

Magnetic dynamics of La_2CuO_4 studied by Mössbauer spectroscopy

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By doping a very small amount of ^{57}Fe into La_2CuO_4 , Mössbauer spectroscopy has been applied to study the magnetic property of the parent compound. From the measurement of the magnetic hyperfine field at the Fe nuclei for various temperatures between 4.2 K and T_N , the temperature dependence of the sublattice magnetization for La_2CuO_4 has been discussed. A theoretical calculation shows that, with temperature increasing a 3D-2D dimensional crossover occurs in the magnetic dynamics of an anisotropic antiferromagnetic, which is indeed confirmed by the data. The best fit to the data using this theory yields $J = 1600$ K and $r = 0.011$.

One of the important characteristics shared by all the high- T_c cuprate superconducting systems is the antiferromagnetic (AFM) ordering of Cu spins in their insulating regimes. Over the past few years, much efforts have been devoted to the study of the magnetism in these systems using neutron scattering,¹⁻⁵ muon-spin rotation,⁶ NMR techniques,⁷ and Mössbauer spectroscopy.⁸⁻¹¹ An accurate determination of the temperature dependence of the sublattice magnetization is of great interest. Such a study of the magnetic dynamics may provide important insight into the nature of the AFM state in these cuprate oxides.

Few techniques are capable of measuring the sublattice magnetization of an antiferromagnetic. Mössbauer spectroscopy, being microscopic in nature, is one such method that provides sufficient accuracy. Previous studies^{8,9,11} have shown that Fe, as a dopant, exclusively goes into the Cu sites in La_2CuO_4 and have also demonstrated antiferromagnetic coupling between the Fe and Cu moments. Therefore, as long as the Fe concentration is low enough such that the magnetic property of the Fe-doped sample is not noticeably altered, the Fe dopants can be used to probe the AFM state of the parent compound with Mössbauer spectroscopy.

Samples of $\text{La}_2\text{Cu}_{0.9945}\text{Fe}_{0.0055}\text{O}_{4+\delta}$ were prepared by using a solid-state reaction method. Appropriate proportions of La_2O_3 , CuO , and $^{57}\text{Fe}_2\text{O}_3$ powders were thoroughly mixed, pressed into a pellet form, and sintered in flowing O_2 at 950°C for a total period of 120 h with three intermediate grindings to ensure full reaction and sample homogeneity. The final cooling rate was $3^\circ\text{C}/\text{min}$. This as-prepared sample will be referred to as LCF. Then, two portions of the LCF sample were annealed in flowing Ar at 600°C for 12 h and at 800°C for 10 h, respectively, to yield two samples with slightly reduced oxygen contents. For convenience, the two Ar-annealed samples will be referred to as ArLCF1 and ArLCF2, respectively.

X-ray-diffraction measurements using $\text{Cu } K\alpha$ radiation revealed that all three samples have a single phase orthorhombic structure as in La_2CuO_4 . A SQUID magnetometer was employed to determine the AFM transition tempera-

tures. The results on magnetization versus temperature are shown in Fig. 1, from which the Néel temperatures have been determined to be approximately 180, 280, and 310 K for samples LCF, ArLCF1, and ArLCF2, respectively. TGA (thermal gravimetric analysis) measurements have shown that the oxygen contents of samples ArLCF1 and ArLCF2 are reduced from that of the as-prepared LCF sample by 0.004 and 0.011 upon Ar annealing. Clearly, T_N is extremely sensitive to the oxygen content. In fact, as suggested in Ref. 12, T_N can also be used to assess the oxygen content in a sample. A sample with $\delta = 0$ yields the highest T_N , which is about 320 K.¹² With $T_N = 310$ K, sample ArLCF2 should have an oxygen content very close to 4, i.e., $\delta \approx 0$. For sample ArLCF1, its oxygen content is slightly above 4 ($\delta \approx 0.007$), but its T_N is still very high, indicating that the AFM state is only weakly disturbed. Therefore, the two Ar-annealed samples are expected to reveal the intrinsic dynamic property of the AFM state of La_2CuO_4 , and will be the focus of our experimental investigation. Mössbauer spectroscopy was performed with a 100-mCi ^{57}Co source in a transmission geometry. The temperature control is better than 1 K. Mössbauer spectra at ten different temperatures from above its T_N to 4.2 K were taken for sample ArLCF1,

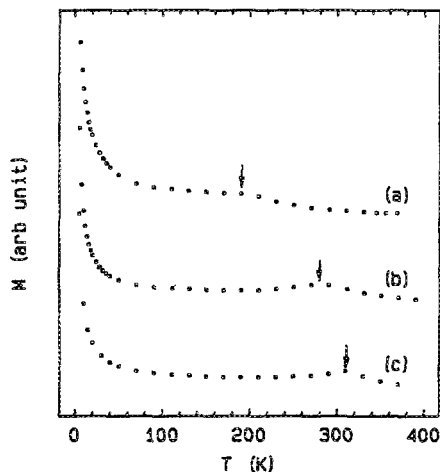


FIG. 1. Magnetization vs temperature for (a) sample LCF, (b) sample ArLCF1, and (c) sample ArLCF2. The arrows indicate the Néel temperatures. The data points have been shifted along the vertical axis so that each set of data is clearly displayed.

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and spectra at three different temperatures were obtained for sample ArLCF2.

A number of Mössbauer spectra at selected temperatures for sample ArLCF1 are shown in Fig. 2. For temperatures below T_N , the spectra all show a magnetic split-out structure, confirming that the Fe moments are indeed magnetically coupled to the Cu moments. However, the spectra at or above 212 K also contain a quadrupole doublet, indicative of a paramagnetic phase due to possible inhomogeneity in oxygen content in the sample. This is in agreement with the observation of the extreme sensitivity of T_N on the oxygen content of the sample and the much broadened peaks that serve as a signature of the AFM ordering as shown in Fig. 1. A slight inhomogeneity in oxygen content suffices to produce different T_N 's throughout the sample. At temperatures close to T_N , certain regions in the sample with slightly higher oxygen contents, and therefore significantly lower T_N 's, are still in a paramagnetic state, while other regions with higher T_N 's are already antiferromagnetically ordered. The Fe in the paramagnetic regions give rise to a doublet, whose intensity represents the paramagnetic fraction of the sample at that particular temperature. The degree of mixing-in of the doublet to the sextet and the temperature range over which such mixing exists furnishes some quantitative information about the degree of oxygen inhomogeneity in the sample.

We have used six independent peaks to obtain excellent fits for the completely split-out six-line spectra or the sextets in the composite spectra. The magnetic hyperfine field, the quadrupole splitting, and the isomer shift are then calculated from the peak positions. The derived Mössbauer parameters are presented in Table I, in which the parameters of the coex-

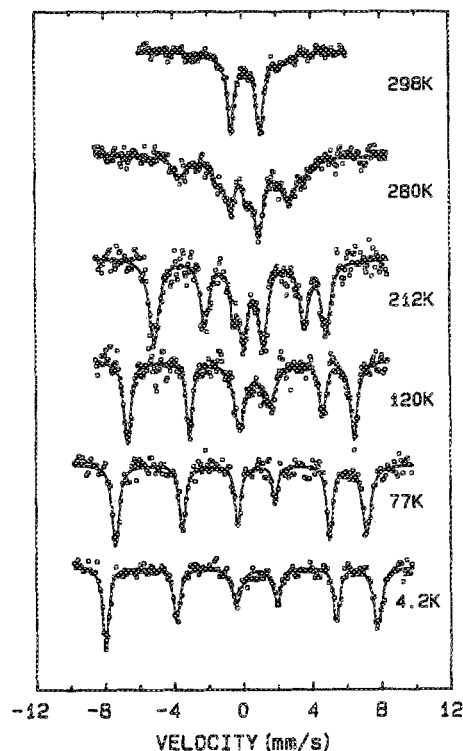


FIG. 2. Mössbauer spectra at the indicated temperatures for sample ArLCF1.

TABLE I. Mössbauer parameters for samples ArLCF1 (upper portion) and ArLCF2 (lower portion) at various temperatures. The isomer shifts are measured with respect to that of α -Fe at room temperature.

T (K)	Sextet			Doublet		wt. %
	H (kOe)	Δ (mm/s)	δ (mm/s)	Δ (mm/s)	δ (mm/s)	
4.2	488.2	-0.85	0.43
77	450.3	-0.86	0.41
99	428.4	-0.87	0.43
120	406.6	-1.00	0.42
140	386.3	-0.95	0.39
160	366.8	-0.87	0.40
212	307.6	-0.91	0.39	1.73	0.42	9
260	247.3	-0.81	0.40	1.70	0.33	15
280	223.6	-0.80	0.44	1.60	0.26	27
298	~95	1.68	0.30	~80
4.2	491.7	-0.83	0.41
77	454.2	-0.84	0.40
298	205.8	1.60	0.23	30

isting doublets in the composite spectra and the results for sample ArLCF2 are also shown. The isomer shift and the magnetic hyperfine field at 4.2 K reveal that the Fe is in a high-spin ($S = \frac{5}{2}$) and trivalent ($3+$) state.

The ordering of the Fe moments below T_N is a result of AFM coupling between the moments of Fe and its host Cu. The low level of doping ensures that the magnetic properties of the Fe-doped sample are barely altered, if at all, from those of its parent compound. Thus, the temperature dependence of the hyperfine field at the Fe nuclei is expected to reflect the genuine temperature dependence of the sublattice magnetization of the AFM Cu spin system. In Fig. 3 we plot the normalized magnetic hyperfine field as a function of temperature for sample ArLCF1.

La_2CuO_4 , with its layered structure, is an *anisotropic* antiferromagnetic in which the planar interaction is much stronger than the interplanar one. At finite temperatures,

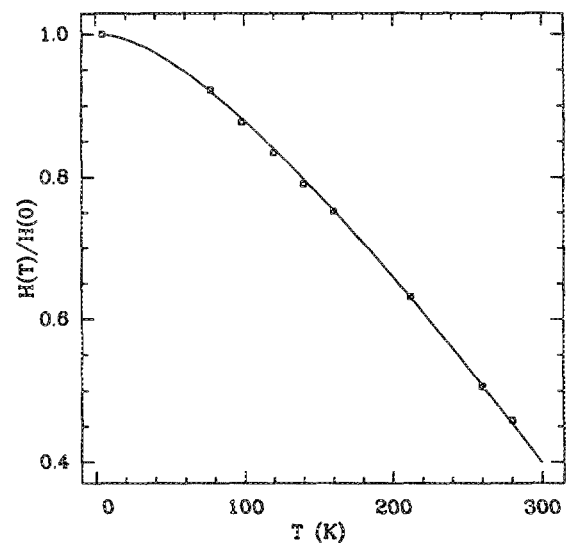


FIG. 3. Temperature dependence of the normalized hyperfine field for sample ArLCF1. The solid line is the best fit to the data.

the sublattice magnetization $M(T)$ reduces due to thermal excitation of spin waves. The anisotropic nature is manifested by the specific temperature dependencies of $M(T)$ in different temperature regimes. At very low temperatures, the significant contribution comes from long-wavelength spin-wave modes in *all* directions, so the temperature dependence of $M(T)$ is that of an isotropic three-dimensional (3D) system with a characteristic T^2 dependence. However, at sufficiently high temperatures (but still sufficiently below T_N so that the complications in the critical region do not come into play) $M(T)$ eventually exhibits an essentially linear temperature dependence, characteristic of a 2D system.

Recently, the reduction in sublattice magnetization¹³ has been obtained by some of us in terms of the Hubbard model with a planar exchange energy of $J_p = 4t^2/U$. In the two limiting temperature regimes, the expression for the reduction in sublattice magnetization has the forms

$$-\delta M(T) = \frac{2}{\pi} \left(\frac{kT}{J} \right) \ln \left(\frac{kT}{2Jr} \sqrt{2} \right) \quad (kT \gg 2Jr), \quad (1)$$

and

$$-\delta M(T) = \frac{\sqrt{2}}{3} \left(\frac{kT}{J} \right) \left(\frac{kT}{2Jr} \right) \quad (kT \ll 2Jr), \quad (2)$$

where J is related to the planar exchange energy by $J = J_p(1 + r^2/2)$, and r is the ratio of an effective interplanar hopping to planar hopping. By fitting the experimentally measured values of $M(T)$ to the full theoretical expression, one can determine the values of J and r .

The effective interplanar coupling is actually subtle in nature. It is not only related to the interplanar hopping, but also related to the structural characteristics of La_2CuO_4 . Because of the orthorhombic distortion in the La_2CuO_4 structure, the four exchange terms by which a Cu spin is coupled to its four out-of-plane nearest (Cu) neighbors are not equal. It is this orthorhombic distortion that breaks the symmetry (which would otherwise lead to spin frustration) and results in a magnetic coupling between planes.

The solid line shown in Fig. 3 is a best fit to the data by numerically evaluating the spin-wave correction to the sublattice magnetization. J and r are used as two parameters in the fitting, and the best fit yields $J = 1600$ K and $r = 0.011$. The characteristic temperature, $2Jr$, at which the dimensional crossover occurs is then about 35 K for sample ArLCF1. Apparently, sample ArLCF2 also exhibits a similar dimensional crossover in its magnetic dynamics. The insufficient data, however, do not allow for an appropriate numerical fit. Such a dimensional-crossover behavior in the temperature dependence of the sublattice magnetization is

characteristic of a highly anisotropic antiferromagnet, which the cuprate oxides with layered structures are.

In conclusion, the antiferromagnetic coupling between the Fe moments and Cu spins has enabled us to investigate the magnetic dynamics of the AFM state in La_2CuO_4 by means of Mössbauer spectroscopy. The temperature dependence of the sublattice magnetization exhibits a T^2 dependence at low temperatures, followed by a quasilinear T dependence at higher temperatures. This is due to a dimensional-crossover behavior of an anisotropic antiferromagnet. By fitting our experimental results to a recent theoretical calculation, we have obtained the planar exchange energy ($J = 1600$) and the ratio ($r = 0.011$) of the interplanar to planar hopping strengths.

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¹D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinga, and H. E. King, Jr., *Phys. Rev. Lett.* **58**, 2802 (1987).

²S. Mitsuda, G. Shirane, S. K. Sinha, D. C. Johnston, M. S. Alvarez, D. Vaknin, and D. E. Moncton, *Phys. Rev. B* **36**, 822 (1987).

³J. M. Tranquada, D. E. Cox, W. Kunmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S. K. Sinha, M. S. Alvarez, A. J. Hacobson, and D. C. Johnston, *Phys. Rev. Lett.* **60**, 156 (1988).

⁴G. Aeppli, S. M. Hayden, H. A. Mook, Z. Fisk, S-W. Cheong, D. Ritz, J. P. Remeika, G. P. Espinosa, and A. S. Cooper, *Phys. Rev. Lett.* **62**, 2052 (1989).

⁵H. R. Ott, P. Birrer, F. N. Gyax, B. Hitti, E. Lippelt, A. Schenk, M. Weber, S. Barth, F. Hulliger, P. Allenspach, S-W. Cheong, P. Fischer, Z. Fisk, A. Furrer, and B. Rupp (unpublished).

⁶Y. J. Vemma, W. J. Kossler, X. H. Yu, J. R. Kempton, H. E. Schone, D. Opie, C. E. Stronach, D. C. Johnston, M. A. Alvarez, and D. P. Goshorn, *Phys. Rev. Lett.* **59**, 1045 (1987).

⁷H. Nishihara, H. Yasuoka, T. Shimizu, T. Tsuda, T. Imai, S. Sasaki, S. Kanbe, K. Kishio, K. Kitazawa, and K. Furki, *J. Phys. Soc. Jpn.* **56**, 4559 (1987).

⁸Y. Nishihara, M. Tokumoto, K. Murata, and H. Unoki, *Jpn. J. Appl. Phys. Lett.* **26**, L1416 (1988).

⁹H. Tang, Y. W. Du, Z. Q. Qiu, J. C. Walker, J. S. Morgan, and W. A. Bryden, *J. Appl. Phys.* **64**, 5950 (1988).

¹⁰Z. Q. Qiu, Y. W. Du, H. Tang, J. C. Walker, J. S. Morgan, and W. A. Bryden, *J. Appl. Phys.* **64**, 5947 (1988).

¹¹S. Jha, C. Mitros, A. Lahamer, S. Yehia, G. M. Julian, R. A. Dunlap, G. Stroink, and Z. M. Stadnik, *Hyperfine Interact.* **50**, 607 (1989).

¹²S.-W. Cheong, J. D. Thompson, and Z. Fisk, *Physica C* **158**, 109 (1989).

¹³A. Singh and Z. Tešanović (unpublished).

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