

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

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(Received 14 May 2003; published 14 October 2003)

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 local-density approximation + 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.

DOI: 10.1103/PhysRevB.68.140405

PACS number(s): 75.10.Jm, 71.27.+a, 76.30.Fc

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 disorder.^{1–3} 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, such as 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.⁴ As an example, the three-dimensional cubic perovskite LaTiO_3 has been proposed to realize a quantum orbital liquid.^{5,6} However, recent x-ray and neutron structural data suggest the ordering of the orbitals.⁷ The structural dimensionality is reduced in TiOCl, where $[\text{TiO}_4\text{Cl}_2]$ octahedra are arranged in bilayers separated from each other along the c axis [Fig. 1(a)]. In fact, for quite a while this compound has been considered as a two-dimensional (2D) antiferromagnet, an electron analog to the high- T_c cuprates,⁹ owing to an almost T -independent magnetic susceptibility reported in Ref. 8. However, very recently TiOCl has emerged in an entirely new light as a 1D antiferromagnet¹⁰ and is proposed as the second example of an inorganic spin-Peierls compound after CuGeO_3 .¹¹ LDA+U (where LDA+U means local-density approximation including Hubbard U) band-structure calculations¹⁰ 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. 1(b)] which form a uniform chain along the b axis. A transition to a nonmagnetic state at $T_c = 67$ K has been observed in the static magnetization.¹⁰ Remarkably, nuclear-magnetic resonance (NMR) data reveal the preexisting pseudo-spin-gap already above T_c which is ascribed to strong orbital fluctuations.¹²

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 signaling the transition to a nonmagnetic 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. 13. 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.¹⁴ Both diffractograms could be indexed in the orthorhombic space group $Pm\bar{m}n$ with $a = 3.789(1)$ Å, $b = 3.365(1)$ Å,

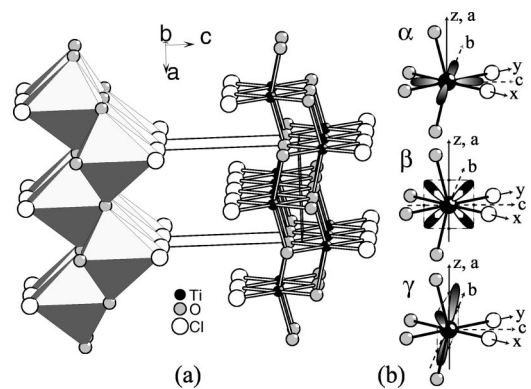


FIG. 1. (a) Crystal structure of TiOCl; (b) sketch of the t_{2g} orbitals (α , β , and γ) in the $[\text{TiO}_4\text{Cl}_2]$ octahedron. The local coordinate frame $\{xyz\}$ is chosen so that $z \parallel a$ axis, and the x and y axes are rotated by 45° with respect to the c and b axes, respectively. Note that in the LDA+U calculation of Seidel *et al.* (Ref. 10) one-dimensional bands are formed from overlapping xy , yz , and xz orbitals, respectively, whereas on a single cluster level $\alpha = xy$, $\beta = (xz + yz)/\sqrt{2}$, and $\gamma = (xz - yz)/\sqrt{2}$ states are the eigenstate orbitals, respectively.

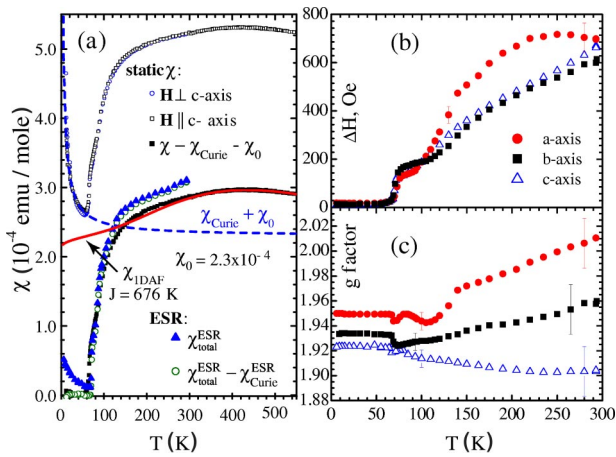


FIG. 2. (a) Static susceptibility $\chi(T)$ of TiOCl together with the ESR spin susceptibility and corresponding fits (see text); (b) and (c) ESR linewidth ΔH and g factor, respectively.

$c = 8.060(3)$ 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 $[\text{TiO}_4\text{Cl}_2]$ 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 T in the temperature range 10–550 K [Fig. 2(a)]. 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 $\chi(T) = \chi(T)_{\text{IDAF}} + \chi(T)_{\text{Curie}} + \chi_0$, where $\chi(T)_{\text{IDAF}}$ is the susceptibility of a uniform 1D Heisenberg antiferromagnet,¹⁵ $\chi(T)_{\text{Curie}}$ is the Curie term, and χ_0 is the sum of the diamagnetic susceptibility of TiOCl and the Van-Vleck susceptibility of 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.¹⁶ After the subtraction of $\chi(T)_{\text{Curie}}$ and χ_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. 2(a)]. Below 130 K the susceptibility rapidly decreases and approaches zero at ~ 60 K.^{17–19}

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 spins.²⁰ A comparison of I of TiOCl with that of a reference sample²² 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 χ^{ESR} obtained from the integrated intensity $I(T)$ is similar to that of the static χ [Fig. 2(a)].²¹ In particular, χ^{ESR} drops sharply almost to zero at $T_c = 67$ K signaling 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

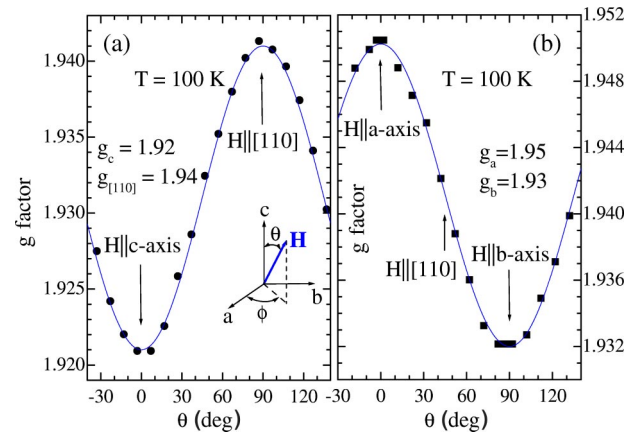


FIG. 3. Angular dependence of the g factor at $T = 100$ K: (a) (1–10) plane; (b) (001) plane.

the samples (e.g., 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 ΔH [Figs. 2(b) and 2(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. 3(a)]. The g factor in the ab plane is larger and also anisotropic, as expected in the orthorhombic symmetry [Fig. 3(b)]: 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 CAMMAG.^{25,26} 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 II. Even if one neglects a plausible anisotropy of the π 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 π bonding, which is quite reasonable owing to the fact the ligands are all bridging, e.g. $[\text{TiO}_{4/4}\text{Cl}_{2/2}]$ (model B).²⁹ In the LDA+U cal-

TABLE I. Observed and calculated g tensor at $T = 293$ K. (A— isotropic, B—anisotropic π 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 $[\text{TiO}_4\text{Cl}_2]$ complex and relative energies of the d orbital states.

ζ	125 cm^{-1}			
B	700 cm^{-1}			
C	2800 cm^{-1}			
e_σ	9500 cm^{-1} ,	$d(\text{Ti-O}) = 1.95 \text{ \AA}$		
e_π	2400 cm^{-1}		z^2	20769 cm^{-1}
e_σ	4900 cm^{-1} ,	$d(\text{Ti-O}) = 2.25 \text{ \AA}$	$x^2 - y^2$	14891 cm^{-1}
e_π	1200 cm^{-1}		$(xz + yz)/\sqrt{2}$	5900 cm^{-1}
e_σ	5700 cm^{-1} ,	$d(\text{Ti-Cl}) = 2.37 \text{ \AA}$	$(xz - yz)/\sqrt{2}$	2456 cm^{-1}
e_π	900 cm^{-1}		xy	0 cm^{-1}
k_x	0.6	$k_y, k_z = 0.9$		

culuation of Seidel *et al.*¹⁰ the two higher-energy 1D bands are derived from unmixed d_{yz} and d_{xz} orbitals, both which 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. 10 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 $[\text{TiO}_4\text{Cl}_2]_\infty^2$ bilayer are shifted in a staggered fashion by $a/2$ and $b/2$ along the a and b axes, respectively [Fig. 1(a)], so that the interchain exchange interaction is expected to be weak and frustrated. Thus almost perfectly isolated spin-1/2 chains with a relatively strong AF exchange $J \sim 700 \text{ K}$, as deduced from the χ data, can be realized. The spin chains undergo the transition to a spin-gap state at $T_c = 67 \text{ K}$. However, NMR data¹² indicate that this is not a conventional spin-Peierls transition as observed, e.g., in CuGeO_3 ¹¹ because of a much larger spin gap Δ_{gap} as compared with T_c ($2\Delta_{gap}/k_B T_c \approx 13$).¹⁴ 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(c)], 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_2O_5 which is another well-known low-D spin-gap TM oxide, the g values do not change with T .^{30,31}

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 superexchange²⁰ $\mathcal{H}' = \sum S_i A S_j$. This interaction yields a second moment of the line $M_2 \sim A \sim (\Delta g/g)^2 J$.³² Here Δg is the deviation of g from the spin-only value of 2, and J is the strength of the isotropic Heisenberg exchange $\mathcal{H} = J \sum S_i S_j$, which in the 3D case narrows the signal so that its width reduces to $\Delta H \sim M_2^2/J$.^{33,34} If the susceptibility $\chi(T)$ deviates from the Curie law, M_2 may acquire a T dependence proportional to $\chi_{\text{Curie}}/\chi(T)$.³⁶ Taking $\Delta g/g \sim 0.05$ and $J \approx 680 \text{ K}$ we obtain ΔH 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. 2(b)] 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 ΔH .³⁷ More serious is the discrepancy of the T dependence of ΔH . Because $\chi_{\text{Curie}}/\chi(T)$ and the average value of Δg both increase with lowering T , the width ΔH is expected to increase, too. However, experimentally one finds the opposite behavior [Fig. 2(b)], suggesting that other mechanisms of spin relaxation, e.g., via orbital and lattice degrees of freedom have to be considered.³⁸ The interplay between orbital and spin fluctuations in TiOCl has been proposed in the discussion of the NMR results.¹² It is argued that the opening of the pseudospin gap at $T^* \sim 135 \text{ K}$ 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 $\sim 150 - 170 \text{ Oe}$ before dropping down at T_c . This implies that the spin fluctuations in this temperature regime are strongly suppressed as expected in the pseudogap regime. The spin dynamics recovers above T^* resulting in the increase of ΔH . An additional T -dependent contribution to ΔH 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.³⁹

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 $T_c = 67 \text{ K}$ 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 temperature dependence of the ESR parameters.

We acknowledge useful discussions with M. Grüninger, T. Lorenz, D. Khomskii, and S. Streltsov, and thank P. Lemmens for pointing our attention to this system. This work was supported by the Deutsche Forschungsgemeinschaft through the Sonderforschungsbereich 608. V.K. acknowledges support of the RAS through Project No. OFN03/032061/020703-996.

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