Spin-Peierls transition in TiPO₄

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We investigated the magnetic and structural properties of the quasi-one dimensional 3d¹-quantum chain system TiPO₄ (J ∼ 965 K) by magnetic susceptibility, heat capacity, ESR, x-ray diffraction, NMR measurements, and by density functional calculations. TiPO₄ undergoes two magnetostructural phase transitions, one at 111 K and the other at 74 K. Below 74 K, NMR detects two different ⁴¹P signals and the magnetic susceptibility vanishes, while DFT calculations evidence a bond alternation of the Ti...Ti distances within each chain. Thus, the 74 K phase transition is a spin-Peierls transition which evolves from an incommensurate phase existing between 111 K and 74 K.

Keywords: TiPO₄, spin-Peierls, magnetic susceptibility, heat capacity, MAS NMR, DFT, ESR

The discovery of high-Tc superconductivity in two-dimensional oxocuprates has stimulated broad interest in the properties of low-dimensional quantum S=1/2 antiferromagnets. The complex interplay between spin, charge, orbital and lattice degrees of freedom in low-dimensional systems with pronounced quantum fluctuation renders a plethora of complex and unusual ground states. ¹,²

Most of the prominent examples of low-dimensional quantum antiferromagnets with exotic ground states contain Cu²⁺ (3d¹, S = 1/2) ions with one hole present in the e_g orbitals.³,⁴ Compounds of early transition-metal elements with one electron in the d shell are less frequently investigated. With a 3d¹ electron in a high-symmetry or slightly distorted octahedral environment, the orbital degeneracy of the t₂g states opens new degrees of freedom, with the possibility of low-energy orbital excitations and the interesting scenario of destabilization of coherent spin/orbital ordering by quantum fluctuations. 3d¹ systems can be easily realized in compounds containing, e.g., Ti³⁺ or V⁴⁺ cations. A paramount example is the vanadium ladder compound α'⁻-NaV₂O₅.⁵ At high temperatures α'⁻-NaV₂O₅ contains mixed-valent vanadium cations with one electron occupying an orbital confined to the rungs of the ladder, hence constituting a quarter-filled ladder system.⁶,⁷ Below ∼ 34 K α'-NaV₂O₅ undergoes charge ordering⁸ leading to a spin-gap of ∼ 100 K indicated by a rapid drop of the magnetic susceptibility. That was initially ascribed to a spin-Peierls transition.⁶,⁷ Other prominent low-dimensional 3d¹ systems that have recently attracted much attention are the Mott insulators TiOX (X=Cl, Br).⁹,¹⁰,¹¹ These compounds crystallizing in the FeOCI-type structure, consisting of Ti - O - X layers made up of TiO₂Cl₂ octahedra. These layers are stacked with van der Waals interactions between them.¹²,¹³ The magnetic susceptibility of TiOCl reveals several unusual features, which led to the proposal that TiOCl may be a manifestation of a resonating valence-bond solid.¹⁰ Subsequently, Seidel et al. demonstrated that the high temperature susceptibility fits very well to a S=1/2 Heisenberg chain model with nearest-neighbor (nn) antiferromagnetic (afm) spin-exchange (SE) interaction of ∼660 K. In view of these findings and their LDA + U electronic structure calculations, Seidel et al. concluded that TiOCl is an example of a Heisenberg chain that undergoes a spin-Peierls transition at 67 K.¹¹ Subsequent low temperature x-ray structure determination showed a slight dimerization of the Ti...Ti distances along the b direction.¹² A further anomaly was detected at T_{c2} = 95 K, which signals a transition into an incommensurate phase with a slight monoclinic distortion of the lattice. It was initially believed and it appears to be now generally accepted to be of continuous or higher order, however, there was a later claim that it was first order.¹⁴,¹⁵,¹⁶,¹⁷

Here, we report the magnetic and structural properties of TiPO₄, which contains Ti³⁺ cations and displays two magneto-structural phase transitions reminiscent of those in TiOX. In contrast to TiOCl, however, TiPO₄ is a structurally one-dimensional compound crystallizing in the CrVO₄ structure-type (SG: Cmcm) (see inset in Fig. 1).²² The Ti³⁺ ions, carrying S=1/2 entities, are subject to axially compressed TiO₆ octahedra. These share their edges to form corrugated TiO₄ ribbon chains along the c-axis with a buckling angle of 156.927(4)° in the a-c plane. The Ti³⁺...Ti³⁺ distance at room temperature (RT) amounts to 3.1745(10)Å with a Ti³⁺-O²⁻-Ti³⁺ angle of 95.484(5)°.²³ The TiO₄ ribbon chains are interconnected by sharing corners with distorted PO₄ tetrahedra.

At high temperature the magnetic susceptibility of a polycrystalline sample (Fig. 1 main panel) is characterized by a broad maximum centered at ∼ 625 K, indicating short range afm correlations. After correction for a temperature independent offset to the susceptibility arising from diamagnetic contributions of the closed shells and van Vleck terms, the high temperature magnetic suscep-
and blue polyhedra represent the TiO tetrahedra, respectively. (b, c) $\chi_m$ in the region of the phase transition. (d, e) Heat capacity, $C_p$, in the region of the anomalies, where the red circles and blue triangles refer to the heating and cooling data, respectively.

The crystal structure of a very high quality single crystal of TiPO$_4$ was determined by x-ray single crystal diffraction measurements at various temperatures between 293 K and 90 K. Down to 90 K the structure was found to be identical to that reported by Glaum et al., except for small changes of the lattice parameters and the general atomic positions. As the temperature is lowered from RT to $\sim$120 K, the lattice parameters $a$ and $b$ increase slightly but the $c$ parameter decreases, such that the cell volume remains almost constant. The residual electron density, i.e. the measured electron density minus the calculated electron density (from the superposition of spherical atom densities) shows considerable residuals located within the $a$ - $c$ plane next to the Ti atoms, at an interstitial position in the ribbon chain, and at a position bisecting the O - Ti - O angle perpendicular to the ribbon chains. Upon cooling there is a gradual migration of the density away from the bisecting position into the interstitial position within the ribbon chains. This change is complemented by a reduction of the distance in the Ti - O - Ti, nn super-exchange pathway, and an increase of the intrachain O - Ti - O angle. Evidence for a structural change was not found in this temperature range, possibly due to the dynamic character of the intermediate phase as observed by NMR (see below).

Magic angle spinning (MAS) $^{31}$P nuclear magnetic resonance (NMR) spectra (center field $\sim$ 8.5 T) operating at a spinning frequency of $\sim$ 25 kHz, were collected on a polycrystalline sample between $\sim$ 35 K and RT. The spectra are displayed versus temperature in the main panel of Fig. Above $\sim$ 140 K we observe a single $^{31}$P symmetric NMR line accompanied by two sets of very weak symmetrically placed spinning sidebands. Near 116 K the line becomes asymmetric and below 111 K it broadens into an asymmetric continuum limited by two boundary peaks. With decreasing temperature the susceptibilities can be described very well by a $S=1/2$ Heisenberg chain with uniform nn afm SE interaction, $J_{nn}$ of 965(10) K and a g-factor of 1.94(3).

Below $\sim$ 120 K the susceptibility reveals two subsequent magnetic phase transitions, indicated by two rapid drops of the susceptibility at 111(1) K and 74(0.5) K. Finally, at lowest temperatures the susceptibility levels off to a value of $75(10)\times10^{-6}$ cm$^3$/mol. At very low temperature a slight increase is seen, which we ascribe to a Curie tail due to $\sim$70 ppm of a free $S=1/2$ spin entities. The anomaly at 74 K shows a thermal hysteresis with a temperature difference of $\sim$ 50 mK between the heating and cooling traces while heating/cooling cycles gave identical susceptibilities for the 111 K anomaly (see Fig. inset (b, c)).

Heat capacities collected on crystals exhibit two $\lambda$-type anomalies at 110.9(0.6) K and 74.1(0.3) K, with the lower temperature anomaly also showing a thermal hysteresis, while again no hysteresis is seen for the higher temperature anomaly (see Fig. inset (d, e)). Angular and temperature dependent Electron Spin Resonance measurements (ESR) on single crystals revealed a single Lorentzian resonance line ($g$-factor 1.93 - 1.95) of very weak symmetrically placed spinning sidebands. Near 116 K the line becomes asymmetric and below 111 K it broadens into an asymmetric continuum limited by two boundary peaks. With decreasing temperature the integrated intensity of the ESR line mimics the temperature dependence of the magnetic susceptibility and drops to zero below 74 K.
continuum expands and its intensity decreases. Towards ~ 76 K the continuum finally washes out, whereupon its lower boundary grows into two symmetric lines indicating the occurrence of two different P atom environments (see inset Fig. 2 (b)). The peak positions and/or boundary edges are shown versus temperature in Fig. 2 (a). There are similarities between NMR measurements of TiPO₄, reported here, and TiOX, reported by Saha et al. [26].

We now probe the SE interactions of TiPO₄ by performing mapping analysis based on density functional calculations.[27] We consider the nn and next-nearest neighbor (nnn) intrachain SE interactions J₁ and J₂, respectively, as well as the interchain SE interaction J₃ (see Fig. 3). To evaluate J₁ - J₃, we determine the relative energies of the four ordered spin states, FM, AF₁, AF₂, and AF₃ shown in Fig. 3 by density functional theory (DFT) electronic band structure calculations. Our DFT calculations employed the Vienna ab initio simulation package (Ref. 28) with the projected augmented-wave method, the generalized gradient approximation (GGA) for the exchange and the correlation functional.[31] We used a plane-wave cut-off energy of 400 eV, a set of 56 k-point irreducible Brillouin zone, and the threshold of 10⁻⁵ eV for the self-consistent-field convergence of the total electronic energy. To account for the electron correlation associated to the Ti 3d state, we performed GGA plus onsite repulsion (GGA+U) calculations (Ref. 31) with an effective U_{eff} = J - J₁ = 2 eV and 3 eV on Ti. The relative energies, per four formula units (FUs), of the four ordered spin states are summarized in Fig. 3.

The total SE energies of the four ordered spin states can be expressed in terms of a Heisenberg spin Hamiltonian, \( H = -\sum J_{ij} \vec{S}_i \cdot \vec{S}_j \), where \( J_{ij} \) is the SE interaction between the spins \( \vec{S}_i \) and \( \vec{S}_j \) on the spin sites \( i \) and \( j \), respectively. By applying the energy expressions obtained for spin dimers with \( N \) unpaired spins per spin site (in the present case, \( N = 1 \)),[29] the total SE energies for the four configurations, per four FUs, are given in Fig. 3.

Thus, by mapping the relative energies of the four ordered spin configurations given in terms of the SE parameters (see Fig. 3) onto the corresponding relative energies obtained from the GGA+U calculations, we obtained the values for the SE parameters J₁ - J₃ (see Table 1).[27, 33] The results of our DFT calculations are in very good quantitative agreement with our experimental findings indicating a very large nn intrachain afm SE interaction. The nnm intrachain SE interaction is almost two orders of magnitude smaller, the interchain interaction J₃ amounts to 2% of J₁.

The low temperature MAS data of TiPO₄ prove a non-magnetic ground state with two distinct P atomic environments, as evidenced especially by the low-temperature spectra. The chemical shifts of the ³¹P lines amount to ~ -20 ppm in good agreement with what has been found for other diamagnetic orthophosphates, proving the non-magnetic character of the ground state of TiPO₄.[34, 35] We ascribe the 74 K phase transition in TiPO₄ to a spin-Peierls transition with the Ti...Ti bond alternation within the Ti chains.

To probe the low temperature crystal structure of TiPO₄, we considered the subgroups Ammm and Pmmn of the RT space group Cmcm. By GGA calculations, we optimized the structures of TiPO₄ starting with the initial settings described by Cmcm, Ammm and Pmmn without symmetry constraints in order to allow the atom positions to relax freely (with a set of 28 k-point irreducible Brillouin zone, and the thresholds of 10⁻⁵ eV and 0.001 eV/Å for the self-consistent-field convergence of the total electronic energy and force, respectively). The lowest-energy structure found was obtained starting from the Pmmn initial setting, and was lower in energy by ~ 48 meV per formula unit than was the Cmcm structure, and by ~ 32 meV per formula unit than the Ammm initial structure. The structure relaxed from the Pmmn initial setting shows a dimerization in the Ti chains with alternating Ti...Ti bond distances of ~2.9 and ~3.5 Å, which is comparable in magnitude to that.

![Figure 3](image)

FIG. 3: (Color online) The four ordered spin configurations, FM, AF₁, AF₂ and AF₃, used to extract the values of J₁, J₂ and J₃, where only the Ti³⁺ ions are shown for simplicity. The up- and down-spin Ti³⁺ sites are indicated by different colors. The numbers in parenthesis (from left to right) represent the relative energies in meV per four FUs obtained from GGA+U calculations with U_{eff} = 2 and 3 eV, respectively. The expression of the total SE energy per four FUs is also given.

| J₁  | U = 2eV  | U = 3eV  |
|-----|----------|----------|
| J₁  | -988     | -751     |
| J₂  | -1.4     | +0.7     |
| J₃  | -20      | -15      |

TABLE I: Values of the SE parameters J₁ - J₃ derived from the mapping analysis (in K).
observed in TiOCl. This structure also has two different environments for the P atoms within the PO₄ units, which is consistent with our MAS NMR spectra. From model calculations using the relaxed crystal structure data, we expect very weak superstructure reflections, which were not resolved in an early neutron powder diffraction experiment.

The incommensurate phase seen between ~111 K and ~74 K is similar to that found for TiOX, where it has been attributed to a frustration between the spin-Peierls pairing and an elastic interchain coupling. Analogous arguments may apply for TiPO₄ as well. In view of the small interchain coupling the incommensurate phase between 111 K and 74 K could also be ascribed to a dynamic equilibrium between short-range-ordered dimmerized segments.

In conclusion, our magnetic susceptibility, heat capacity, ESR and ³¹P MAS NMR measurements supported by our density functional calculations show that TiPO₄ undergoes a spin-Peierls transition at 74.1(0.3) K, which is preceded by an incommensurate phase extending up to ~111 K. The thermal hysteretic behavior of these transitions is consistent with the pattern of discontinuous and continuous transitions seen for TiOCl and TiOBr. At high temperatures the magnetic susceptibility of TiO₄ is described by a $S=1/2$ Heisenberg antiferromagnetic chain with an unprecedented nn SE of ~1000 K.

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