

ANTIFERROMAGNETISM IN ^{57}Co -DOPED $\text{La}_2\text{CuO}_{4-y}$ STUDIED BY MÖSSBAUER SPECTROSCOPYS. JHA, C. MITROS, Amer LAHAMER¹ and Sherif YEHIA²*University of Cincinnati, Ohio 45221, U.S.A.*

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Mössbauer effect studies of ^{57}Co -doped $\text{La}_2\text{CuO}_{4-y}$ were performed at temperatures between 4.2 K and room temperature. These confirm the antiferromagnetic ordering of these compounds below room temperature. Temperature dependence of the quadrupole splitting shows that the hyperfine field is at an angle with the c -axis.

1. Introduction

Antiferromagnetic order in the layered perovskite compound $\text{La}_2\text{CuO}_{4-y}$ has been detected by neutron scattering [1–3], muon spin rotation [4], and nmr [5,6] techniques. The Néel temperature T_N is found to depend strongly on sample preparation [3,7], ranging from $T_N \sim 0$ for $y = 0$ to $T_N \sim 290$ K for $y \sim 0.03$. Some oxygenated samples have been reported to be superconductors [8,9].

Mössbauer spectroscopy is well suited to study of the antiferromagnetic ordering. Nishihara et al. have studied [10–12] the Mössbauer effect of ^{57}Fe in $\text{La}_2\text{Cu}_{0.995}\text{Fe}_{0.005}\text{O}_4$. They reported Zeeman splitting below 220 K with broadening of the spectrum attributed to a distribution of hyperfine fields; extra absorption near zero velocity and asymmetry of the spectrum were attributed to iron in an extra phase or to relaxation effects. In the present work Mössbauer effect studies of ^{57}Co -doped $\text{La}_2\text{CuO}_{4-y}$ were performed at temperatures between 4.2 K and room temperature; this source experiment allows use of much less impurity, perturbing less the environment of ^{57}Fe .

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2. Experimental methods

Samples of $\text{La}_2\text{CuO}_{4-y}$ were prepared by dissolving stoichiometric quantities of La_2O_3 and CuO in HNO_3 . The precipitate formed by the addition of oxalic acid was calcified for 3 hours at 600°C , ground and annealed in air at 950°C for one day. This was followed by pressing, heating in air for 12 hours at 950°C and slow cooling. Finally samples were annealed under He for 15 hours at 500°C and slow cooled. Carrier-free ^{57}Co in the form of CoCl_2 solution was deposited on the sample and the final anneal repeated. X-ray diffraction measurements showed the sample to be single phase with the correct structure [13,14]. The value of y was not measured.

Mössbauer measurements were carried out with a source mounted on an Elscint constant acceleration spectrometer and using a stationary absorber, or with a WissEl II spectrometer with the source stationary at low temperature and a room-temperature potassium ferrocyanide absorber vibrated sinusoidally. Positive velocity corresponds to source and absorber becoming closer.

3. Results and discussion

Figure 1 shows room-temperature Mössbauer spectra for a $^{57}\text{Co}(\text{La}_2\text{CuO}_{4-y})$ source with a potassium ferrocyanide (PFC) absorber, and for a $^{57}\text{Co}(\text{Rh})$ source

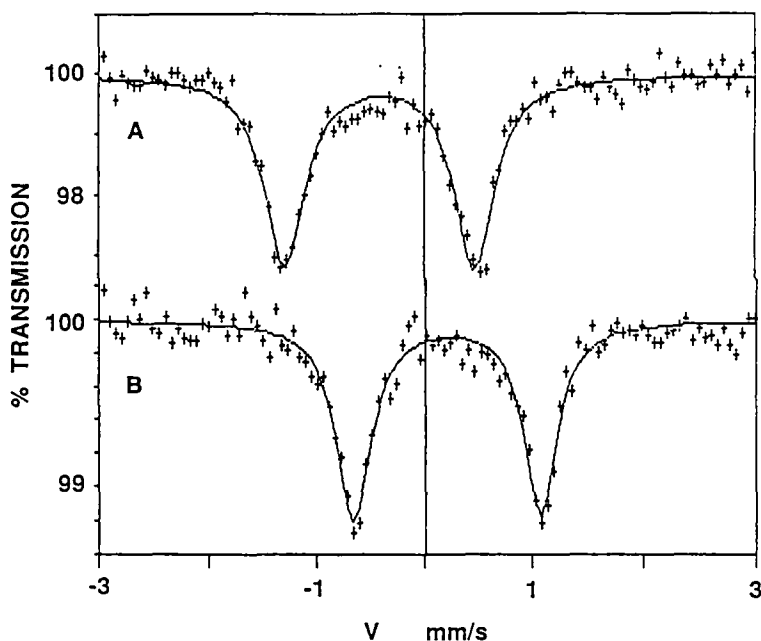


Fig. 1. Mössbauer spectra at 295 K: A) $^{57}\text{Co}(\text{La}_2\text{CuO}_{4-y})$ versus PFC, and B) $^{57}\text{Co}(\text{Rh})$ versus $^{57}\text{Fe}(\text{La}_2\text{CuO}_{4-y})$. Sources have constant acceleration.

with a $\text{La}_2\text{Cu}_{0.98}^{57}\text{Fe}_{0.02}\text{O}_4$ absorber. Each spectrum is fitted with a doublet; in the former case the individual lines are only slightly broader (0.44 mm/s FWHM versus 0.38 mm/s FWHM), which indicates that the electron capture aftereffect

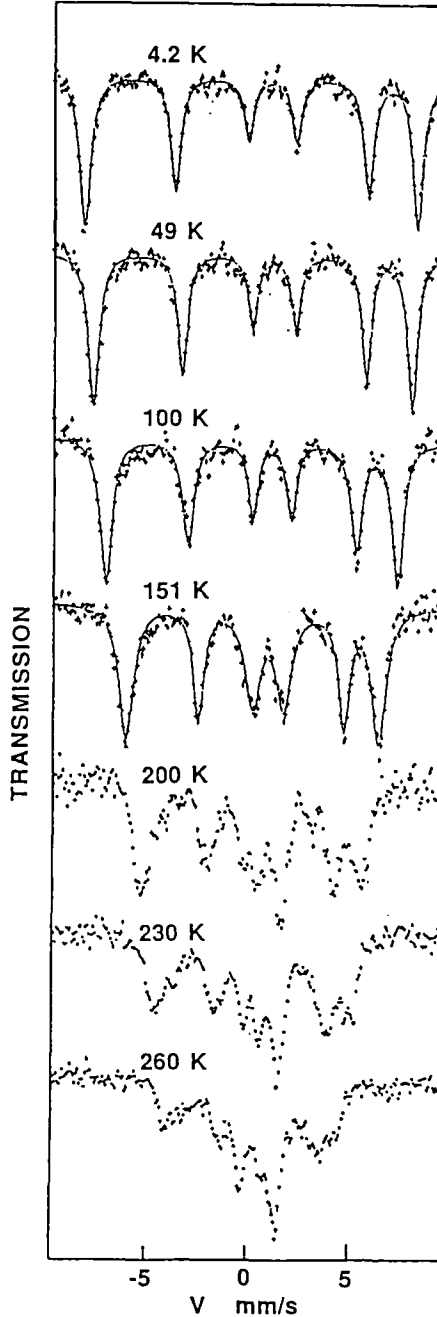


Fig. 2. Mössbauer spectra of $^{57}\text{Co}(\text{La}_2\text{CuO}_{4-y})$, at indicated temperatures, versus room-temperature PFC absorber vibrated sinusoidally.

is negligible for the case of $^{57}\text{Co}(\text{La}_2\text{CuO}_{4-y})$. In both cases the lines are broader than the natural linewidth [0.24 mm/s FWHM for a $^{57}\text{Co}(\text{Rh})$ source with a PFC absorber]. This broadening may be due to residual hyperfine field associated with 2D ordering above $T_N \sim 290$ K [15,16].

Figure 2 shows Mössbauer spectra as a function of temperature for a $^{57}\text{Co}(\text{La}_2\text{CuO}_{4-y})$ source and PFC absorber. The data have been linearized to correspond to equal times at equal velocity intervals. Below about 100 K there is a clearly resolved 6-line Zeeman pattern, without the extra absorption near zero velocity or the extreme broadening of the outer lines reported by Nishihara et al. [10–12] for $^{57}\text{Fe}(\text{La}_2\text{CuO}_{4-y})$.

Above 150 K there is a marked change in the shape of the spectra, and they cannot be fitted with a sextet. A number of factors may be contributing, including a distribution of magnetic fields due to parts of the sample having different values of T_N , or possibly the onset of relaxation effects [17].

The magnetic field H , obtained from the spectra of fig. 2 and normalized to $T=0$, is plotted in fig. 3 as a function of temperature. For comparison the temperature dependence for magnetization in the molecular field model for $J = 1/2$ is also shown, with T_N assumed to be 290 K. Yamada et al. [3] found the sublattice magnetization, deduced from the intensity of the (100) neutron diffraction peak, rather closely followed the $J = 1/2$ Brillouin curve. In contrast, the large deviation of H from the Brillouin curve, found in the present study, resembles the temperature dependence of the sublattice magnetization deduced from ^{139}La NQR by Nishihara et al. [5], and of the muon precession signal, observed by Uemura et al. [4].

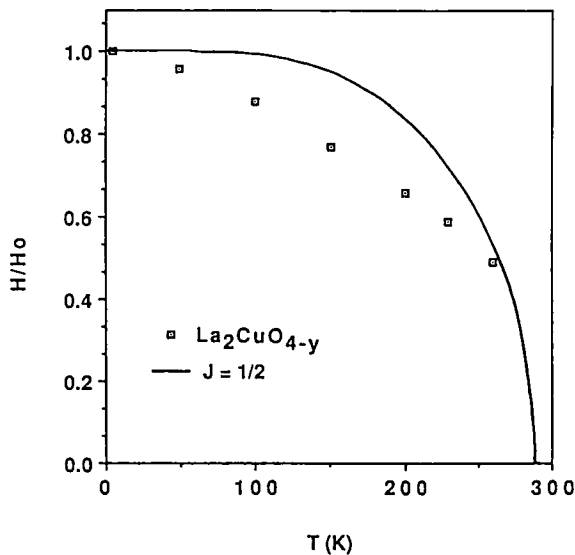


Fig. 3. Temperature variation of normalized hyperfine field from fig. 2, and $J=1/2$ Brillouin function for $T_N = 290$ K.

Table 1

Fitted Mössbauer parameters for ^{57}Co in $\text{La}_2\text{CuO}_{4-y}$, as a function of temperature T . H , δ , Δ are respectively the hyperfine field, the isomer shift relative to $\alpha\text{-Fe}$, and the quadrupole splitting. Γ_i is the linewidth (FWHM) in mm/s of the i^{th} line pair, and I_i the intensity relative to lines 3 and 4. Error in the least significant digit is given in ().

T (K)	H (kOe)	δ (mm/s)	Δ (mm/s)	$I_{1,6}$	$I_{2,5}$	$\Gamma_{1,6}$	$\Gamma_{2,5}$	$\Gamma_{3,4}$
4.2	494 (5)	-0.19 (1)	-0.93 (1)	2.64	1.91	0.31	0.29	0.28
49.4	475 (5)	-0.12 (1)	-0.98 (1)	2.24	1.61	0.31	0.28	0.29
100.2	434 (5)	-0.19 (1)	-0.97 (1)	2.18	1.59	0.34	0.34	0.29
151.0	378 (5)	-0.15 (1)	-0.92 (1)	1.27	0.79	0.42	0.31	0.46
295	-	-0.30 (1)	1.76 (2) ^a					

^a sign not determined.

Table 1 gives values of parameters for Mössbauer spectra from fig. 2. In the fit, both lines of a pair (i.e. 1-6, 2-5, and 3-4) are constrained to have the same width and depth.

An average value of $H = 395 \pm 1$ kOe at 77 K was obtained by Nishihara et al. [10-12] from the broadened spectra of ^{57}Fe in $\text{La}_2\text{Cu}_{0.995}\text{Fe}_{0.005}\text{O}_{4-y}$, where their sample had $T_N \sim 220$ K. This may be compared to the value of $H = 434 \pm 5$ kOe at 100.2 K in the present experiment; allowing for the difference in T_N , which may be due to oxygen content [3], the absorber experiment is reasonably consistent with the more clean-cut source experiment.

In the antiferromagnetic region in magnitude of the quadrupole splitting Δ is about half that measured at room temperature, and it shows a slight decrease in magnitude with increasing T . This is consistent with orientation of the magnetic field at about 90 degrees to the c -axis, the principal axis of the electric field gradient.

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References

- [1] D. Vaknin et al., Phys. Rev. Lett. 58 (1987) 2802.
- [2] S. Mitsuda et al., Phys. Rev. B 36 (1987) 822.
- [3] K. Yamada et al., Solid State Comm. 64 (1987) 753.
- [4] Y.J. Uemura et al., Phys. Rev. Lett. 59 (1987) 1045.

- [5] H. Nishihara et al., *J. Phys. Soc. Japan* 56 (1987) 4559.
- [6] S. Sasaki et al., *J. Phys. Soc. Japan* 57 (1988) 1151.
- [7] D.C. Johnston et al., *Phys. Rev. B* 36 (1987) 4007.
- [8] R.L. Greene et al., *Solid State Commun.* 63 (1987) 379.
- [9] P.M. Grant et al., *Phys. Rev. Lett.* 58 (1987) 2482.
- [10] Y. Nishihara et al., *Jpn. J. Appl. Phys.* 26 (1987) L1416.
- [11] Y. Nishihara et al., *J. Phys. Soc. Japan* 57 (1988) 384.
- [12] Y. Nishihara, K. Oka, and H. Unoki, *Physica B* 149 (1988) 91.
- [13] V.B. Grande, Hk. Muller-Buschbaum and M. Schweizer, *Z. Anorg. Allg. Chem.* 428 (1977) 120.
- [14] J.D. Jorgensen et al., *Phys. Rev. Lett.* 58 (1987) 1024.
- [15] D.C. Johnston et al., *Physica C* 153–155 (1988).
- [16] Y. Endoh et al., *Phys. Rev. B* 37 (1988) 7443.
- [17] F. van der Woude and A.J. Dekker, *Phys. Stat. Sol.* 9 (1965) 775.