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Field-induced magnetic form factor of La_2CuO_{4-y}

C. Stassis and B. N. Harmon
Ames Laboratory and Department of Physics, Iowa State University, Ames, Iowa 50011

T. Freltoft* and G. Shirane
Brookhaven National Laboratory, Upton, New York 11973

S. K. Sinha
Exxon Research and Engineering Company, Annandale, New Jersey 08801

K. Yamada and Y. Endoh
Department of Physics, Tohoku University, Sendai 980, Japan

Y. Hidaka and T. Murakami
Nippon Telegraph and Telephone Corporation Electrical Communications Laboratories, Tokai, Ibaraki 319-11, Japan

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Polarized-neutron-scattering techniques have been used to study the spatial distribution of the induced magnetization (by a magnetic field of 50 kG) in a single crystal of La_2CuO_{4-y}. The induced-moment magnetic form factor was obtained by measuring at $T=330$ K ($>T_N=304$ K) the polarization ratios of eight Bragg reflections. The measured induced-moment magnetic form factor was found to be in good agreement with the $3d$ magnetic form factor of the Cu^{2+} free ion. This observation implies that if any moment is induced on the in-plane oxygen sites, it is certainly much smaller than that predicted from recent band-theoretical calculations.

I. INTRODUCTION

The physical properties of La_2CuO_{4-y}, the parent compound of the $A_{2-x}B_xCuO_{4-y}$ (A=lanthanide, B=Ca, Sr, or Ba), have been the subject of many experimental and theoretical investigations. La_2CuO_{4-y} is tetragonal at high temperatures and undergoes an orthorhombic distortion between 440 K and 530 K, depending on y.[1-5] Susceptibility and neutron-diffraction measurements have established that La_2CuO_{4-y} is antiferromagnetic with a Néel temperature T_N that depends strongly on the oxygen deficiency y.[5-10] The intensities of the antiferromagnetic reflections observed in the neutron-diffraction experiments[6] are consistent with a model in which the moments, assumed to be localized on the Cu sites, are aligned along the c axis while the antiferromagnetic modulation is along the a axis. Assuming this magnetic structure, the magnetic form factor was found[6,9] to be in reasonable agreement with that of the Cu^{2+} free ion. The measured form factor did however deviate slightly from the smooth, monotonically decreasing ionic form factor. This could be caused either by some anisotropy in the magnetization density on the copper site or, as suggested by band theory,[11] by some small magnetic moment on the out-of-plane oxygen sites. To within the experimental precision of these measurements, however, it is difficult to ascertain whether there is a moment on the in-plane oxygen sites.

In the paramagnetic state, on the other hand, the field-induced magnetic form factor can be measured quite accurately by utilizing polarized neutrons. The induced-moment form factor is quite sensitive to any small moment induced on the in-plane oxygen sites because of interference effects with the moment induced on the Cu sites. Actually this sensitivity and the desire to assess the magnetic contribution of the oxygens were the principal motivations for the present study. A large in-plane oxygen moment was, in fact, predicted by recent spin-polarized band-theoretical calculations.[11]

In a metal with the application of a magnetic field the induced-magnetization density is just the charge density of the uncompensated spin up states at the Fermi level. A common feature in all the electronic structure calculations for the high-T_c copper oxides is that at the Fermi level there is a nearly half-filled band derived from copper $d_{x^2-y^2}$ and in-plane oxygen p_x and p_y antibonding states. Therefore, if La_2CuO_4 is a typical metal as described by band theory, one would expect a large contribution from both the copper and the in-plane oxygens. The applicability of band theory has been questioned for La_2CuO_4 because it predicts incorrectly that the stoichiometric material is a metal and does not order antiferromagnetically. This apparent breakdown of band theory suggests that the strong on-site Coulomb correlations and low density of states place stoichiometric La_2CuO_4 on the insulating side of the so-called Mott-Hubbard transition. Since such systems are rare (or at least have been rarely studied in detail), it is important to assess the degree to which a mean-field approach like band theory breaks down and to establish key experimental results which must be explained by theories which include the strong correlations.

II. EXPERIMENT

The single crystal (of dimensions $6\times4\times1$ mm^3) used in the present experiment was grown by the CuO flux method described in detail in Ref. 12. To obtain an oxygen-deficient specimen, the crystal was annealed at 740 °C for two hours in an argon atmosphere. The bulk susceptibility of the crystal was measured[13] by the Faraday method with the external field applied parallel as well as perpendicular to the b axis of the crystal (the b axis is perpendicular to the Cu-O layers). Under the same conditions as those of the neutron experiments ($T=330$ K, $\mathbf{H}\perp\mathbf{b}$) the bulk susceptibility was found to be 1.77 ± 0.05 cm^3/g. From both the susceptibility measurements[13] and neutron-diffraction studies,[14] the Néel temperature of the crystal was determined to be 304 ± 1 K.

The neutron measurements were performed, at $T=330$ K, in a magnetic field of 50 kG provided by a split coil superconducting magnet installed on the sample table of a polarized neutron spectrometer at the HFBR reactor of the Brookhaven National Laboratory. The experiment simply consists of measuring the polarization ratio R defined as the ratio of the Bragg peak intensities for the two neutron spin orientations, parallel and antiparallel to the applied magnetic field, respectively. After some corrections (see below), R provides a measure of the ratio $F_M(\theta)/F_N(\theta)$ of the induced moment magnetic structure factor $F_M(\theta)$ to the nuclear structure factor $F_N(\theta)$ (θ denotes here the Bragg scattering angle)

$$R=\left(\frac{F_M+F_N}{F_M-F_N}\right)^2\cong1+4\frac{F_M(\theta)}{F_N(\theta)}.$$

The last relation is valid if $F_M(\theta)\ll F_N(\theta)$, a condition fulfilled for all reflections measured in the present experiment. Thus $R-1$ provides a direct measurement of the induced-moment magnetic structure factor [$F_N(\theta)$ can be calculated from the known coherent nuclear-scattering amplitudes].

The data were corrected for background and the incomplete polarization of the neutron beam. Although the crystal was quite thin (~1 mm) secondary extinction effects were not negligible. The appropriate corrections ($\sim25\%$ for the strongest reflection) were assessed by measuring under the same conditions the integrated reflectivities of a number of reflections and fitting the data to an extinction curve. In order to be able to compare the data with the paramagnetic induced-moment form factor evaluated from band theory we corrected the data for the contribution of the field-induced diamagnetic moment.[15] This contribution was appreciable mainly because of the large core-diamagnetism of La. The neutron-spin–neutron-orbit contribution,[16] on the other hand, was estimated and found to be small in comparison to that of the field-induced diamagnetic moment.

III. RESULTS AND DISCUSSION

To determine the paramagnetic form factor, we measured the polarization ratios of the (020), (040), (200), (220), (060), (080), (460), and (0140) reflections. The results are tabulated in Table I. The experimental results for the paramagnetic response were fitted to $Af(\theta)/F_N(\theta)$, where A is a scale parameter and $f(\theta)$ the magnetic form factor of the Cu^{2+} free ion (Fig. 1). It is seen from the figure that this function provides a satisfactory fit to the experimental data. The fit to the experimental data extrapolates to a forward value of 6.4 ± 0.5. This value is in good agreement with that (7.0 ± 0.2) obtained from bulk-susceptibility measurements[13] performed on the sample used in the present experiments (the paramagnetic susceptibility was obtained by subtracting the core-diamagnetic contribution from the experimental value of the bulk susceptibility). We, therefore, conclude that the induced paramagnetic moment is predominantly of Cu $3d$ electronic character.

In particular, no evidence was found, to within experimental precision, of any significant deviation from the Cu^{2+} form factor of the (200) and (220) polarization ratios. This result is in contradiction with the predictions of recent band-theoretical calculations[11] of the induced-moment paramagnetic form factor. In these calculations, the induced moment was found to contain a significant contribution of oxygen $2p$ electronic character, and as a result of destructive interference of this moment with the Cu $3d$ component, the form factor at the (200) and (220) positions is considerably lower than the Cu^{2+} magnetic

TABLE I. Results of the field-induced magnetic-form-factor measurements. The measured values of the polarization ratio $R-1$ have been corrected for background, incomplete polarization of the neuron beam, secondary extinction, and field-induced diamagnetic contributions. F_N and F_M are, respectively, the calculated nuclear, and the measured paramagnetic structure factors.

Reflection (hkl)	$\sin\theta/\lambda$ (Å^{-1})	$10^3(R-1)$	F_N (10^{-12} cm)	F_M (10^{-15} cm)
(020)	0.076	1.65 ± 0.25	3.38	1.39 ± 0.21
(040)	0.152	5.10 ± 1.00	0.98	1.25 ± 0.25
(200)	0.187	0.67 ± 0.10	9.48	1.61 ± 0.24
(220)	0.202	-0.73 ± 0.17	−5.63	1.01 ± 0.24
(060)	0.228	0.28 ± 0.11	14.46	1.01 ± 0.40
(080)	0.304	0.67 ± 0.18	7.83	1.31 ± 0.35
(460)	0.436	0.36 ± 0.24	13.83	1.24 ± 0.83
(0140)	0.530	-0.41 ± 0.51	8.80	-0.90 ± 1.12

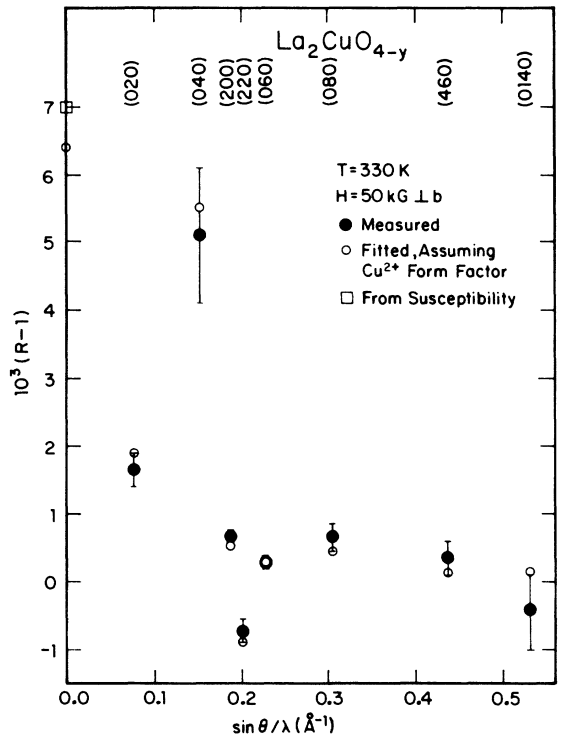

FIG. 1. Measured field-induced paramagnetic response in La_2CuO_{4-y} (solid circles). The points represented by open circles were obtained by fitting the data, using the $3d$ magnetic form factor of Cu^{2+}. The point in the forward direction, represented by a square, was calculated from the measured susceptibility (see text).

form factor. Thus the present experimental results are not in agreement with the prediction of band-theory calculations of the electronic properties of this compound. As mentioned in the introduction, this may be due to the fact that the on-site Coulomb repulsion, which is believed to play an important role in determining the electronic properties of these compounds, is not adequately treated by the local-density functional approximation used in the band theoretical treatment.[11] A similar problem has been encountered[17] in FeO and CoO, which are also Mott insulators.

Actually our results are consistent with a picture of local moments on the copper sites which disorder in three dimensions at T_N but maintain their spatial distribution above T_N. Inelastic-neutron-scattering experiments[18] have shown strong two-dimensional correlation of moments above T_N, so it seems clear that an applied magnetic field will tend to line up preexisting moments and that the Pauli paramagnetism picture associated with a band model is inappropriate. If in fact the local-moment model is correct and the state of the copper is close to the free Cu^{2+} ion, then the prevalent concept of Cu $d_{x^2-y^2}$ orbitals interacting with the in-plane oxygen p orbitals to form antibonding states at the highest occupied levels is highly questionable. Indeed, our experiments indicate very little or no magnetic response from the oxygen sites. It would be interesting to investigate whether the hybridization of the Cu $d_{x^2-y^2}$ orbitals with the oxygen p orbitals is present in the metallic compounds which arise from doping.

If the antibonding states are an inappropriate description for states at the Fermi level in La_2CuO_4, then band-theoretical treatments[19] of the electron-phonon interaction cannot be correct. However, this does not mean that the electron-phonon mechanism is necessarily invalid for producing high-temperature superconductivity. Before reaching such a conclusion, one should use the appropriate electronic states to evaluate the electron-phonon interaction.

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*Present address: A/S Nordiske Kabel-og Traadfabriker, Corporate R&D, 22 Vibeholms Allé, DK-2605 Brøndby, Denmark.

[1]B. Grande, H. R. Müller-Buschbaum, and M. Schweizer, Z. Anorg. Allg. Chem. **428**, 120 (1977).

[2]C. Michel and B. Raveau, Rev. Chim. Miner. **21**, 407 (1984).

[3]J. D. Jorgensen, H. B. Schuttler, D. G. Hinks, D. W. Capone, II, K. Zhang, M. B. Brodsky, and D. J. Scalapino, Phys. Rev. Lett. **58**, 1024 (1987).

[4]D. C. Johnston, S. K. Sinha, A. J. Jacobson, and J. M. Newsam, in *Proceedings of the International Conference on High Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, Switzerland, 1988,* edited by J. Müller and J. L. Olsen [Physica C **153–155**, 572 (1988)].

[5]D. C. Johnston, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski, Phys. Rev. B **36**, 4007 (1987), and references therein.

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

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

[8]T. Freltoft, J. E. Fischer, G. Shirane, D. E. Moncton, S. K. Sinha, D. Vaknin, J. P. Remeika, A. S. Cooper, and D. Harshman, Phys. Rev. B **36**, 826 (1987).

[9]T. Freltoft, G. Shirane, S. Mitsuda, J. P. Remeika, and A. S. Cooper, Phys. Rev. B **37**, 137 (1988).

[10]S. K. Sinha, D. E. Moncton, D. C. Johnston D. Vaknin, G. Shirane, and C. Stassis, J. Appl. Phys. **63**, 4015 (1988).
[11]T. C. Leung, X. W. Wang, and B. N. Harmon, Phys. Rev. B **37**, 384 (1988).
[12]Y. Hidaka, Y. Enomoto, M. Suzuki, M. Oda, and T. Murakami, J. Cryst. Growth **85**, 581 (1987).
[13]D. C. Johnston *et al.* (unpublished).
[14]K. Yamada, E. Kudo, Y. Endoh, Y. Hidaka, M. Oda, M. Suzuki, and T. Murakami, Solid State Commun. **64**, 753 (1987).
[15]C. Stassis, Phys. Rev. Lett. **24**, 1415 (1970).
[16]J. Schwinger, Phys. Rev. **73**, 407 (1948).
[17]K. Terakura, T. Oguchi, A. R. Williams, and J. Kubler, Phys. Rev. B **30**, 4734 (1984).
[18]G. Shirane, Y. Endoh, R. J. Birgineau, M. A. Kastner, Y. Hidaka, M. Oda, M. Suzuki, and T. Murakami, Phys. Rev. Lett. **59**, 1613 (1987).
[19]W. Weber, Phys. Rev. Lett. **58**, 1371 (1987).