Strong Anisotropy of Superexchange in the Copper-Oxygen Chains of $La_{14-x}Ca_xCu_{24}O_{41}$

V. Kataev,[1,*] K.-Y. Choi,[1] M. Grüninger,[1] U. Ammerahl,[1] B. Büchner,[1] A. Freimuth,[1] and A. Revcolevschi[2]

[1]*II. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*

[2]*Laboratoire de Chimie des Solides, Université Paris-Sud, 91405 Orsay Cédex, France*

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Electron spin resonance data of Cu^{2+} ions in $La_{14-x}Ca_xCu_{24}O_{41}$ single crystals ($x = 9, 11, 12$) reveal a very large width of the resonance line in the paramagnetic state. This signals an unusually strong anisotropy of ~10% of the isotropic Heisenberg superexchange in the Cu-O chains of this compound. The strong anisotropy can be explained by the specific geometry of two symmetrical 90° Cu-O-Cu bonds, which boosts the importance of orbital degrees of freedom. Our data show the apparent limitations of the applicability of an isotropic Heisenberg model to the low-dimensional cuprates.

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Magnetic interactions in strongly correlated transition metal oxides have attracted much interest during the past decade due to their intimate relationship with high-T_c superconductivity, and also in connection with novel quantum magnetic phenomena in spin-chain and spin-ladder materials. The superexchange interaction between magnetic ions in oxides is mediated via oxygen ligands and is described by the Hamiltonian

$$\mathcal{H} = J_{\rm iso}\sum_{ij}\mathbf{S}_i\mathbf{S}_j + \sum_{ij}\mathbf{d}_{ij}[\mathbf{S}_i \times \mathbf{S}_j] + \sum_{ij}\mathbf{S}_i A_{ij}\mathbf{S}_j\,, \tag{1}$$

where the first term denotes the isotropic Heisenberg exchange, and the second and third terms represent antisymmetric and symmetric *anisotropic* contributions caused by spin-orbit coupling. In the case of $3d^9$ Cu^{2+} with a single hole with $S = 1/2$, the orbital angular momentum is quenched by the crystal field. In general, spin-orbit coupling and the corresponding anisotropies play only a minor role in cuprates. For instance, the undoped parent compounds of the high-T_c cuprates such as La_2CuO_4 are thought to be the best representatives of a 2D $S = 1/2$ square-lattice *isotropic* Heisenberg antiferromagnet with $J_{\rm iso} \approx 1500$ K. This large value of $J_{\rm iso}$ is typical for the 180° Cu-O-Cu bond angle present in 2D cuprates. Both anisotropic magnetic couplings $A_{ij} \ll |\mathbf{d}_{ij}|$ do not exceed 1% of $J_{\rm iso}$ in La_2CuO_4 [1]. Nevertheless, this small anisotropy determines the orientation of spins with respect to the lattice in the magnetically ordered state and is responsible for such remarkable phenomena as weak ferromagnetism or the presence of spin wave gaps.

According to the Goodenough-Kanamori-Anderson rules [2] the strength of the leading isotropic coupling $J_{\rm iso}$ can be considerably reduced by decreasing the Cu-O-Cu bond angle from 180° to 90°. In the case of a 180° bond the antiferromagnetic (AF) coupling is mediated via a single ligand orbital, whereas the exchange in a 90° bond proceeds via orthogonal orbitals (see Fig. 3 below) which are coupled via Hund's rule, resulting in a *ferromagnetic* coupling [3]. Experimentally, one still finds an AF $J_{\rm iso} \approx 120$ K [4] in the Cu-O chains of the spin-Peierls compound $CuGeO_3$ with a bond angle ~98°. Still closer to 90° $J_{\rm iso}$ indeed changes sign and becomes ferromagnetic, as in $(La, Ca)_{14}Cu_{24}O_{41}$ [5]. The dependence of the *anisotropic* corrections on the bond angle has not been studied to the same extent. Recently, it was theoretically predicted that the magnetic anisotropy of two symmetrical 90° bonds may be unusually large [6,7]. This bonding geometry is found in several systems such as $(La, Ca)_{14}$-$Cu_{24}O_{41}$ [8], Li_2CuO_2 [9], or $Ca_2Y_2Cu_5O_{10}$ [10].

Electron spin resonance (ESR) is a very sensitive tool to study the spin-spin coupling anisotropy which is the main source of the finite width ΔH of an ESR signal in concentrated paramagnets [11]. In this letter we present ESR data of the Cu-O chains of $La_{14-x}Ca_xCu_{24}O_{41}$ (LCCO), which show a very broad linewidth $\Delta H \sim 1500$–2000 Oe in the paramagnetic regime at $T > 60$ K. We show that the observed linewidth requires an unusually large anisotropic coupling of ~10% of the leading isotropic exchange $J_{\rm iso}$. This cannot be explained by conventional estimates of the dipole-dipole or anisotropic exchange interactions which neglect the geometry. The data thus give evidence for a significantly enhanced contribution of spin-orbit coupling to the magnetism of copper oxides in certain bonding geometries.

ESR measurements were carried out at 9.47 GHz. The magnetic susceptibility $\chi_{\rm stat}$ was measured with a SQUID magnetometer at 1 T. $La_{14-x}Ca_xCu_{24}O_{41}$ single crystals with $x = 9$, 11, and 12 were grown by the traveling solvent floating zone method [12]. Their single phase structure and stoichiometry have been verified by x-ray, energy dispersive x-ray, and thermogravimetric analyses. The Ca content determines the average oxidation state of $Cu^{2+\delta}$. The average number of holes per Cu site increases from $\delta \approx 0.04$ for $x = 9$ to $\delta \approx 0.17$ for $x = 12$. The Cu-O chains are parallel to the c axis and lie in one crystallographic plane (ac plane). The exchange interaction in the chains is found to be small and ferromagnetic, $J_{\rm iso} \approx -20$ K [5], as expected for the nearly 90° Cu-O-Cu bond angle. Parallel to the chains, LCCO contains Cu_2O_3 two-leg spin-ladders [8] with a singlet ground state with a spin gap of ~400–500 K [13,14].

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Representative ESR spectra of the $x = 9$ sample and the fitting curves are shown in the left panels of Fig. 1 at $T = 100$ and 14 K. Since the linewidth ΔH is comparable to the value of the resonance field $H_{\rm res}$, the fitting function $f(H)$ has to include Lorentzian absorption derivatives corresponding to both right and left circularly polarized components $A(H_+)$ and $A(H_-)$ of the linearly polarized microwave field [11]. Moreover, we add to $f(H)$ the correction due to the nondiagonal contributions to the dynamic susceptibility which appears as an admixture of the Lorentzian dispersion $D(H_+)$ [15]:

$$f(H) = A(H_+) + A(H_-) + D(H_+), \qquad (2)$$

$$A(H_\pm) = -\frac{16ah_\pm}{(3 + h_\pm^2)^2}, \qquad D(H_\pm) = \frac{3d(3 - h_\pm^2)}{(3 + h_\pm^2)^2}.$$

Here, $h_\pm = 2(H \mp H_{\rm res})/\Delta H$, and a and d ($<a$) are the amplitudes of the Lorentzian absorption and dispersion signals, respectively. From this fit we obtain the values of $H_{\rm res}$, ΔH, and the integrated intensity I of the ESR line. The temperature dependence of these quantities for $H \parallel c$ [16] is shown in Figs. 1 (right panel) and 2. From the dependence of $H_{\rm res}$ on the orientation of the magnetic field we derive g-factors of $g_c = 2.02 \pm 0.02$ and $g_b = 2.30 \pm 0.05$ [17], which are typical for Cu^{2+} ions in a fourfold square oxygen coordination [11].

In the *paramagnetic* regime, the ESR intensity $I(T)$ is per definition proportional to the static susceptibility of the resonating spins $\chi_{\rm ESR}^{\rm spin}$ [11]. In order to obtain $\chi_{\rm ESR}^{\rm spin}$ in absolute units we have calibrated $I(T)$ of the samples at $T = 100$ K against the intensity of the simultaneously measured spectrum of the standard reference material $Al_2O_3 + 0.03\%Cr^{3+}$, which gives rise to small background lines at 840, 3340, and 7740 Oe (top left panel of Fig. 1). For $T > 30$ K, $\chi_{\rm ESR}^{\rm spin}$ and $\chi_{\rm stat}$ are very similar (right panel of Fig. 1). The deviations at $T \lesssim 30$ K are related to a transition to a long-range ordered AF state (see below). For $50 < T < 300$ K, $\chi_{\rm stat}$ in LCCO is entirely described in terms of weakly interacting Cu-O spin chains, the contribution from the ladders is negligible due to their large spin gap [5]. From the similarity between $\chi_{\rm ESR}^{\rm spin}$ and $\chi_{\rm stat}$ we conclude that the ESR signal can be ascribed solely to the Cu spins in the chains [18].

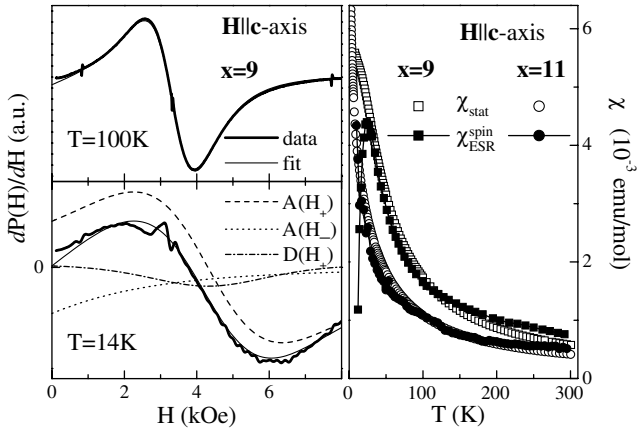

FIG. 1. Left: representative ESR spectra (derivatives of the absorbed microwave power $dP(H)/dH$, thick lines) of a LCCO crystal and the respective fits according to Eq. (2) (thin solid lines). Dashed lines: different contributions to the 14 K fit. Right: comparison of the spin susceptibility $\chi_{\rm ESR}^{\rm spin}$ derived from the intensity $I(T)$ with the static susceptibility $\chi_{\rm stat}$.

The ESR linewidth in magnetic insulators is usually decomposed into noncritical and critical parts [20]:

$$\Delta H = \Delta H(\infty) + \Delta H_{\rm crit}(T). \qquad (3)$$

The first term reflects spin-spin interactions in the high-temperature *paramagnetic* regime, where spins are uncorrelated. The second term $\Delta H_{\rm crit}(T)$ defines an additional contribution to ΔH arising at low T, when long-range magnetic order is approached. It is caused by fluctuations of the staggered magnetization in the short-range ordered state. These enhance the spin-spin relaxation rate $1/T_2$ and, consequently, additionally broaden the ESR line [20]. Insulating LCCO is paramagnetic above 50 K [5]. At lower temperatures, spin correlations grow and finally result in long-range AF order, which has been observed for $x = 9$ at $T_N \approx 10$ K [19,21]. Indeed, both the considerable shift of $H_{\rm res}$ to higher fields and the increase of ΔH below 60 K (see Fig. 2) are obviously due to the development of short-range magnetic order [$\Delta H_{\rm crit}(T)$ in Eq. (3)] [22]. The ESR intensity already drops rapidly above T_N due to the growth of short-range AF ordered regions. Most of the spins within these regions do not contribute to the ESR signal since their resonance frequency is outside the range of our spectrometer. This explains the discrepancy between $\chi_{\rm ESR}^{\rm spin}$ and $\chi_{\rm stat}$ at low T (right panel of Fig. 1). With increasing Ca content the critical behavior of the ESR response gets less pronounced, thus giving evidence for a rapid suppression of AF correlations in LCCO by hole doping.

The main concern of this paper is the large value of $\Delta H(T)$ of about 1500–2000 Oe for temperatures far above

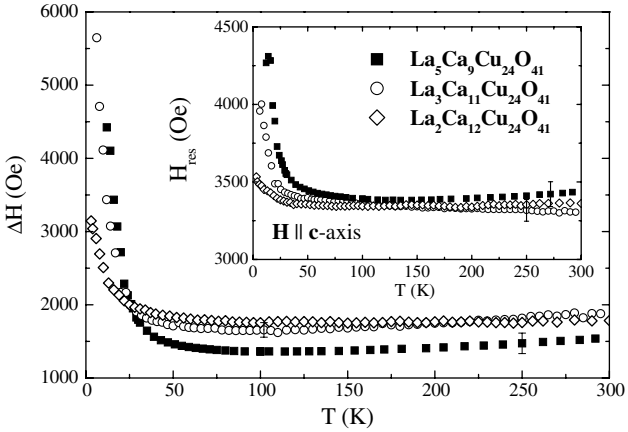

FIG. 2. Temperature dependence of the ESR linewidth $\Delta H(T)$ and of the resonance field $H_{\rm res}(T)$ (inset) for $La_{14-x}Ca_xCu_{24}O_{41}$ crystals with $x = 9$, 11, and 12 ($H \parallel c$).

the magnetically ordered state (see Fig. 2). It is reasonable to assume that the almost T-independent linewidth in the paramagnetic regime above $\sim$60 K is determined by the Cu spin-spin interactions, i.e., by $\Delta H(\infty)$ in Eq. (3) [23]. Magnetic resonance in paramagnetic insulators is usually discussed in terms of the "moments" of a Gaussian absorption line [11]. In particular, $\Delta H(\infty)$ is proportional to the second moment M_2, which is determined only by various *anisotropic* interactions between spins. However, the isotropic Heisenberg exchange interaction $J_{\rm iso}$ influences the line shape via the well-known effect of "exchange narrowing" of the magnetic resonance which takes place if $|J_{\rm iso}|/g\mu_B \gg H_{\rm res} \gtrsim \Delta H$. In this case the ESR signal acquires a Lorentzian shape, which is indeed observed in LCCO (see Fig. 1). The corresponding "exchange narrowed" linewidth reads [24,25]

$$\Delta H(\infty) \simeq \frac{\hbar^2}{g\mu_B}\,\frac{M_2}{|J_{\rm iso}|}\,. \tag{4}$$

The most obvious anisotropic interaction which broadens the resonance line is a dipole-dipole interaction between the spins $\mathbf{S}_i$ and $\mathbf{S}_j$ separated by a distance $\mathbf{r}_{ij}$: $\mathcal{H}_{\rm dd} = g^2\mu_B^2 \sum_{ij} r_{ij}^{-3}[\mathbf{S}_i\mathbf{S}_j - 3r_{ij}^{-2}(\mathbf{S}_i\mathbf{r}_{ij})\,(\mathbf{S}_j\mathbf{r}_{ij})]$. This yields an exchange narrowed dipole-dipole contribution to the width of $\Delta H^{\rm dd} \approx 1$ Oe, which is negligible compared to the experimental result.

Now we focus on the contributions to ΔH arising from the *anisotropy* of exchange [last two terms in Eq. (1)]. The antisymmetric Dzyaloshinsky-Moriya interaction [28,29] $\sum_{ij} \mathbf{d}_{ij}[\mathbf{S}_i \times \mathbf{S}_j]$ is zero in LCCO due to the presence of an inversion center between two nearest neighbor Cu sites [8]. The only possible source of the large ΔH in LCCO is hence the symmetric anisotropic exchange $\sum_{ij} \mathbf{S}_i A_{ij} \mathbf{S}_j$. In this case $M_2 \simeq A_{ij}^2$ [11]. With the observed value of $\Delta H \approx 1500$ Oe and $J_{\rm iso} \approx 20$ K [5], we get from Eq. (4) a surprisingly strong anisotropy A_{ij} of about 10% of $J_{\rm iso}$. This value of A_{ij} is 10 times larger than the conventional estimate [28], $A_{ij}^{\rm conv} \simeq (\Delta g/g)^2 J_{\rm iso} \approx 1\%$ of $J_{\rm iso}$, where $\Delta g \approx 0.2$ is the average deviation of the g-factor of Cu^{2+} in LCCO from its spin-only value $g = 2$. In terms of experimentally accessible quantities, the conventional estimate yields $\Delta H \approx 15$ Oe, whereas the experimental result is 2 orders of magnitude larger.

In the following we discuss the basic physics that may cause such an unusually strong exchange anisotropy in LCCO [6,7]. For a qualitative understanding it is sufficient to consider only two nearest neighbor ions, Cu_L and Cu_R, in the Cu-O chain (see Fig. 3). The crystal field splits the $3d^9$ state of Cu^{2+}. The lowest orbital $d_{x^2-y^2}$ is occupied by a single hole with $S = 1/2$. In perturbation theory, the superexchange interaction arises from virtual hopping processes via the two intermediate oxygen ligands A and B, which couple the Cu spins by 90° bonds. Note that the oxygen orbitals are empty in hole notation. The leading isotropic exchange is ferromagnetic because Hund's rule coupling favors a parallel alignment of spins

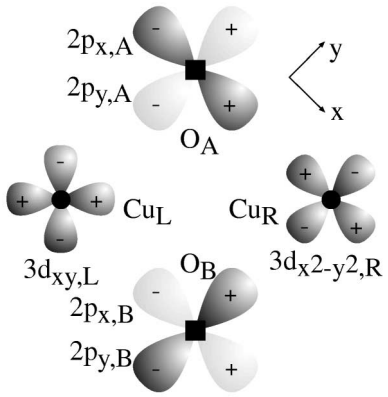

FIG. 3. Copper and oxygen orbitals of two symmetric 90° Cu-O-Cu bonds relevant to the anisotropic coupling.

in the virtually excited state, where the two spins occupy orthogonal oxygen orbitals. However, a finite spin-orbit coupling $\lambda\mathbf{L}\cdot\mathbf{S}$ couples the $|x^2 - y^2\rangle$ state with the orbital states $|xy\rangle$, $|yz\rangle$, and $|zx\rangle$. The central point is that the relevance of these orbitals for superexchange depends on the geometry of the considered bond. In the present case, higher order exchange processes involving the $|xy\rangle$ orbital are strongly enhanced with respect to those involving $|yz\rangle$ and $|zx\rangle$. This strong anisotropy in orbital space is directly translated into a strong anisotropy in spin space via spin-orbit coupling. The dominant contribution to *anisotropic* exchange is the "ring exchange" [7] which avoids unfavorable doubly occupied sites: one spin virtually hops from, e.g., $|xy, \mathrm{L}\rangle$ via $|p_{x,A}\rangle$ to $|x^2 - y^2, \mathrm{R}\rangle$, whereas the second spin takes the opposite route via $|p_{y,B}\rangle$. The sign of this contribution is negative because of the different signs of the hopping from $|x^2 - y^2, \mathrm{R}\rangle$ to $|p_{x,A}\rangle$ and $|p_{y,B}\rangle$, respectively (see Fig. 3), and causes an easy-axis out-of-plane anisotropy. Because of the presence of a competing process where the two spins meet on the *same* ligand in the intermediate state, the total leading order anisotropy scales with the oxygen on-site Coulomb interaction, whereas all processes involving $|yz\rangle$ and $|zx\rangle$ states depend on Hund's rule coupling and are much smaller [7]. In the case of a 180° bond directed, e.g., along the x axis with a single oxygen ligand at the midpoint between the two Cu sites, the symmetry of the $|xy\rangle$ and $|zx\rangle$ states is *identical* with respect to the Cu-O-Cu bond, and the anisotropy is dominated by Coulomb exchange [30]. Compared to a 180° bond, the anisotropy is additionally enhanced in the present geometry due to the strongly reduced isotropic superexchange, which may further be reduced for bond angles slightly larger than 90° because of a cancellation of the leading order ferromagnetic and antiferromagnetic contributions [7].

Our ESR data clearly show a strong anisotropy of the spin-spin interactions in the Cu-O chains of LCCO in the paramagnetic regime. In this respect LCCO may not be unique. For instance, in Li_2CuO_2 a surprisingly broad ESR signal ($\Delta H \sim 4000$ Oe) was reported in the submillimeter wavelength range [31]. Complementary to our result,

specific heat measurements of $La_5Ca_9Cu_{24}O_{41}$ in a magnetic field reveal a strong magnetic anisotropy in the AF *ordered* state at low T, suggesting even an Ising-like character of the magnetism of the chains [19]. Moreover, our analysis is in agreement with the recent observations of a large spin-wave gap in Li_2CuO_2 [32] and of a large size of the ordered moment in $Ca_2Y_2Cu_5O_{10}$ [10], which both point toward a strong easy-axis anisotropy of edge-sharing Cu-O plaquettes.

In summary, a very broad ESR signal of the Cu^{2+} ions in the chains of $(La, Ca)_{14}Cu_{24}O_{41}$ single crystals is observed in the paramagnetic regime. Our analysis reveals that the linewidth is 2 orders of magnitude larger than one expects from conventional estimates of the anisotropy of the magnetic exchange interaction. This gives strong experimental evidence for a significant amplification of the influence of spin-orbit coupling on magnetic exchange in edge-sharing Cu-O structures, as suggested recently by theoretical calculations [6,7]. The commonly accepted point of view on copper oxides as good model systems for studies of the isotropic Heisenberg spin magnetism has thus to be revised for certain bonding geometries.

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*On leave from Kazan Physical Technical Institute, Russian Academy of Sciences, 420111 Kazan, Russia.

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[16] As expected in the case of exchange narrowing (see Ref. [24] and the text), we find that ΔH depends on the angle θ between H and the b axis approximately as $(1 + \cos^2\theta)$. Since the experimental accuracy is higher for small ΔH, we restrict the discussion to $H \parallel c$, i.e., $\theta = 90°$.
[17] These values were obtained for T between 80 and 150 K, where $H_{\rm res}$ is not affected by the low-temperature AF spin correlations. Above 150 K the uncertainty and the systematic error in the determination of $H_{\rm res}$ considerably increase due to the reduced amplitude of the signal.
[18] Although $\chi_{\rm ESR}^{\rm spin}$ and $\chi_{\rm stat}$ were measured at different fields ($\sim$0.3 and 1 T, respectively), their comparison is reasonable because $\chi_{\rm stat}$ is field independent for $T \gtrsim 25$ K and $0 < H \leq 14$ T [19].
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