum. **65**, 3787 (1994).
[14] A. H. Muir, Jr. and H. Wiedersich, J. Phys. Chem. Solids **28**, 65 (1967).
[15] F. Van der Woude and A. J. Dekker, Phys. Status Solidi **9**, 775 (1965).
[16] D. P. Landau, Phys. Rev. B **27**, 5604 (1983).
[17] M. Hasegawa, M. I. Batrashevich, T. R. Zhao, H. Takei, and T. Goto, Phys. Rev. B **63**, 184437 (2001).