Strong anisotropy of superexchange in the copper-oxygen chains of La$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$

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(November 16, 2000)

Abstract

Electron spin resonance data of Cu$^{2+}$ ions in La$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ 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 $\sim 10\%$ 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 $90^\circ$ 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.

PACS numbers: 76.30.-v, 71.27.+a, 71.70.Gm, 75.40.Gb
Magnetic interactions in strongly correlated transition metal oxides have attracted much interest during the past decade due to their intimate relationship with high temperature superconductivity in the cuprates, but 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

\[ \mathcal{H} = J_{iso} \sum_{ij} S_i S_j + \sum_{ij} d_{ij} [S_i \times S_j] + \sum_{ij} A_{ij} S_i S_j , \]  

(1)

where the first term denotes the isotropic Heisenberg exchange, and the second and third represent antisymmetric and symmetric anisotropic contributions caused by spin-orbit coupling. In the case of a Cu$^{2+}$ ion with a single hole with $S=1/2$ in the 3$d$ shell, the orbital angular momentum is quenched in the solid due to crystal field splitting. In general spin-orbit coupling and the corresponding anisotropies play only a minor role in cuprates. For instance the CuO$_2$ planes of the parent compounds of high temperature superconductors like La$_2$CuO$_4$ or Sr$_2$CuO$_2$Cl$_2$ are thought to be the best representatives of a 2D $S=1/2$ square lattice isotropic Heisenberg antiferromagnet with $J_{iso} \approx 1500$ K. This large value of $J_{iso}$ is typical for the 180° Cu-O-Cu bond angle present in 2D cuprates. The anisotropic magnetic couplings $A_{ij} \ll |d_{ij}|$ both do not exceed 1% of $J_{iso}$ in La$_2$CuO$_4$ [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 [4] the strength of the leading isotropic coupling $J_{iso}$ 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) which are coupled via Hund’s rule, resulting in a ferromagnetic coupling [3]. Experimentally, one still finds an AF $J_{iso} \approx 120$ K [4] in the quasi-one-dimensional Cu-O chains of the spin-Peierls compound CuGeO$_3$ with a bond angle $\sim 98°$. Still closer to 90° $J_{iso}$ indeed changes sign and becomes ferromagnetic, as in La$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ [4]. The
dependence of the anisotropic corrections on the bond angle have not been studied to the same extent. Recently, it has been predicted theoretically that the magnetic anisotropy of two symmetrical $90^\circ$ Cu-O-Cu bonds may be unusually large \[6,7\]. This bonding geometry arises if Cu-O plaquettes (i.e. four oxygens forming a square with a Cu ion at the center) are connected along their edges and is found in several systems like La$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ [8], Li$_2$CuO$_2$ [9] or Ca$_2$Y$_2$Cu$_5$O$_{10}$ [10].

Electron spin resonance (ESR) is a very sensitive tool to study the anisotropy of the spin-spin coupling which, in particular, is the main source of the finite width $\Delta H$ of an ESR signal in concentrated paramagnets \[11\]. In this paper we present ESR data of La$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ (LCCO) single crystals, which show a very broad Cu$^{2+}$ ESR signal of $\Delta H \sim 1500-2000$ Oe from the Cu-O chains in the paramagnetic regime at $T > 60$ K. Our analysis shows that the observed width of the ESR signal requires an unusually large anisotropic coupling of about 10% of the leading isotropic exchange $J_{iso}$. 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 a frequency of 9.47 GHz. The magnetic susceptibility $\chi_{\text{static}}$ was measured with a SQUID-magnetometer at a field of 1 Tesla. La$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ single crystals with $x=9$, 11 and 12 were grown by the travelling 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 chains of edge-sharing Cu-O plaquettes 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 ($J_{iso} \approx -20$ K \[5\]), as expected for the nearly $90^\circ$ Cu-O-Cu bond angle. Additionally, La$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ contains planes of Cu$_2$O$_3$ two-leg spin ladders running parallel to the chains \[8\]. The ladders show a spin-singlet ground state with a spin gap of the order of 500-600 K \[13,14\].
Representative ESR spectra of the sample with $x=9$ and the fitting curves are shown in the left panels of Fig. 1 at $T = 100$ and 14 K. Since the width of the signal $\Delta H$ is comparable to the value of the resonance field $H_{\text{res}}$, the fitting function $f(H)$ has to include Lorentzian absorption derivatives corresponding to both, right and left circularly polarized components $A(H_\pm)$ and $A(H_-)$ of the linearly polarized microwave field \[11\]. Moreover, we add to $f(H)$ the correction due to the non-diagonal contributions to the dynamic susceptibility which appears as an admixture of the Lorentzian dispersion $D(H_\pm)$ \[15\]:

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

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

Here, $h_{\pm} = 2(H \pm H_{\text{res}})/\Delta H$, and $a$ and $d ( < a)$ are the amplitudes of the Lorentzian absorption and dispersion signals, respectively. From this fit we obtain the values of $H_{\text{res}}$, $\Delta H$ 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 $H_{\text{res}}$ 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 four-fold 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 $\chi_{\text{ESR}}^{\text{spin}}$ \[11\]. In order to obtain $\chi_{\text{ESR}}^{\text{spin}}$ 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$_2$O$_3 + 0.03%$Cr$^{3+}$ (the latter spectrum is visible in the top left panel of Fig. 1 as three small background lines at 840, 3340 and 7740 Oe). The $T$ dependences of $\chi_{\text{ESR}}^{\text{spin}}$ and $\chi_{\text{static}}$ are very similar for $T > 30$ K (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 $50$ K $< T < 300$ K, $\chi_{\text{static}}$ 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 \[1]. From the similarity between $\chi_{\text{ESR}}^{\text{spin}}$ and $\chi_{\text{static}}$ we therefore conclude that the ESR spectrum can be ascribed solely to the Cu
spins in the chains.

The ESR line width in magnetic insulators is usually decomposed into non-critical and critical parts [20]:

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

The first term in Eq. 3 is determined by spin-spin interactions at high temperatures, where spins are uncorrelated (paramagnetic regime). The second term \(\Delta H_{\text{crit}}(T)\) defines an additional contribution to the line width which arises at low temperatures, when long-range magnetic order is approached. It is caused by the fluctuations of the staggered magnetization in the short-range ordered state. These enhance the rate of the spin-spin relaxation \(1/T_2\) and consequently broaden the ESR line additionally [20]. According to the analysis of \(\chi_{\text{static}}\) in Ref. [5], insulating LCCO is paramagnetic above 50 K, whereas at lower temperatures spin correlations grow and finally result in long range AF order, which has been observed in \(\text{La}_5\text{Ca}_9\text{Cu}_{24}\text{O}_{41}\) at \(T_N \approx 10\) K [19,21]. Indeed, both the considerable shift of \(H_{\text{res}}\) to higher fields and the broadening of the ESR line at \(T < 60\) K (see Fig. 2) are obviously due to the development of short-range magnetic order (\(\Delta H_{\text{crit}}(T)\) in Eq. 3) [22]. The intensity of the ESR signal drops rapidly already 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 spectrum since their resonance frequency is outside the range of our spectrometer. This explains the discrepancy between \(\chi_{\text{ESR}}^{\text{spin}}\) and \(\chi_{\text{static}}\) 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 the present paper is the large value of \(\Delta H(T)\) of about 1500-2000 Oe for temperatures far away from the magnetically ordered state (see Fig. 2). It is reasonable to assume that the almost \(T\)-independent ESR line width in the paramagnetic regime above 60-80 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. On the other hand, the isotropic Heisenberg exchange interaction $J_{\text{iso}} \sum S_iS_j$ influences the shape of the line via the well known effect of “exchange narrowing” of the magnetic resonance which takes place if $|J_{\text{iso}}|/g\mu_B \gg H_{\text{res}} \gg \Delta H$. In this case the ESR signal acquires a Lorentzian line shape, which is indeed observed in LCCO (see Fig. 1). The corresponding “exchange narrowed” line width reads [24,25]:

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

(4)

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

Now we focus on the contributions to $\Delta H$ arising from the anisotropy of exchange (last two terms in Eq. 1). The term $\sum_{ij} d_{ij} [S_i \times S_j]$ is known as the antisymmetric Dzyaloshinsky-Moriya (DM) interaction [28,29]. However, in LCCO the DM vector $d_{ij}$ is zero due to the presence of an inversion center between two nearest neighbor Cu sites [8]. The only possible source of the large $\Delta H$ in LCCO is hence the symmetric anisotropic exchange $\sum_{ij} S_i A_{ij} S_j$. In this case $M_2 \simeq A_{ij}^2$ [11]. With the observed value of $\Delta H \approx 1500$ Oe and $J_{\text{iso}} \approx 20$ K [3] we get from Eq. 1 a surprisingly strong anisotropy $A_{ij}$ of about 10% of $J_{\text{iso}}$. This value of $A_{ij}$ is ten times larger than the conventional estimate [28] $A_{ij}^{\text{conv}} \simeq (\Delta g/g)^2 J_{\text{iso}} \approx 1\%$ of $J_{\text{iso}}$, 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 two orders of magnitude larger.

In the following we discuss the basic physics that may cause such an unusually strong anisotropy of superexchange in LCCO [3,4]. For a qualitative understanding it is sufficient to consider only two nearest neighbor Cu ions, $\text{Cu}_L$ and $\text{Cu}_R$ in the Cu-O chain (see Fig. 3). 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. In hole notation oxygen orbitals are empty. The crystal field splits the $3d^9$ state of a Cu$^{2+}$ ion, and the lowest orbital $d_{x^2−y^2}$ is non-degenerate and singly occupied. Only the twofold Kramers spin degeneracy remains in the ground state. However, a finite spin-orbit coupling $\lambda \mathbf{L} \cdot \mathbf{S}$ couples the $|x^2−y^2>$ state with the orbital states $|xy>$, $|yz>$ and $|zx>$. The central point is that the relevance of these orbitals for superexchange depends on the geometry of the considered bond. In 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 and the contribution of the $|xy, \text{Cu}_L>$ and $|zx, \text{Cu}_L>$ states are identical with respect to the Cu-O-Cu bond. In the present case, on the other hand, exchange processes involving virtual hopping of the hole from the $|x^2−y^2>$ ground state to the $|xy>$ orbital are strongly enhanced with respect to the exchange via $|yz>$ and $|zx>$ states. This strong anisotropy in orbital space is directly translated into a strong anisotropy in spin space via spin-orbit coupling. A strong ferromagnetic coupling arises e.g. due to virtual hopping processes via $|xy, \text{Cu}_L>$ into the $|p_x,A>$ and $|p_y,B>$ ligand states. The hopping process takes the form of ”ring exchange” which avoids unfavorable doubly occupied sites by involving the excitations along the ring $\text{Cu}_L \rightarrow \text{O}_A \rightarrow \text{Cu}_R \rightarrow \text{O}_B \rightarrow \text{Cu}_L$ [7]. The predominant contribution of the $|xy>$ orbital to superexchange causes an easy-axis out-of-plane anisotropy. In the present geometry this anisotropy, as compared to a 180° bond, is additionally enhanced due to a strongly reduced isotropic superexchange between $|x^2−y^2, \text{Cu}_L>$ and $|x^2−y^2, \text{Cu}_R>$, which may be reduced furthermore for bond angles slightly larger than 90° because of a cancellation of the leading order ferro- and antiferromagnetic contributions to the isotropic exchange [7].

Our ESR data clearly show that the spin dynamics of the Cu-O chains of LCCO is governed by a strong anisotropy of the magnetic interactions in the paramagnetic regime. In this respect LCCO may not be unique. For instance, in Li$_2$CuO$_2$ a surprisingly broad ESR signal ($\Delta H \sim 4000$ Oe) has been reported in the submillimeter wavelength range [30]. Complementary to our result, specific heat measurements of La$_5$Ca$_9$Cu$_{24}$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$_2$CuO$_2$ [31] and of a large size of the ordered moment in Ca$_2$Y$_2$Cu$_5$O$_{10}$ [10], which both point towards a strong easy-axis anisotropy of edge-sharing Cu-O plaquettes.

In summary, a very broad ESR absorption line of Cu$^{2+}$ ions in the chains of La$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ single crystals is observed in the paramagnetic regime. Our analysis reveals that the line width is two 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 superexchange 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.

We gratefully acknowledge useful discussions with G.A. Sawatzky, B. Keimer, and E. Müller-Hartmann. This work was supported by the Deutsche Forschungsgemeinschaft through SFB 341.
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\[ \Delta H \] depends on the angle \( \theta \) between \( H \) and the \( b \)-axis approximately as \( (1 + \cos^2 \theta) \) which is expected in the case of the exchange narrowing effect (see Ref. \[24\] and the text). The value of \( \Delta H \) is thus nearly twice as large for \( H \parallel b \) than for \( H \parallel c \). We therefore restrict ourselves to the discussion of the parameters for \( H \parallel c \), which can be determined more accurately.

These values were obtained for \( T \) between 80 and 150 K, where \( H_{\text{res}} \) is not affected by the low temperature AF spin correlations. Above 150 K the uncertainty and the systematic error in the determination of \( H_{\text{res}} \) considerably increase due to the reduced amplitude of the signal.

Although \( I \) and \( \chi_{\text{static}} \) were measured at different fields (~0.3 and 1 Tesla, respectively), their comparison is reasonable because \( \chi_{\text{static}} \) is field independent for \( T \gtrsim 25 \text{ K} \) and \( 0 < H \leq 14 \text{ T} \). \[19\].

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We consider sample inhomogeneities as a rather improbable source of the broadening of the ESR signal. In principal, structural disorder may cause local deviations of the \( g \)-factors of the Cu ions from their mean values \( g_b \) and \( g_c \). However, the observed linewidth would require a spread of the \( g \)-factors of the order \( \Delta g \sim \pm 0.5 \), which is unrealistic. In the case of magnetic inhomogeneity the broadening should be proportional to the magnetization of the sample \( \chi(T) \cdot H \). Thus the linewidth would decrease with increasing temperature which is not observed in the experiment. Moreover in both cases one expects
rather a Gaussian and not a Lorentzian line profile, but the former does not describe our data.

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FIG. 1. Left: Representative ESR spectra (derivatives of the absorbed microwave power \( dP(H)/dH \), thick lines) of a La\(_{14-x}\)Ca\(_x\)Cu\(_{24}\)O\(_{41}\) crystal (\( x=9 \)) at \( T=100 \) and 14 K and the respective fits according to Eq. 2 (thin solid lines). Different contributions to the \( T=14 \) K fitting curve are shown by broken lines. Right: A comparison of the spin susceptibility \( \chi^{\text{spin}} \) derived from the ESR intensity \( I(T) \) with the static susceptibility \( \chi^{\text{static}} \) for \( x=9 \) and 11.
FIG. 2. Temperature dependence of the ESR line width $\Delta H(T)$ and of the resonance field $H_{\text{res}}(T)$ (inset) for La$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ crystals with $x=9$, 11 and 12 ($H \parallel c$).
FIG. 3. Copper and oxygen orbitals of two symmetric 90° Cu-O-Cu bonds relevant for the anisotropic coupling.