Orbital order in the low-dimensional quantum spin system TiOCl probed by ESR

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We present electron spin resonance data of Ti$^{3+}$ ($3d^{1}$) ions in single crystals of the novel layered quantum spin magnet TiOCl. The analysis of the $g$ tensor yields direct evidence that the $d_{xy}$ orbital from the $t_{2g}$ set is predominantly occupied and owing to the occurrence of orbital order a linear spin chain forms along the crystallographic $b$ axis. This result corroborates recent theoretical LDA+U calculations of the band structure. The temperature dependence of the parameters of the resonance signal suggests a strong coupling between spin and lattice degrees of freedom and gives evidence for a transition to a nonmagnetic ground state at 67 K.

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Transition metal (TM) oxides with low-dimensional structural elements provide a fascinating playground to study novel phenomena such as high-temperature superconductivity, spin-charge separation, spin-gap states and quantum disorders. $^{1,2}$ Until recently, the emphasis has been put on Cu-based oxides, where a Cu$^{2+}$ ($3d^{9}$) ion has a single hole in the $e_g$ orbitals with spin $S=1/2$, and its orbital momentum is almost completely quenched by the crystal field. The ions at the beginning of the TM elements row, like Ti$^{3+}$ and V$^{4+}$, have, in contrast, a single $d$-electron which occupies one of the $t_{2g}$ orbitals. Because these orbitals are much less Jahn-Teller active, their near degeneracy may yield more complicated physics, involving not only the spin and charge, but also the orbital sector. $^{3}$ As an example, the three-dimensional cubic perovskite LaTiO$_3$ has been proposed to realize a quantum orbital liquid. $^{4}$ However recent x-ray and neutron structural data suggest the ordering of the orbitals. $^{5}$

The structural dimensionality is reduced in TiOCl, where [TiO$_4$Cl$_2$] octahedra are arranged in bilayers separated from each other along the $c$ axis (Fig. 1). In fact, for quite a while this compound has been considered as a 2D antiferromagnet, an electron analog to the high-$T_c$ cuprates, owing to an almost $T$-independent magnetic susceptibility reported in Ref. $^{6}$ However, very recently TiOCl has emerged in an entirely new light as a 1D antiferromagnet and is proposed as the second example of an inorganic spin-Peierls compound after CuGeO$_3$. $^{7,8}$ LDA+U band-structure calculations suggest ordering of the $t_{2g}$ orbitals in TiOCl which produces quasi-1D antiferromagnetic (AF) $S=1/2$ chains. This calculation favors the occupancy of the $d_{xy}$ orbitals (Fig. 1b) which form a uniform chain along the $b$ axis. A transition to a non-magnetic state at $T_c=67$ K has been observed in the static magnetization. $^{9}$ Remarkably, NMR data reveal the pre-existing pseudo spin-gap already above $T_c$ which is ascribed to strong orbital fluctuations. $^{10}$

In this paper we present electron spin resonance (ESR) data of Ti$^{3+}$ ($3d^{1}$) in single crystals of TiOCl. By measuring the anisotropy of the $g$ factor and comparing it with our theoretical estimates in the framework of the angular overlap model we conclude that the single $d$ electron occupies the $d_{xy}$ orbital which lies in the $bc$ plane. This result suggests a formation of a spin-1/2 chain along the $b$ direction, owing to the overlap of the orbital states, and supports recent LDA+U calculations. $^{10}$ The ESR signal vanishes at $T_c=67$ K signalling the transition to a non-magnetic ground state. A pronounced dependence of the linewidth and the $g$ factor on temperature suggests a strong coupling of spins to the lattice which may play an important role for the opening of the spin gap.

Single crystals of TiOCl have been prepared from TiCl$_3$ (Aldrich) and TiO$_2$ (Kronos Titan) according to experimental details given in Ref. $^{12}$ The purity of the product was checked by x-ray powder diffraction at 293 K and 10 K. The latter measurement has been carried out in order to check for a possible structural phase transition, which we do not find. Both diffractograms could

FIG. 1: (a) Crystal structure of TiOCl; (b) sketch of the $t_{2g}$ orbitals ($\alpha$, $\beta$ and $\gamma$) in the [TiO$_4$Cl$_2$] octahedron. The local coordinate frame $\{xyz\}$ is chosen so that $z\parallel a$ axis, and the $x$ and $y$ axes are rotated by 45° with respect to the $c$ and $b$ axes, respectively. Note that in the LDA+U calculation of Seidel et al. one-dimensional bands are formed from overlapping $xy$, $yz$, and $xz$ orbitals, respectively, whereas on a single cluster level the $\alpha=xy$, $\beta=(xz+yz)/\sqrt{2}$ and $\gamma=(xz-yz)/\sqrt{2}$ states are the eigenstate orbitals, respectively.

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be indexed in the orthorhombic space group $Pmmn$ with $a = 3.789(1)$ Å, $b = 3.365(1)$ Å, $c = 8.060(3)$ Å at 293 K and $a = 3.7946(3)$ Å, $b = 3.3584(2)$ Å, $c = 8.057(1)$ Å at 10 K. It is interesting to note that the $a$ axis is longer and the $b$ and $c$ axes are shorter at lower temperatures, which means that the already distorted $[TiO_4Cl]$ octahedra are slightly less compressed at 10 K. The static magnetic susceptibility $\chi(T)$ has been measured in a Faraday balance in a field of 1 Tesla in the temperature range 10–550 K (Fig. 2a). Within the experimental accuracy $\chi(T)$ is isotropic and shows a behavior similar to that reported in Ref. 10. The fit of the data with the formula $\chi(T) = \chi(T)_{\text{DADF}} + \chi(T)_{\text{Curie}} + \chi_0$, where $\chi(T)_{\text{DADF}}$ is the susceptibility of a uniform 1D Heisenberg antiferromagnet $\chi(T)_{\text{Curie}}$ is the Curie term and $\chi_0$ is the sum of the diamagnetic susceptibility of TiOCl and the Van-Vleck susceptibility of $\text{Ti}^{3+}$, yields the number of free $S = 1/2$ spins (paramagnetic defects), responsible for the low-$T$ Curie upturn of $\chi(T)$ of order 0.6%, and $\chi_0 = 2.3 \times 10^{-4}$ emu/mole. After the subtraction of $\chi(T)_{\text{Curie}}$ and $\chi_0$ from the raw data one sees that the model of a 1D antiferromagnet with the nearest neighbor exchange $J = 676$ K and the $g$ factor of 1.91 (see below) describes the data in the high-$T$ regime quite well (Fig. 2a). Below 130 K the susceptibility rapidly decreases and approaches zero at $\sim 60$ K $^{17,18,19}$.

ESR has been measured using a Bruker spectrometer at X-band frequency 9.48 GHz and at temperatures between 2 and 300 K. A single resonance line of a Lorentzian shape has been observed. The intensity of the ESR signal $I$ is proportional to the susceptibility of the resonating spin $^{20}$. A comparison of $I$ of TiOCl with that of a reference sample $^{25}$ gives evidence that within the experimental uncertainty practically all spins contributing to the static susceptibility participate in ESR. The $T$-dependence of the spin susceptibility $\chi_{\text{ESR}}$ obtained from the integrated intensity $I(T)$ is similar to that of the static $\chi$ (Fig. 2c). $^{22}$ In particular, $\chi_{\text{ESR}}$ drops sharply almost to zero at $T_c = 67$ K signalling the transition to a non-magnetic state. In addition a small kink can be seen at 90–95 K, which is ascribed in Ref. 12 to the onset of the structural instability. A small signal arising at $T < T_c$ is obviously due to a small amount of paramagnetic impurities in the samples (e.g. $\text{Ti}^{3+}$ in structural defects). The bulk signal observed above $T_c$ is anisotropic and exhibits a strong temperature dependence of the $g$ factor and the linewidth $\Delta H$ (Fig. 2b and c).

A representative example of the dependence of $g$ on the direction of the external magnetic field $H$ is shown in Fig. 3. One notices that the $c$ axis is a symmetry axis of the $g$ tensor, where $g$ reaches its minimum value (Fig. 3b). The $g$ factor in the $ab$ plane is larger and also anisotropic, as expected in the orthorhombic symmetry (Fig. 3a): The situation is typical for a Ti octahedron strongly compressed along the $z$ axis with smaller distortions in the equatorial plane, where the $xy$ orbital ground state is realized. $^{23}$ On the quantitative level we compare the experimental data with the results of the angular overlap model (AOM). The AOM has been a tool to rationalize spectroscopic and magnetic properties of TM and rare-earth metal ions in various ligand fields and provides a mathematical approach to calculating relative energies of molecular orbitals of a TM complex from the overlap of the central-atom orbitals with the ligand orbitals. $^{24}$ We calculated the $g$ values for TiOCl using the program package CAMMAG25,26. The best fit of the $g$ tensor with experimental data (Table I) clearly identifies the $d_{xy}$ orbital as the ground state orbital. The relative energies of the orbital states and the bonding parameters used in the calculation are listed in Table I. Even if one neglects a plausible anisotropy of the $\pi$ interactions (Model A) the AOM predicts correctly a minimum value of the $g$ factor along the $c$ axis and larger values in the $ab$ plane ($g_c < g_b < g_a$). The agreement becomes even quantitative if one accounts for the anisotropy of the $\pi$ bonding, which is quite reasonable owing to the fact the ligands are all bridging, e.g. $[\text{TiO}_4/\text{Cl}_2/2]$ (Model B).$^{22}$ In the LDA+$U$ calculation of Seidel et al. the
A considerable decrease of the $g$ anisotropy at low $T$ signals a reduction of the distortion of the Ti complex, in agreement with our x-ray data. Such an appreciable coupling of the spin to the lattice should affect the $T$ dependence of the ESR linewidth as well. In a concentrated paramagnet spin-spin interactions produce a finite ESR linewidth owing to the anisotropic part of the superexchange $\hat{H}' = \sum S_i S_j$. This interaction yields a second moment of the line $M_2 \sim A \sim (\Delta g/g)^2 J$. Here $\Delta g$ is the deviation of $g$ from the spin-only value of 2, and $J$ is the strength of the isotropic Heisenberg exchange $\hat{H} = J \sum S_i S_j$ which in the 3D case narrows the signal so that its width reduces to $\Delta H \sim M_2/\gamma^2$, if $\Delta g \sim 0.05$ and $J \sim 680$ K we obtain $\Delta H$ of the order of 30 Oe. The much smaller value of this rough estimate as compared with the experimental data for $T > T_c$ (Fig. 2b) may be in part due to the fact that it neglects the peculiarities of the bonding geometry in the 1D spin chain which in certain cases may considerably boost $\Delta H$. More serious is the discrepancy of the $T$ dependence of $\Delta H$. Because $\chi_{\text{Curie}}/\chi(T)$ and the average value of $\Delta g$ both increase with lowering $T$, the width $\Delta H$ is expected to increase, too. However, experimentally one finds the opposite behavior (Fig. 2b), suggesting that other mechanisms of spin relaxation e.g. via orbital and lattice degrees of freedom have to be considered. The interplay between orbital and spin fluctuations in TiOCl has been proposed in the discussion of the NMR results. It is argued that the opening of the pseudo-spin gap at $T^* \sim 35$ K is related to the suppression of the spin-Peierls transition caused by fluctuations of the orbital states. Remarkably, in the temperature interval $T_c < T < T^*$ the ESR linewidth levels off at a minimum value of $\sim 150 - 170$ Oe before dropping down at $T_c$. This implies that the spin fluctuations in this temperature regime are strongly suppressed as expected in the pseudo-gap regime. The spin dynamics recovers above $T^*$ resulting in the increase of $\Delta H$. An additional $T$-dependent contribution to $\Delta H$ could arise due to the spin-phonon coupling, which may be significant as suggested by the strong sensitivity of the $g$ factor to the change of the lattice parameters.

In summary, we have studied electron spin resonance of Ti$^{3+}$ ions in single crystals of the novel low-dimensional spin magnet TiOCl. The analysis of the $g$ tensor justifies the scenario that in an apparently 2D structure uniform spin $S = 1/2$ chains are formed along the $b$ direction. The bulk ESR signal vanishes at $T_c = 67$ K evidencing the transition to a nonmagnetic, possibly a spin-Peierls state. The $T$ dependence of the $g$ values and the linewidth suggests that orbital and lattice degrees of freedom may play a key role in the magnetic properties of TiOCl. In particular, strong spin and probably also orbital fluctuation effects above $T_c$ may be responsible for a peculiar $T$ dependence of the ESR parameters.

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**TABLE I:** Observed and calculated $g$ tensor at $T = 293$ K. (A - isotropic, B - anisotropic $\pi$ interactions).

| | experiment | Model A | Model B |
|---|------------|---------|---------|
| $g_a$ | 2.01 | 1.946 | 1.976 |
| $g_b$ | 1.96 | 1.935 | 1.959 |
| $g_c$ | 1.91 | 1.926 | 1.911 |

**TABLE II:** AOM parameters for [TiO$_4$Cl$_2$] complex and relative energies of the $d$ orbital states.

| | $\zeta$ | B | C | $c_a$ | $d(Ti-O)$ | $c_x$ | $d(Ti-O)$ | $c_y$ | $d(Ti-O)$ | $c_z$ | $d(Ti-CI)$ |
|---|---------|---|---|-------|---------|---|---------|---|---------|---|---------|
| | 125 cm$^{-1}$ | 700 cm$^{-1}$ | 2800 cm$^{-1}$ | 9500 cm$^{-1}$ | 1.95 Å | 2400 cm$^{-1}$ | 2.25 Å | 1200 cm$^{-1}$ | 1.95 Å | 5700 cm$^{-1}$ | 2.37 Å |
| | $z^2$ | 20769 cm$^{-1}$ | $x^2-y^2$ | 14891 cm$^{-1}$ | $(xz+y^2)/\sqrt{2}$ | 5900 cm$^{-1}$ | $(xy-z^2)/\sqrt{2}$ | 2456 cm$^{-1}$ | $xy$ | 0 cm$^{-1}$ |
| $k_x$ | 0.6 | $k_y$, $k_z$ | 0.9 |

Two higher-energy 1D bands are derived from unmixed $d_{yz}$ and $d_{xz}$ orbitals, which both make an angle of $\sim 45^\circ$ with the $c$ axis and the $ab$ plane. Their occupation by the $d$ electron can be excluded, as the symmetry of these states is different from the symmetry of the $g$ tensor.

The above discussion strongly supports the scenario proposed in Ref. [24] on the basis of the band structure results. The occupation of the $d_{xy}$ states favors the occurrence of AF spin chains along the $b$ axis owing e.g. to the direct overlap of the $d_{xy}$ orbitals (Fig. 1). The neighboring chains in the [TiO$_4$Cl$_2$]$_\infty$ bilayer are shifted in a staggered fashion by $a/2$ and $b/2$ along the $a$ and $b$ axes, respectively (Fig. 1), so that the inter-chain exchange interaction is expected to be weak and frustrated. Thus almost perfectly isolated spin-1/2 chains with a relatively strong AF exchange $J \sim 700$ K, as deduced from the $\chi$ data, can be realized. The spin chains undergo the transition to a spin-gap state at $T_c = 67$ K. However, NMR data indicate that this is not a conventional spin-Peierls transition as observed e.g. in CuGeO$_3$ because of a much larger spin gap $\Delta_{\text{gap}}$ as compared with $T_c (2\Delta_{\text{gap}}/k_B T_c \approx 13)$. Probably additional orbital degrees of freedom play an important role in TiOCl. Indeed, the components of the $g$ tensor exhibit a strong $T$ dependence (Fig. 2), suggesting that the energy of the orbital states alters appreciably with $T$. This is a rather unusual feature; for example, in CuGeO$_3$ as well as in NaV$_2$O$_5$ which is another well-known low-D spin-gap TM oxide, the $g$ values do not change with $T$.\[9035\]

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