Zero-Field Incommensurate Spin-Peierls Phase with Interchain Frustration in TiOCl

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(Received 17 March 2005; published 26 August 2005)

We report on the magnetic, thermodynamic, and optical properties of the quasi-one-dimensional quantum antiferromagnets TiOCl and TiOBr, which have been discussed as spin-Peierls compounds. The observed deviations from canonical spin-Peierls behavior, e.g., the existence of two distinct phase transitions, have been attributed previously to strong orbital fluctuations. This can be ruled out by our optical data of the orbital excitations. We show that the frustration of the interchain interactions in the bilayer structure gives rise to incommensurate order with a subsequent lock-in transition to a commensurate dimerized state. In this way, a single driving force, the spin-Peierls mechanism, induces two separate transitions.

DOI: 10.1103/PhysRevLett.95.097203 PACS numbers: 75.10.Jm, 71.70.Ch, 75.40.Cx, 78.30.−j

Low-dimensional quantum spin systems exhibit a multitude of interesting phenomena. For instance, a one-dimensional (1D) $S = 1/2$ chain coupled to the lattice may show a spin-Peierls transition to a nonmagnetic, dimerized ground state. In recent years, detailed studies of the first inorganic spin-Peierls compound $CuGeO_3$ have deepened the understanding of spin-Peierls systems substantially [1]. Even richer physics is expected if the spins are coupled additionally to orbital or charge degrees of freedom. A prominent example is the complex behavior of NaV_2O_5, which arises from the interplay of spin dimerization, orbital order, and charge order [1]. Recently, TiOCl and TiOBr have been discussed as spin-Peierls compounds with strong orbital fluctuations [2–9], assuming a near degeneracy of the t_{2g} orbitals in these $3d^1$ systems. Different quantities such as the magnetic susceptibility [2], the specific heat [9], ESR data [3], and NMR spectra [4] point towards the existence of two successive phase transitions, which clearly goes beyond a canonical spin-Peierls scenario in which a single second-order phase transition is expected. The high transition temperatures of $T_{c1} = 67$ K and $T_{c2} = 91$ K found in TiOCl are fascinating in a spin-Peierls context.

The structure of Ti*OX* consists of 2D Ti-O bilayers within the *ab* plane which are well separated by $X = \mathrm{Cl/Br}$ ions [10]. Quasi-1D $S = 1/2$ chains are formed due to the occupation of the $d_{y^2-z^2}$ orbital in the ground state (see below), giving rise to strong direct exchange between neighboring Ti sites along the *b* axis and negligible coupling in the other directions [unlike, e.g., Ref. [2], we use $x \| a$, $y \| b$, and $z \| c$]. Accordingly, the magnetic susceptibility of TiOCl is well described at high temperatures by the 1D $S = 1/2$ Heisenberg model with an exchange constant of $J \approx 676$ K [2,3]. In the nonmagnetic low-temperature phase, a doubling of the unit cell along the chain direction has been observed by x-ray measurements for both TiOCl [10] and TiOBr [11], supporting a spin-Peierls scenario. However, the following experimental facts are not expected in a canonical spin-Peierls system: (i) the existence of two successive phase transitions [2–4,9], (ii) the first-order character of the low-temperature phase transition [9–11], (iii) the observation of inequivalent Ti sites by NMR at low temperatures [4], and (iv) the appearance of incommensurate superstructure satellites between T_{c1} and T_{c2} [12,13], which arise in a generic spin-Peierls system only in a sufficiently high magnetic field. Testing whether Ti*OX* displays the generic *H*-*T* phase diagram of a spin-Peierls system [14] is difficult due to the large energy scale.

The aim of the present study is to determine the ingredients necessary to understand the peculiar properties of Ti*OX*. Using optical spectroscopy, we show that the t_{2g} subshell on the Ti sites experiences a pronounced crystal-field splitting of 0.65 eV. Thus the orbital degree of freedom is quenched and can be neglected for the description of the low-energy physics. All of the above mentioned points can be attributed to the coupling of spin and lattice degrees of freedom in the bilayer structure, which gives rise to a frustration of interchain interactions.

Single crystals of TiOCl and TiOBr have been grown by the chemical vapor transport technique [15]. The purity of the crystals was checked by x-ray powder diffraction. Typical crystal dimensions are a few mm^2 in the *ab* plane and 10–100 μm along the *c* axis, i.e., the stacking direction. We have measured the magnetic susceptibility χ in a Faraday balance [TiOCl; 4–550 K, see also Ref. [3]] and a SQUID magnetometer (TiOBr; 4–300 K) in an applied magnetic field of $B = 1$ Tesla. In order to obtain a large enough signal we have coaligned several crystals ($\simeq 10$ mg; TiOCl: $B \| c$; TiOBr: $B \perp c$). The specific heat C_p has been determined on pressed pellets from crashed single crystals in different calorimeters using the continuous heating method ($\simeq$29 mg TiOCl; 40–300 K) and the relaxation time method ($\simeq$ 3 mg TiOBr; 2–300 K). The linear thermal expansion $\alpha = \partial \ln L / \partial T$ has been measured on 7 single crystals stacked on top of each other with $L \| c$ by a home-built capacitance dilatometer. Optical data have been collected on thin single crystals using a Fourier spectrometer.

In Fig. 1 we plot χ, α, and C_p/T of TiOCl and TiOBr. The existence of two distinct phase transitions at T_{c1} and T_{c2} (67 and 91 K in TiOCl; 28 and 48 K in TiOBr) is most clearly detected in α, but anomalies are also observed in χ and C_p/T at both T_{c1} and T_{c2}. The very similar behavior of TiOCl and TiOBr proves that the occurrence of *two* transitions is an intrinsic property of these compounds. The sharp and symmetric anomaly of α at T_{c1} signals an almost jumplike decrease of the lattice parameter c with increasing temperature indicating a first-order transition, in agreement with an analysis of C_p of TiOCl [9] and x-ray data of the superstructure satellites [10,11]. The anomaly of α at T_{c2} does not display the typical shape of a phase transition, neither of first nor of second order, but rather resembles a glass transition [16]. Recently, the appearance of incommensurate superstructure satellites below T_{c2} has been reported [12,13], which may be reconciled with a transition with glasslike features due to pinning to impurities. Below T_{c1}, χ is dominated by the van Vleck term and by contributions of impurities and of remnants of organic solvents [3]. Well above T_{c2}, χ can be described by the 1D $S = 1/2$ Heisenberg model [17] with exchange constant $J \approx 676$ K in TiOCl [2,3]. For TiOBr the position $T_{\max} \approx 240$ K of the maximum of χ allows us to estimate $J \approx 375$ K from $T_{\max}/J \approx 0.64$ [17], but $\chi(T)$ deviates from the theoretical curve [11,18]. The weak anomalies of C_p show that only a small amount of entropy is released at the phase transitions [9], in agreement with the expectations for a spin-Peierls transition of a 1D $S = 1/2$ chain, where most of the magnetic entropy $R \ln 2$ is connected with short-range correlations which are present up to temperatures of order $J \gg T_{c1}, T_{c2}$.

In the literature, the peculiar properties of TiOX have been attributed tentatively to strong orbital fluctuations [2–9]. We have determined the orbital excitation energies, i.e., the crystal-field splitting of the $3d$ levels, by measuring the transmittance of thin single crystals (Fig. 2). The transmittance is suppressed below ≈ 0.1 eV by phonon absorption and above ≈ 2 eV by interband excitations, i.e., excitations across the charge gap. The absorption at 0.6–0.7 eV for $E \| a$ and at 1.3–1.6 eV for $E \| b$ can be identified as orbital excitations which are infrared active due to the lack of inversion symmetry on the Ti sites. Both the excitation energies and the polarization dependence are in good agreement with the predictions of a cluster calculation of the crystal-field levels [19]. The observed features correspond to transitions from the ground state (predominantly $d_{y^2-z^2}$ with a small admixture of p_z character) to the second and third excited states. Transitions to the first excited state, d_{xy}, are not directly infrared active in the 300 K structure. Our cluster calculation [19] indicates a value of ≈ 0.25 eV ($\approx$2900 K) for the d_{xy} level. Moreover, we can exclude a significant admixture of the xy orbital to the ground state since a population of the xy orbital would lead to an entirely different polarization dependence [19]. Finally, we observe only a small change of the respective absorption features as a function of tem-

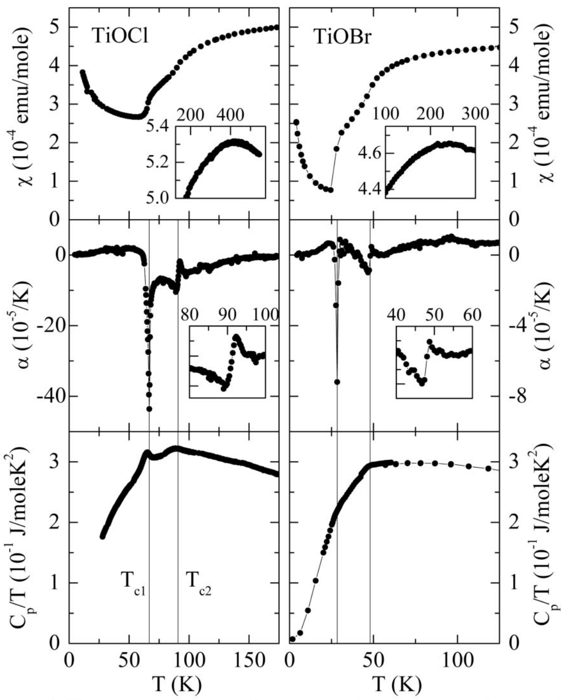

FIG. 1. Magnetic susceptibility χ, thermal expansion α, and specific heat C_p of TiOCl (left panels) and TiOBr (right).

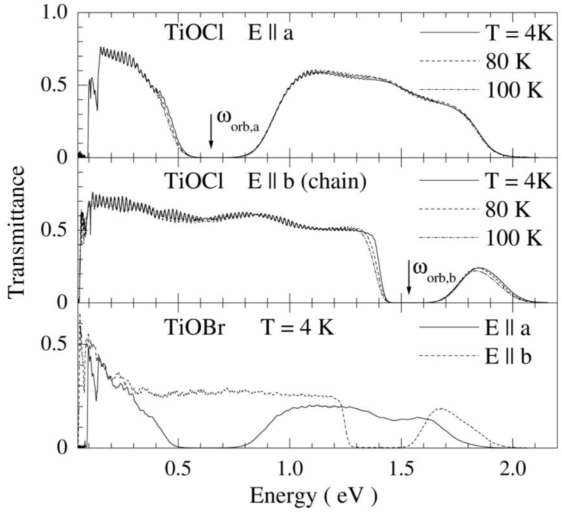

FIG. 2. Transmittance $T(\omega)$ of TiOX. For large values of $T(\omega)$, the spectra are dominated by interference fringes.

perature (see Fig. 2). We conclude that orbital fluctuations are strongly suppressed and do not constitute the origin of the peculiar properties of Ti*OX*. A sizeable splitting between $d_{y^2-z^2}$ and d_{xy} is in agreement with recent LDA + U and LDA + DMFT results [20–22] and with ESR data [3].

With a charge gap of ≈ 2 eV and an orbital excitation gap of the order of 0.25 eV, it is sufficient to consider spin and lattice degrees of freedom for the explanation of the low-energy physics. Clear evidence for structural changes at both T_{c1} and T_{c2} is provided by an analysis of the phonon spectra. We have observed changes of the number of infrared-active phonons in far-infrared reflectance and transmittance measurements on TiOCl and TiOBr at both T_{c1} and T_{c2}. As an example we show the temperature dependence of a phonon observed for $E \| a$ in TiOBr in Fig. 3. At 4 K, the energy of this mode amounts to 21.8 meV in TiOBr and 22.3 meV in TiOCl. This small difference shows that the Br/Cl ions hardly contribute to this mode. The energy, polarization, and temperature dependence indicate a displacement of mainly Ti ions along the a axis, with neighboring Ti ions within a chain moving out of phase. In the dimerized superlattice structure this mode is folded back to the Brillouin zone center. It becomes weakly infrared active if neighboring Ti sites are inequivalent, as observed by NMR [4]. The left panel of Fig. 3 shows that this mode gains finite spectral weight at about $T_{c2} = 48$ K in TiOBr. The linewidth is reduced by a factor of 3 upon cooling from 45 to 29 K, and also the peak energy is strongly temperature dependent, showing a jump at T_{c1}. These observations are in agreement with an incommensurate intermediate phase [12,13], which locally resembles the low-temperature phase.

We now turn to the bilayer geometry and discuss different scenarios for the existence of two phase transitions. In a single $S = 1/2$ chain, the dimers may reside either on the even or on the odd bonds. In an array of chains, the dimerization on nearest-neighbor chains may be in phase or out of phase with respect to each other. In the bilayer structure of Ti*OX*, a Ti ion of layer 1 is located on top of the center of a plaquette of four Ti ions on layer 2 [dashed box in Fig. 4(b)]. First we discuss in-phase and out-of-phase dimer patterns within the individual layers. In the out-of-phase case, all Ti sites are equivalent [circles in Fig. 4(b)], each facing one dimer on the surrounding plaquette. However, there are two inequivalent Ti sites in the in-phase case, facing either two or zero dimers [up/down triangles in Fig. 4(a)]. The observation of two distinct Ti sites in NMR [4] at low temperatures thus clearly indicates that an in-phase pattern is realized. This is corroborated by structural data [10], which show that two Ti ions forming a dimer are displaced with opposite signs perpendicular to the layers.

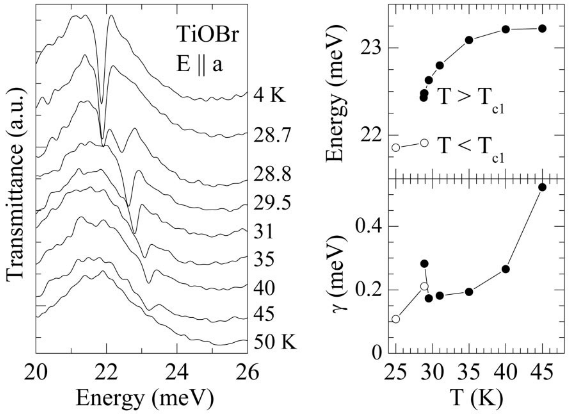

FIG. 3. Left: far-infrared transmittance of a thin single crystal of TiOBr for $E \| a$. The broad sinusoidal feature corresponds to a Fabry-Perot interference fringe. The sharp dip shifting from 23 to 22 meV reflects absorption by a phonon which becomes infrared active due to structural changes at T_{c2}. Right: temperature dependence of the phonon energy and of the linewidth γ.

For a single bilayer there are four degenerate in-phase patterns, with dimers on the even/even, even/odd, odd/even, or odd/odd bonds of layers 1/2 [see Fig. 4(a)]. In principle, this allows for several phase transitions between different superstructures, e.g., from an undimerized high-temperature phase to a dimerized phase where all bilayers realize the even/even pattern and finally to a low-temperature phase in which the dimerization alternates between even/even and odd/odd on adjacent bilayers. However, in this scenario both the NMR signal of two inequivalent Ti sites and the commensurate superstructure satellites are expected to appear at the high-temperature phase transition at T_{c2}, in contrast to the experimental observation.

Our second scenario focuses on the observation of two inequivalent Ti sites at low temperatures [4,10]. In principle, this inequivalence may serve as a second-order parameter; i.e., the system may undergo both a spontaneous spin-Peierls transition and, at a different temperature, a spontaneous transition to a state with Ti site inequivalence. In the present bilayer structure these two order parameters are coupled. Roughly, this scenario predicts the onset of dimerization with some admixture of site inequivalence at T_{c2} and the development of full site inequivalence below T_{c1} (or vice versa). In this scenario, commensurate superstructure satellites are predicted to appear at the high-

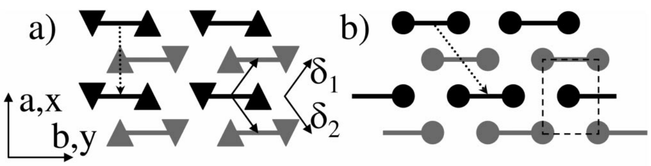

FIG. 4. Patterns of Ti spin dimers in the bilayer structure of Ti*OX*. Black (gray): Ti sites in layer 1 (2) of a single bilayer. (a) In-phase arrangement of neighboring chains within a layer. (b) Out-of-phase arrangement (see dashed arrows). The choice of δ_1 and δ_2 is convenient for the theoretical description.

temperature phase transition at T_{c2}, in disagreement with the experimental data on both TiOCl and TiOBr [4,10,11].

In the intermediate phase, superstructure satellites have been reported which are incommensurate both in b and a direction [12,13]. Incommensurate order was also proposed in order to explain the very broad NMR signal in the intermediate phase [4]. In compounds with commensurate band filling, incommensurability may arise from the frustration of competing interactions which favor different ordering wave vectors. We propose that the incommensurability arises from the frustration inherent to the bilayer structure. Therefore we discuss the following Landau expansion for the free energy as a function of the displacement ϕ_i^y of the Ti ion i parallel to the chains (to quadratic order)

$$\begin{aligned}\Delta F &= \frac{a_0}{2}\sum_i (\phi_i^y)^2 + \frac{a_1}{2}\sum_i \phi_i^y \phi_{i+\delta_1+\delta_2}^y \\ &\quad + \frac{b}{2}\sum_i \phi_i^y(\phi_{i+\delta_1}^y + \phi_{i-\delta_2}^y) \\ &= \frac{1}{2}\sum_{(h,k)} |\phi_{(h,k)}^y|^2 \left[a_0 + a_1\cos(k) + 2b\cos\left(\frac{h}{2}\right)\cos\left(\frac{k}{2}\right)\right], \end{aligned} \tag{1}$$

where h and k denote the momenta perpendicular and parallel to the chains, respectively. See Fig. 4(a) for the definition of δ_1 and δ_2. The a_1 term describes the tendency towards a spin-Peierls distortion ($a_1 > 0$). For vanishing interlayer coupling, i.e., $b = 0$, the system undergoes spontaneous dimerization with $k = \pi$ if $a_0 - a_1 < 0$. However, for $b \neq 0$ the free energy is minimized for $h = 0$ and $k = 2\arccos(-b/2a_1) \approx \pi + b/a_1$; i.e., the system becomes incommensurate for any finite value of the interlayer coupling b. This is due to the fact that the interlayer coupling described by the b term vanishes for $k = \pi$. The system has to become incommensurate in order to gain energy from the interlayer coupling.

In order to explain the additionally observed incommensurability perpendicular to the chains we have to consider a coupling of ϕ_i^y to the displacements ϕ_j^x and ϕ_j^z in a and in c direction, where i and j are neighbors on adjacent chains as described for the b term above. The formation of a dimer on sites i and $i + \delta_1 + \delta_2$ and the corresponding ϕ_i^y and $\phi_{i+\delta_1+\delta_2}^y$ push away the Ti ion on site $i + \delta_1$; i.e., they couple to $\phi_{i+\delta_1}^{x,z}$. This gives rise to an effective *intralayer* coupling between the chains, i.e., between site i and $i + \delta_1 - \delta_2$. The coupling via ϕ^z leads to a term approximately proportional to $-\cos(h/2)$, favoring the in-phase pattern [Fig. 4(a)]. In contrast, the coupling via ϕ^x produces a term approximately proportional to $\sin(h/2)$, favoring the out-of-phase pattern. In total this yields an incommensurate value of h.

Experimental evidence for a coupling between ϕ^y and $\phi^{x,z}$ stems from the observation of finite values of ϕ^z in the distorted low-temperature phase showing the in-phase pattern [10], and from the strong temperature dependence of the phonon observed for $E \| a$ depicted in Fig. 3. Furthermore, this scenario has two consequences which can be tested experimentally. First, it predicts finite values of ϕ_i^x in the intermediate phase. Second, the incommensurability $\Delta k \approx b/a_1$ is predicted to decrease with decreasing temperature, because the tendency a_1 towards a spin-Peierls distortion grows with decreasing temperature. Considering in addition $\Delta F_{\text{quartic}} = \Sigma_i(\phi_i^y)^4$, a first-order lock-in transition to commensurate order is to be expected for small enough Δk at low temperatures, as observed.

In conclusion, TiOCl and TiOBr do not display canonical spin-Peierls behavior. The peculiar properties of TiO*X* cannot be attributed to orbital fluctuations due to the large crystal-field splitting of the 3*d* levels. The bilayer structure offers a clear explanation for the existence of two distinct phase transitions. The incommensurate phase at intermediate temperatures arises due to the frustration of interchain interactions. These compounds offer the possibility to study a spin-Peierls transition in a predominantly two-dimensional, frustrated lattice.

It is a pleasure to acknowledge fruitful discussions with D. I. Khomskii, R. Valenti, S. Scheidl, D. Fausti, P. van Loosdrecht, M. Mostovoy, S.-L. Drechsler, and M. Lang. This project is supported by the DFG via SFB 608.

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