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Antisymmetric exchange and its influence on the magnetic structure and conductivity of La_2CuO_4

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Measurements of the magnetic moment of antiferromagnetic La_2CuO_4 at high fields reveal a new phase boundary originating from a previously undetected canting of the Cu^{2+} spins out of the CuO_2 planes. This canting, together with the exponential temperature dependence of the two-dimensional correlation length, accounts quantitatively for the susceptibility peak at the Néel temperature. Enhancement of the conductivity in the ferromagnetic phase demonstrates a strong connection between the magnetism and charge transport.

The discovery[1] of antiferromagnetic spin fluctuations in $La_{2-x}Sr_xCuO_{4-\delta}$ has provided substantiation for a variety of theoretical models[2] based on the idea that the magnetism is the progenitor of high-temperature superconductivity.[3] This idea and the observation that La_2CuO_4 is a good approximation to the two-dimensional (2D) $S=\frac{1}{2}$ Heisenberg antiferromagnet make a thorough understanding of its magnetic properties very important. The general features of the phase diagram in T-x space are known: for x and $\delta=0$, the system is an antiferromagnetic insulator below $T_N \approx 300$ K; and for $x \sim$ a few percent there is no long-range order, but the antiferromagnetic fluctuations are still strong in samples with x large enough to result in the insulator-metal transition and superconductivity. The structure of the Néel state is quite simple,[4] but two features have been disturbing. One is the sharp ferromagneticlike peak[4] in the uniform magnetic susceptibility χ at T_N. The second is the relatively large magnetic anisotropy in the Cu-O planes leading to a large gap[5] in the spin-wave spectrum. Also surprising is the absence of evidence for strong coupling of the magnetism to the charge transport, a crucial link in the connection to superconductivity.

We report here measurements of the magnetic moment and magnetoresistance as functions of field and temperature for pure single crystals of La_2CuO_4 that provide solutions to these puzzles. We have discovered a new phase boundary in the H-T plane which terminates at $H=0$, $T=T_N$, suggesting that it is intimately connected with the antiferromagnetism. Above the critical field $H_c(T)$ an induced ferromagnetic moment appears indicating that La_2CuO_4 possesses hidden ferromagnetism.[6] The measurements thus demonstrate that the spins do not lie exactly in the Cu-O planes in the Néel state, as previously thought, but are canted out of the plane by a small angle (0.17°). This canting is driven by the rotation of the CuO_6 octahedra in the orthorhombic phase which allows an antisymmetric superexchange term in the spin Hamiltonian; it is, in fact, the largest term after the isotropic exchange itself. Each Cu-O layer thus carries a ferromagnetic moment, but the net moment at $H=0$ is zero because the antiferromagnetic interlayer coupling causes alternate layers to cant in opposite directions. Above $H_c(T)$ the layers cant in the same direction; we also observe an increase in conductance as large as a factor ~ 2 for $H > H_c(T)$, demonstrating a strong coupling between the transport and magnetic order. Because of the antisymmetric exchange, the external field H generates staggered fields in the layers which account for the susceptibility peak at the Néel temperature. Treating the interlayer coupling by mean-field theory we obtain an excellent quantitative fit for the susceptibility and for $H_c(T)$.

The high-purity single crystals used for this study were grown by the top-seeded solution method described recently[7] from CuO flux. Single crystals as large as $2.5 \times 2.5 \times 0.5$ cm^3 have been grown in this way and were used for neutron-scattering experiments. Oriented pieces were cut from these, large enough to allow conventional four-probe resistivity measurements along the orthorhombic b (tetragonal c) axis as well as in the a-c plane;[8] contacts were made with silver paint (see inset of Fig. 2). The resistance follows $\exp(T_0/T)^{1/4}$ indicative of variable-range hopping with $T_0 \sim 10^5$ K, similar to the values reported previously.[9]

The magnetic moment M, and hence the susceptibility χ, were measured at temperatures from 10 to 400 K and at magnetic fields up to 5 T with a superconducting-quantum interference device (SQUID) magnetometer; the magnetoresistance was measured up to 15 T. Neutron scattering measurements were carried out at the Brookhaven High Flux Beam Reactor using the triple-axis spectrometer H4M set for zero energy transfer and with pyrolitic graphite filters before and after the sample; the neutron energy was 3.5 meV. Further details may be found in recent publications.[1]

Figure 1 shows the unusual behavior of the magnetic moment and magnetoresistance at high fields for **H**∥**b**. There is a jump in the moment and a corresponding decrease in the resistance R at $H_c(T)$; the transition shows hysteresis in R below ~ 200 K, but in M only below ~ 150 K, probably because measurements of M are made much more slowly. The transition moves to lower field and broadens as T approaches T_N, suggesting that the transition may become second order at some $T < T_N$. The phase boundary, plotted as H_c^2, is shown in Fig. 2 together with neutron data for the square of the order parameter divided by the square of the symmetric staggered susceptibility $\chi_+^\dagger$ (discussed below). Clearly the antiferromagnetism and this new phase transition are closely related. We shall give a detailed theory for this transition and the associated magnetic properties below. There is no evidence for a transition in $M(H)$ or $R(H)$ when **H**⊥**b**, as shown by the top trace in Fig. 1. The resistance change varies in magnitude by ~ 2 from sample to sample.

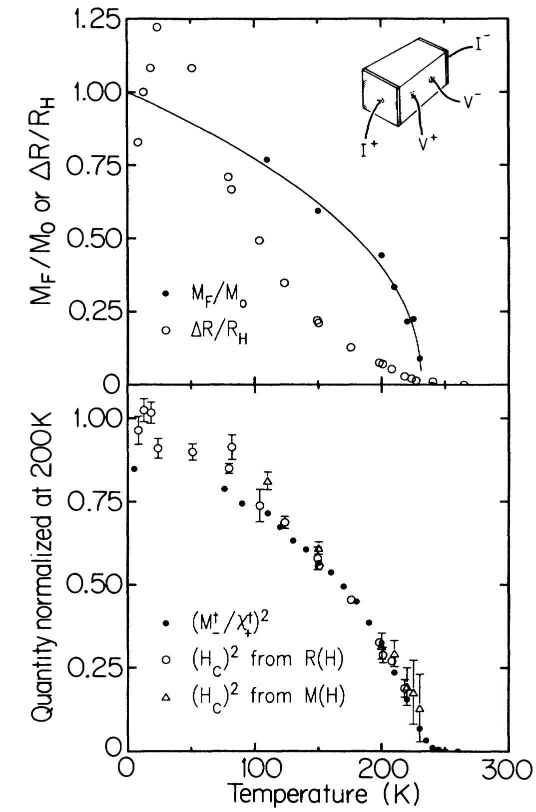

FIG. 2. Lower panel: $(M_-^\dagger/\chi_+^\dagger)^2$ and $(Hc)^2$ vs temperature. $(M_-^\dagger)^2$ is the intensity of the (100) Bragg peak and $\chi_+^\dagger$ is calculated from Eq. (3) using the parameters from the fit in Fig. 3. Note that $H_c(T)$ measured from $R(H)$ agrees well with that from $M(H)$. Upper panel: Change in resistance divided by its high-field value $\Delta R/R_H$ and M_F vs T. The solid curve is a guide to the eye. The inset shows a schematic of the electrode geometry. The large current electrodes are on a-c planes for $j \parallel b$ or twinned a/c-b planes for $j \perp b$.

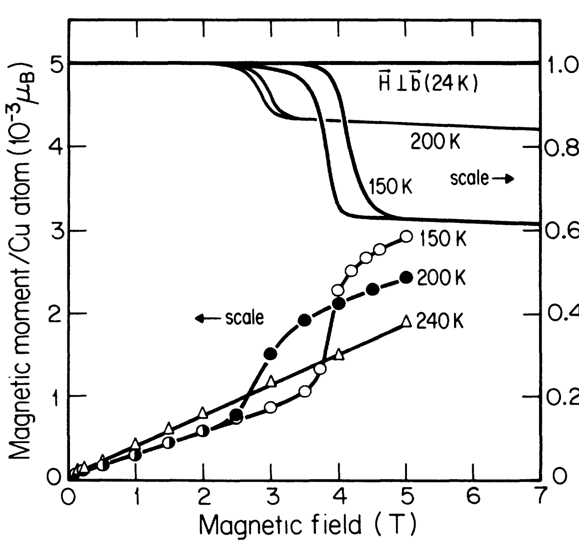

FIG. 1. Resistance and magnetic moment vs magnetic field in the b direction (except as noted).

The data for $M(H)$ at 200 K show that the differential susceptibility is practically the same for fields far above and below the transition field. Assuming that this is the case at all T, we extract the induced ferromagnetic moment $M_F(T)$ from the displacement of the two straight lines; we emphasize that this is to be interpreted as a first-order jump in M only at low T. The resistance change ΔR is extracted in a similar way; both quantities are plotted in Fig. 2. The inducing field H_c is determined from the maximum derivative of $M(H)$ and $R(H)$. Extrapolation to $T=0$ gives $H_c(0) = (5.3 \pm 0.3)$ T, and $M_F(0) = (2.1 \pm 0.2) \times 10^{-3} \mu_B$ per Cu atom.

This transition may be readily understood as the reorientation of a small 2D ferromagnetic moment in alternate layers. This hidden ferromagnetism arises from antisymmetric terms[10,11] in the spin Hamiltonian, which, as mentioned above, are made possible by the rotation (by an angle ϕ_0) of the CuO_6 octahedra. The exchange Hamiltonian may be written

$$H=\sum_{\langle NN\rangle} \mathbf{S}_i\cdot\bar{\bar{J}}_{NN}\cdot\mathbf{S}_{i+\delta} \text{ with } \bar{\bar{J}}_{NN}=\begin{pmatrix} J^{aa} & 0 & 0 \\ 0 & J^{bb} & J^{bc} \\ 0 & -J^{bc} & J^{cc}\end{pmatrix}, \quad (1)$$

where $|J^{cc}|>|J^{aa}|>|J^{bb}|$, and, as noted by Moriya,[11] J^{bc} is of order $J_{NN}\Delta g/g$, with $J_{NN}=(J^{aa}+J^{bb}+J^{cc})/3$, multiplied by the overlap between crystal-field-split levels on neighboring sites. The latter is[12] of order ϕ_0, leading to $J^{bc}\sim\phi_0 J_{NN}\Delta g/g$. We expect this to be much larger than the symmetric anisotropic terms $(J^{aa}-J^{cc})$ and $(J^{bb}-J^{cc})$, which are higher order in $\Delta g/g$.

At $T=0$, the antisymmetric term causes a canting along **b** with angle (Ref. 6) $\theta=M_F/(g\mu_B S)=J^{bc}/2J_{NN}$. Our measured M_F, with (Ref. 13) $g=2.2$ and S reduced from $\frac{1}{2}$ by a factor 0.63 for quantum renormalization,[6] gives $\theta=0.0030\pm0.0006$. We compare this with a value of θ determined in a different way: From infrared and neutron measurement of the spin-wave gap[5] one may infer $J^{bc}=0.55$ meV. The measurement of two-magnon Raman scattering, after quantum renormalization,[14] gives $J_{NN}=116$ meV. Using these values gives $\theta=0.0025$ in good agreement with our measured value. This agreement, in turn, makes the identification of $4J^{bc}S$ with the spin-wave gap unambiguous. These measurements of θ are also in good agreement with the order of magnitude estimate $\theta\sim\phi_0\Delta g/g\sim5\times10^{-3}$ using $\Delta g/g\approx0.1$ and the measured (Ref. 15) $\phi_0=0.049$.

At $H=0$ alternate layers cant in opposite directions because of the interlayer antiferromagnetic coupling $J_\perp$. A simple argument indicates that, at $T=0$, the field at which all layers cant in the same direction is given by $H_c(0)M_F(0)=J_\perp S^2$. Using our measurements of $H_c(0)$ and $M_F(0)$ gives $J_\perp=(0.0026\pm0.003)$ meV.

We now outline how the antisymmetric exchange together with the large 2D correlation length ξ_{2D} provides a natural explanation of the hitherto unexplained peak in the uniform susceptibility χ near T_N in La_2CuO_4. Let $\mathbf{M}_1^\dagger$ and $\mathbf{M}_2^\dagger$ be the staggered magnetizations of the successive a-c layers 1 and 2 with canted moments alternating in the b direction. In the absence of J^{bc} we would set $\mathbf{M}_i^\dagger=\chi_{2D}^\dagger\mathbf{h}_i^\dagger+O(h_i^\dagger)^3$ where $\mathbf{h}_i^\dagger$ is an external field and $\chi_{2D}^\dagger$ is the staggered susceptibility of the 2D spin-$\frac{1}{2}$ Heisenberg model $\chi_{2D}^\dagger=(\xi_{2D}/a)^2/kT$ where a is the Cu-Cu distance. Since the interplane coupling $J_\perp$ is weak, we may treat it in a mean-field approximation.[16] We then have, for symmetric and antisymmetric staggered fields,

$$\mathbf{h}_\pm^\dagger=\mathbf{h}_1^\dagger\pm\mathbf{h}_2^\dagger=[(\chi_{2D}^\dagger)^{-1}\pm J_\perp]\mathbf{M}_\pm^\dagger+A[(|\mathbf{M}_+^\dagger|^2+|\mathbf{M}_-^\dagger|^2)\mathbf{M}_\pm^\dagger+2(\mathbf{M}_+^\dagger\cdot\mathbf{M}_-^\dagger)\mathbf{M}_\mp^\dagger] , \quad (2)$$

where $\mathbf{M}_\pm^\dagger=\mathbf{M}_1^\dagger\pm\mathbf{M}_2^\dagger$, and A is weakly T dependent. Differentiating Eq. (2) with respect to $\mathbf{M}_\pm^\dagger$ gives the inverse symmetric and antisymmetric staggered susceptibilities $(\chi_\pm^\dagger)^{-1}$. Below T_N, where the nonlinear terms are important, setting $\mathbf{h}_i^\dagger=0$ and $\mathbf{M}_+^\dagger=0$ in Eq. (2) gives $A|\mathbf{M}_-^\dagger|^2=[J_\perp-(\chi_{2D}^\dagger)^{-1}]$; hence

$$(\chi_\pm^\dagger)^{-1}=\begin{cases}(\chi_{2D}^\dagger)^{-1}\pm J_\perp+3[J_\perp-(\chi_{2D}^\dagger)^{-1}], & T\le T_N,\\ (\chi_{2D}^\dagger)^{-1}\pm J_\perp, & T\ge T_N\ .\end{cases} \quad (3)$$

Thus, the three-dimensional antisymmetric staggered susceptibility $\chi_-^\dagger$ diverges at the Néel temperature given by $J_\perp\chi_{2D}^\dagger=1$.

In terms of magnetizations, the antisymmetric term in the Hamiltonian has the form $2J^{bc}(M_{1c}^\dagger M_{1b}+M_{2c}^\dagger M_{2b})$. This implies that an external field H in the b direction generates a field $h_+^\dagger=2J^{bc}\chi_0 H$ which yields a staggered moment $M_+^\dagger=2J^{bc}\chi_0 H\chi_+^\dagger$, where χ_0 is the uniform susceptibility of the 2D system. The proportionality of $h_+^\dagger$ to H now adds a singular term to the uniform susceptibility,

$$\chi=\chi_0+\chi_0^2(2J^{bc})^2\chi_+^\dagger\ . \quad (4)$$

Chakravarty *et al.*[17] found good agreement between their calculated ξ_{2D} and neutron scattering experiments in the paramagnetic phase. We therefore use their form $\xi_{2D}=0.9(\hbar c/kT)\exp(2\pi\rho_s/kT)$ with sets of constants which gave the best fit: the spin-wave dispersion $\hbar c=0.6$ eV Å and the quantum-renormalization spin-stiffness constants $\rho_s=8.9$ meV or $\hbar c=0.425$ eV Å and $\rho_s=10.3$ meV. Figure 3 shows one of these fits of Eqs. (3) and (4) to the susceptibility data for **H**||**b** using J^{bc}, $J_\perp$, and χ_0 as parameters, demanding that $J_\perp\chi_{2D}^\dagger(T_N)=1$; the fits for the two sets of $\hbar c$ and ρ_s are almost indistinguishable. The fits give $J_{bc}=0.7\pm0.1$ meV, in agreement with the value deduced from the spin-wave gap as discussed above, and $J_\perp=(1.3\pm0.1)\times10^{-6}$, about two times smaller than the value measured from $H_c(0)M_F(0)$. In addition, substitution of the value for $\chi_0=2\times10^{-4}$ cm^3/mol into the

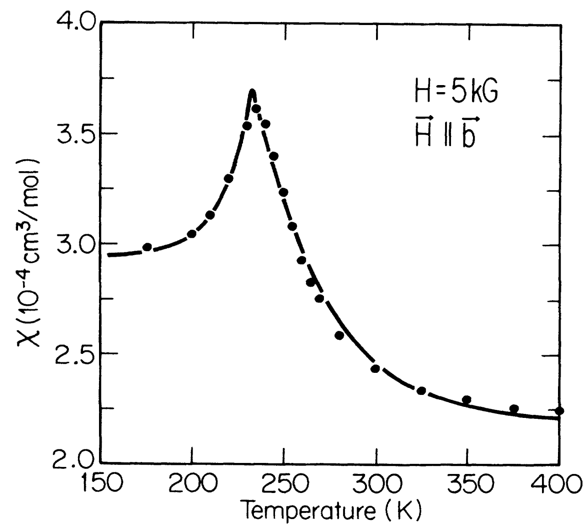

FIG. 3. Susceptibility as a function of temperature corrected for core susceptibility (9.9×10^{-5} cm^3/mol) [P.W. Selwood, *Magnetochemistry*, 2nd ed. (Interscience, New York, 1956)]. The solid curve is the theoretical fit to the data using $\hbar c=0.425$ eV Å and $\rho_s=10.3$ meV.

zero-temperature prediction $(g\mu_B)^2/8J_{\mathrm{NN}}$ gives $J_{\mathrm{NN}}=100$ meV, in good agreement with the value 116 meV from two-magnon Raman scattering quoted above. Thus the uniform susceptibility is explained quantitatively using our theory with parameters which agree well with independently obtained values.

At $H\neq 0$ and $h^{\dagger}_{-}=0$, Eq. (2) yields

$$A|M^{\dagger}_{-}|^2=J_{\perp}-(\chi^{\ddagger}_{2\mathrm{D}})^{-1}-3A|M^{\ddagger}_{+}|^2$$
$$=A(|M^{\dagger}_{-}(H=0)|^2-3|M^{\ddagger}_{+}|^2)\ .$$

Therefore, a second-order transition at which $M^{\dagger}_{-}$ vanishes occurs when $|M^{\ddagger}_{+}|^2=|M^{\dagger}_{-}(H=0)|^2/3$. Substituting $M^{\ddagger}_{+}=2J^{bc}\chi^{\ddagger}_{+}\chi_0 H$ thus predicts that H_c^2 is proportional to the Bragg intensity $(M^{\dagger}_{-})^2$ divided by $(\chi^{\ddagger}_{+})^2$. This comparison is made in Fig. 2; clearly the agreement is excellent. This proportionality should hold only when the transition is continuous. At high fields, the fluctuations in $M^{\ddagger}_{+}$ are expected to turn the transition first order, via a tricritical point, similar to other metamagnets.[18]

The antisymmetric change is crucial for understanding the magnetism in La_2CuO_4. Surprisingly, it has a profound effect on the conductivity as well. First note in Fig. 1 that the increase of M with H above and below the phase transition, resulting from χ, is comparable to M_F, the jump at H_c. However, the variation of R in these regions is negligible compared to the change near H_c. This shows that the variation of R depends only on the ordering of the canted layers and not on the size of the net moment. That this holds true up to at least 200 K indicates a very strong coupling of the spins of the excess holes, which carry the current, to the extremely small canted component ($\sim 10^{-3}$) of the Cu^{2+} spins.

At the peak of $\Delta R/R_H$ near 20 K (see Fig. 2) the resistance at low field is roughly twice that above H_c. The $\exp[(T_0/T)^{1/4}]$ dependence and the absence of large anisotropy indicate[8] that the conductivity is limited by hopping between layers. The most extreme assumption, that hopping is only allowed between layers of the same canting, would explain the factor 2 change in R, but we have, as yet, no explanation of the T dependence of $\Delta R/R_H$. The downturn below 20 K may result from the reentrant spin-glass phase.[2]

In conclusion, we have demonstrated a new phase boundary in La_2CuO_4 which is related to hidden ferromagnetism created by the rotation of the CuO_6 octahedra. We find that the susceptibility peak at the transition into the Néel state can be quantitatively[19] explained using a mean-field theory once $\xi_{2\mathrm{D}}(T)$ and the antisymmetric exchange are understood. The large jump in conductance[20] at the antiferromagnetic to ferromagnetic transition remains to be explained quantitatively, but shows a strong connection between the transport and the magnetism.

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