

# Magnetic properties of the antiferromagnetic spin- $\frac{1}{2}$ chain system $\beta$ -TeVO<sub>4</sub>

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(Received 5 June 2011; published 30 September 2011)

The magnetic susceptibility and magnetization of high-quality single-crystal  $\beta$ -TeVO<sub>4</sub> are reported. We show that this compound, made of weakly coupled infinite chains of VO<sub>5</sub> pyramids sharing corners, behaves as an  $S = \frac{1}{2}$  one-dimensional Heisenberg antiferromagnet. From magnetic experiments, we deduce the intrachain antiferromagnetic coupling constant,  $J/k_B = 21.4 \pm 0.2$  K. Below 5 K, a series of three phase transitions at 2.26, 3.28, and 4.65 K is observed.

DOI: [10.1103/PhysRevB.84.104447](https://doi.org/10.1103/PhysRevB.84.104447)

PACS number(s): 75.50.Ee, 75.40.Cx, 75.30.Et, 75.10.Pq

## I. INTRODUCTION

Vanadium oxides with the V<sup>4+</sup> ions ( $S = \frac{1}{2}$ ) are excellent model systems for one-dimensional spin- $\frac{1}{2}$  quantum magnets. Most studies have been focused on two classes of vanadium oxide chains with edge- and corner-shared VO<sub>n</sub> polyhedra (VO<sub>5</sub> square pyramids or VO<sub>6</sub> octahedra). Compounds in which adjacent building blocks share their edges are good realizations of the one-dimensional (1D) Heisenberg Hamiltonian.<sup>1</sup> In compounds built up of the corner-sharing topology, nearest-neighbor (NN) exchange coupling may be more than an order of magnitude smaller,<sup>2,3</sup> and the next-nearest-neighbor (NNN) interactions play an important role. The interplay between frustration and quantum spin fluctuations results in a rich phase diagram with commensurate/incommensurate phases and unusual magnetic properties of these materials.

Recently,  $\alpha$ -TeVO<sub>4</sub> with the zigzag chains formed by distorted VO<sub>6</sub> octahedra sharing edges have been discovered as a quasi-one-dimensional spin- $\frac{1}{2}$  Heisenberg system with alternating NN ferromagnetic (FM) interactions and NNN antiferromagnetic (AF) interaction.<sup>4</sup> As it was known,<sup>5</sup> the compound TeVO<sub>4</sub> can be prepared in two different crystalline forms with a reversible polymorphic transformation at 650 °C ( $\alpha \leftrightarrow \beta$ ). In contrast to  $\alpha$ -phase,  $\beta$ -TeVO<sub>4</sub> has a significant difference in its structure: The zigzag chains are formed by distorted VO<sub>5</sub> pyramids sharing their corners. Thus, the corner-sharing of VO<sub>5</sub> pyramids can lead to the considerable reduction in the scale of the existing exchange interactions in the 1D spin system.

In this paper, we report on the single-crystal magnetic properties of a quasi-one-dimensional spin- $\frac{1}{2}$  chain system,  $\beta$ -TeVO<sub>4</sub>. Though this compound phase has been known for a long time,<sup>5</sup> to our knowledge, its magnetic properties on powdered or single-crystal samples were hitherto not reported at all. We discuss that the actual topology of magnetic couplings for such system might indeed be more complex than originally envisioned.

## II. EXPERIMENTAL DETAILS

The growth of  $\beta$ -TeVO<sub>4</sub> single crystals has been described elsewhere.<sup>5</sup> A sample with dimensions of  $3 \times 2 \times 4$  mm<sup>3</sup> was oriented using x-ray Laue diffractometry. Variable-temperature magnetic susceptibility measurements in the

temperature range 1.9–400 K and at magnetic fields of 0.001–0.1 T along three crystallographic axes were carried out on a single-crystal sample of  $\beta$ -TeVO<sub>4</sub> ( $m = 128.33$  mg) using a Quantum Design SQUID magnetometer MPMS-XL5. Susceptibility measurements were complemented by isothermal magnetization runs at temperatures between 2 and 50 K for fields up to 5 T.

## III. RESULTS AND DISCUSSION

### A. Structure description and important parameters

The compound  $\beta$ -TeVO<sub>4</sub> crystallizes in the monoclinic system with the space group  $P2_1/c$  and the parameters:  $a = 4.379 \pm 0.002$  Å,  $b = 13.502 \pm 0.004$  Å,  $c = 5.446 \pm 0.002$  Å, and  $\beta = 91.72 \pm 0.05^\circ$  with  $Z = 4$  (f.u. TeVO<sub>4</sub> per unit cell).<sup>5</sup> The crystal structure of  $\beta$ -TeVO<sub>4</sub> is shown in Fig. 1. The structure consists of zigzag chains (double chains) parallel to the  $c$  axis formed by slightly distorted square pyramids of VO<sub>5</sub> sharing corners. There are two identical zigzag chains, in which all apices of square pyramids are pointing alternatively below and above the  $bc$  plane. The lone pair cation Te<sup>4+</sup> leads to a magnetic separation of chains with respect to each other. A twofold axis  $C_2$  is directed along the  $b$  axis of the crystal. In accordance to the symmetry properties, there is only one symmetry-independent position for the vanadium atom, and only one NN exchange path for the V<sup>4+</sup> ions through the corner oxygens (the V–O–V angle is  $133.7^\circ$ ) into a chain is expected. The nearest intrachain distance is V–V =  $3.6427$  Å. The nearest V–V distances perpendicular to the chain direction are  $4.9149$  (along the  $b$  axis) and  $4.3790$  Å (along the  $a$  axis), respectively.

Figure 2 shows the nearest oxygen environment of a vanadium atom in the crystal structure  $\beta$ -TeVO<sub>4</sub>. Each vanadium atom is surrounded by five nearest-neighbor oxygen atoms forming a slightly distorted square pyramid VO<sub>5</sub>. A sixth oxygen neighbor, O<sub>ap</sub>', which can be also interpreted as an apical oxygen of the next VO<sub>5</sub> pyramid, is found at a much longer distance (V–O<sub>ap</sub>' =  $2.772$  Å,  $\angle[\text{O}_{\text{ap}}\text{--V--O}_{\text{ap}}'] = 173.6^\circ$ ) in the position usually issued from a highly distorted octahedron VO<sub>6</sub> (see Figs. 1 and 2). The apical distance V–O<sub>ap</sub> ( $1.613$  Å) is much smaller than the V–O distances involving either the oxygens contained in the pyramid basal plane ( $1.927\text{--}2.035$  Å), or the sixth oxygen O<sub>ap</sub>' ( $2.772$  Å).

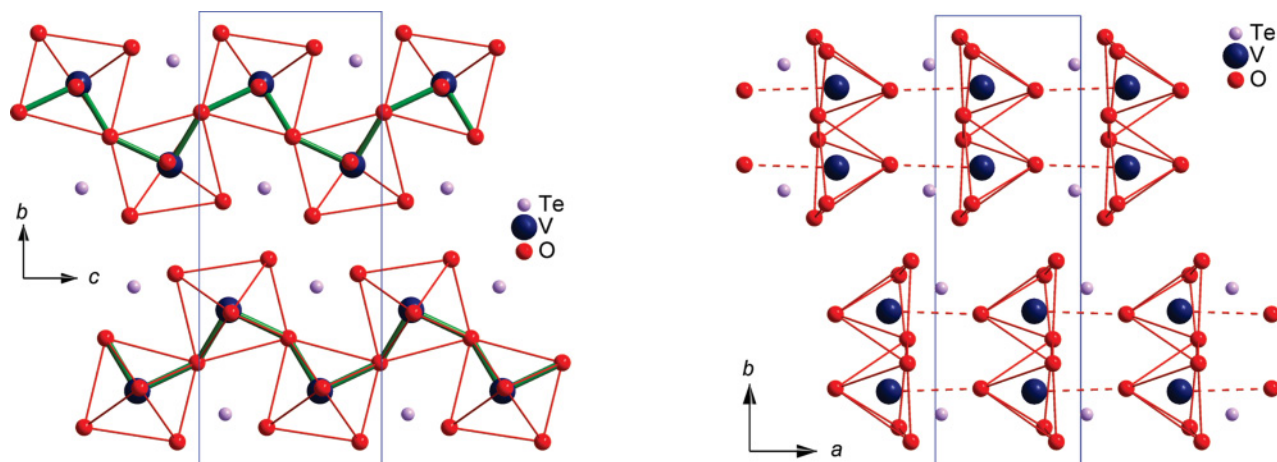


FIG. 1. (Color online) Crystal structure of  $\beta$ -TeVO<sub>4</sub>, viewed along  $a$  (left) and  $c$  (right) axis. The corner-sharing paths in a zigzag chain responsible for nearest-neighbor exchange interactions are shown by the thick green lines. The V–O bonds between the nearest VO<sub>5</sub> pyramids along the  $a$  axis are shown as dashed lines.

The presence of additional long bond V–O<sub>ap</sub>' might give a possibility to ascribe the nearest environment of the vanadium atoms as a highly distorted octahedron, but the obtained large shift of 0.515 Å for a vanadium atom from the basal oxygen plane is in favor of a square pyramidal environment. Additionally, note that the typical range of the longest apical bonds for a distorted octahedron VO<sub>6</sub> is usually  $2.10 < d(V^{4+}-O_{ap}) < 2.70$  Å.<sup>6</sup> In the case of the “octahedron presentation,” the crystal structure of  $\beta$ -TeVO<sub>4</sub> might be regarded as a two-dimensional framework with well-separated layers of the distorted VO<sub>6</sub> octahedra perpendicular to the  $b$  axis. As was shown in Ref. 7, the exchange pathway through common apical corners of VO<sub>6</sub> octahedra leads to a very weak magnetic interaction between the V<sup>4+</sup> ions with a magnitude smaller than 2 K, and therefore pronounced two-dimensional magnetic behavior of  $\beta$ -TeVO<sub>4</sub> is not expected.

Each square pyramid VO<sub>5</sub> may actually be seen as a vanadyl V≡O<sub>ap</sub> cation lying above a slightly distorted square of O<sup>2-</sup> anions. The apical V–O<sub>ap</sub> bond is not rigorously perpendicular to the basal oxygen plane of the square pyramids (the angle is 87.831°). As was mentioned in Ref. 8, the existence of an apical oxygen O<sub>ap</sub> is crucial in such compounds, since the shortest V–O<sub>ap</sub> distance allows the possibility of a strong delocalization to occur between these two atoms and a

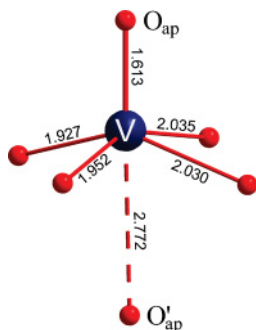


FIG. 2. (Color online) Oxygen environment of the V<sup>4+</sup> ion in crystal structure of  $\beta$ -TeVO<sub>4</sub>. The length of V–O bonds is shown in Å.

multiple vanadium-oxygen covalent bond to take place. The experimental signature of such a strong multiple bond in the Raman spectra is the presence of a sharp peak at relatively high energy, corresponding to the stretching mode. This peak, for example, occurs at 969 cm<sup>-1</sup> for  $\alpha'$ -NaV<sub>2</sub>O<sub>5</sub>,<sup>9</sup> and at 932 cm<sup>-1</sup> and 1002 cm<sup>-1</sup> for CaV<sub>2</sub>O<sub>5</sub> and MgV<sub>2</sub>O<sub>5</sub>,<sup>10</sup> respectively.

The corner linkages of the VO<sub>5</sub> pyramids in the chain of  $\beta$ -TeVO<sub>4</sub> revealed here are almost identical to those of the zigzag chain compounds CdVO<sub>3</sub><sup>2</sup> and CaV<sub>2</sub>O<sub>5</sub><sup>3</sup> formed by sharing edges and corners of VO<sub>5</sub> pyramids. The V–O–V angles for the corner-sharing paths in CdVO<sub>3</sub> and CaV<sub>2</sub>O<sub>5</sub> are 136.1° and 135.3°, respectively. Both compounds have a nearest-neighbor V–V distance of around 3.60 Å. Magnetic study of the zigzag chain of CdVO<sub>3</sub> has demonstrated that the corner-sharing exchange coupling is quite small and is not relevant to the magnetic properties of this compound. This statement is also consistent with an isolated dimer model for the zigzag chain compound CaV<sub>2</sub>O<sub>5</sub>. Therefore, the NN exchange interactions (see  $J_1$  in Fig. 3), which are due to corner-sharing paths in the chain of  $\beta$ -TeVO<sub>4</sub>, are expected to be weak in magnitude. In this case, we should take also into account the possible NNN exchange paths like V–O–O–V (see  $J_2$  in Fig. 3), which has connectivity through two oxygens of the basal plane. Thus, an

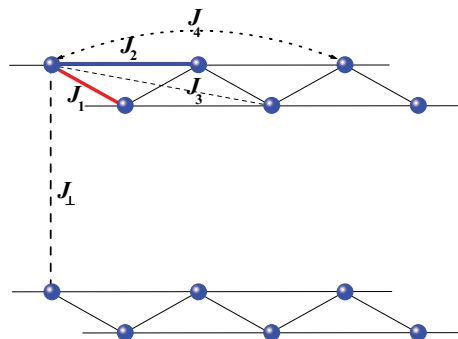


FIG. 3. (Color online) A schematic view of exchange interactions between the V<sup>4+</sup> ions in  $\beta$ -TeVO<sub>4</sub>. The most important magnetic interactions are sketched.

effective 1D magnetic model might also be seen as a network of isolated two-leg ladders (double chains) with two different exchange integrals,  $J_1$  and  $J_2$  ( $J_1$ - $J_2$  model). The period of each “leg” of the double spin chains is equal to  $c$ . The two legs are offset by  $c/2$  relative to each other and thus form a “triangular ladder.” In the purely 1D case, depending on the sign and magnitudes of  $J_1$  and  $J_2$ , the ground state of the isolated  $J_1$ - $J_2$  model might be either the quantum disordered gapped state (with commensurate or incommensurate spin correlations) or the gapless state with commensurate spin correlations. Note, for  $J_1 \gg J_2 \rightarrow 0$  or  $J_2 \gg J_1 \rightarrow 0$ , the  $J_1$ - $J_2$  model transforms to a uniform spin- $\frac{1}{2}$  chain system. In the case of weakly coupled chains in three dimensions, a large variety of magnetic ground states of the system might be realized: a disordered gapped state (nonmagnetic at  $T = 0$ ), a collinear long-range Neel state, a helimagnetic long-range order, and, finally, in a certain temperature range, a chiral long-range order with broken symmetry of left/right spirals and helimagnetic incommensurate short-range correlations without magnetic long-range order.

Further complicating the model, similar to the “NNN” case, we can even consider the nearest-neighbor pathways of the higher order: *third-* or *fourth-* nearest-neighbor exchange interactions through the V-O-O-O-V or V-O-O-O-O-V bridges, respectively. A total scheme of possible exchange interactions between the  $V^{4+}$  ions in  $\beta$ -TeVO<sub>4</sub> is illustrated in Fig. 3. It should be noted that for a  $J_1$ - $J_2$  model, the presence of the third interchain interaction  $J_{\perp}$  (possibly quite weak in its amplitude) through the bridge V-O<sub>ap</sub>-V between neighboring pyramids in  $\beta$ -TeVO<sub>4</sub> and/or the existence of the nonzero

*third-* or *fourth-*nearest-neighbor coupling constant (see  $J_3$  or  $J_4$  in Fig. 3) gives a total similarity with the exchange model topology, which have been proposed and discussed for quasi-one-dimensional helimagnets LiCu<sub>2</sub>O<sub>2</sub><sup>11</sup> and NaCu<sub>2</sub>O<sub>2</sub><sup>12</sup>.

Thus, the structural data allow us to consider the compound  $\beta$ -TeVO<sub>4</sub> as a uniform spin- $\frac{1}{2}$  chain system (for the small exchange magnitudes, possibly with competing NN and NNN interactions, alternating AF/FM exchange interactions, anisotropic and antisymmetric Dzyaloshinskii-Moriya interactions).

## B. Magnetic susceptibility and magnetization

The magnetic susceptibilities  $\chi(T) = M(T)/H$  of single-crystal  $\beta$ -TeVO<sub>4</sub> ( $M$  denotes the magnetic moment of the sample) measured along three principal crystallographic  $a$ ,  $b$ ,  $c$  axes are shown in Fig. 4. The inverse magnetic susceptibility  $\chi^{-1}(T)$  and the product  $\chi(T)T$  for the same data are shown in the insert of Fig. 4 and in Fig. 5, respectively. The magnetic data were found to be reversible upon cooling and heating with no indications for hysteretic behavior. The collapse of the susceptibility data onto a single curve for various measured fields indicates that no significant field dependence occurs over the whole temperature (5–400 K) and magnetic field (0.001–0.1 T) range under investigation. We have estimated a diamagnetic contribution from the closed atomic shells for  $\beta$ -TeVO<sub>4</sub> as  $-9.5 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$  by using tabulated values for Pascal’s constants.<sup>13</sup>

In Fig. 4, magnetic susceptibility data show a noticeable axial anisotropy of magnetic properties of single-crystal  $\beta$ -TeVO<sub>4</sub> with respect to the crystallographic  $b$  axis. The ratio

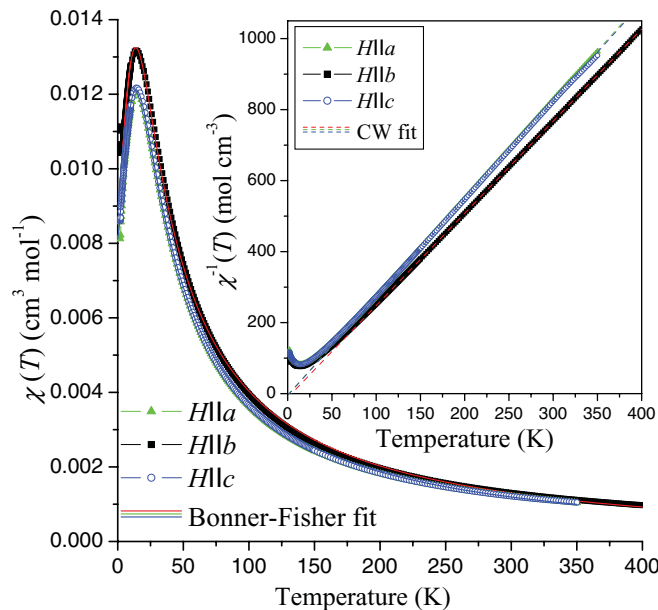


FIG. 4. (Color online) Temperature dependence of molar magnetic susceptibility  $\chi(T)$  of single-crystal  $\beta$ -TeVO<sub>4</sub> measured in a magnetic field  $H = 0.02$  T applied along three crystallographic axes. The solid lines show the best fit for a uniform AF spin- $\frac{1}{2}$  chain (Bonner-Fisher model) with parameters specified to Table II. The insert shows temperature dependence of the inverse magnetic susceptibility  $\chi^{-1}(T)$  and the best fit by using a Curie-Weiss law (dashed lines, examined in the range 150–400 K).

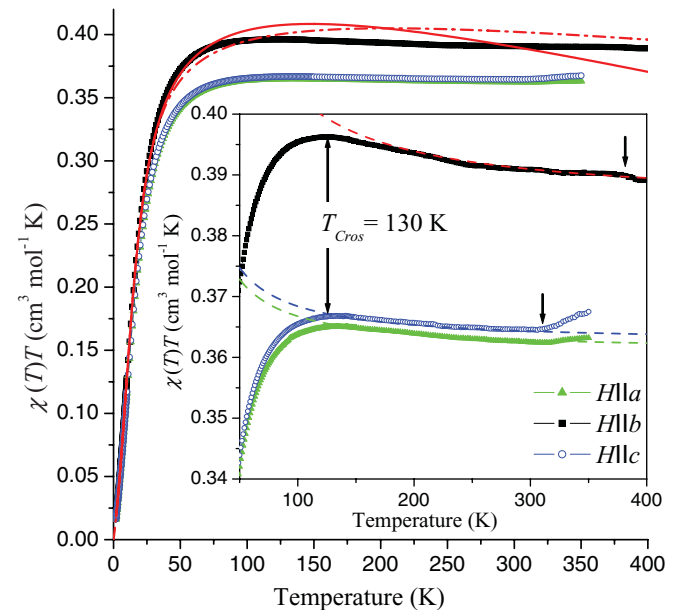


FIG. 5. (Color online) The product  $\chi(T)T$  of single-crystal  $\beta$ -TeVO<sub>4</sub> as a function of temperature  $T$  for three crystallographic directions. The solid line shows the result of a fit to the uniform 1D chain model, whereas the dot-dashed line is the best fit for the weakly coupled AF chain model ( $H||b$ ). The insert shows the enlarged scale of high-temperature behavior. The dashed lines are the results for Curie-Weiss law with magnetic parameters specified to the Table I.

TABLE I. Effective magnetic parameters for a Curie-Weiss model used in high-temperature range (150–400 K).

Field direction	Curie constant $C$ ( $\text{cm}^3 \text{mol}^{-1} \text{K}$ )	Curie-Weiss temperature $\theta$ (K)	$g$ -value for the $\text{V}^{4+}$ ion extracted from $C$
$H \parallel b$	0.3852	+4.418	2.027
$H \parallel a$ ( $H \perp b$ )	0.3609	+1.598	1.962
$H \parallel c$ ( $H \perp b$ )	0.3623	+1.658	1.965

between magnetic susceptibility for  $H \parallel b$  and  $H \perp b$  keeps a constant value of  $\chi_{\parallel}/\chi_{\perp}$  ( $\chi_{\parallel} \gg \chi_{\perp}$ ) in the whole temperature range. For magnetic fields applied within the  $ac$  plane ( $H \perp b$ ), we did not find any significant difference in magnetic behavior of the studied system. The most probable explanation of such magnetic anisotropy is due to an axial symmetry of the  $g$ -tensor for the  $\text{V}^{4+}$  ions with a square-pyramidal environment. For example, the estimated  $g$ -values extracted from Curie constants (see Table I) show good agreement with the expected ones from the literature.<sup>14</sup> The fact that the  $b$  axis is a preferential magnetic direction of the crystal might be contradicted by the obtained crystallographic data, especially with the spatial orientation of the  $\text{VO}_5$  pyramids, in which all apical axes (a short  $\text{V}-\text{O}_{\text{ap}}$  bond) are located along the crystallographic  $a$  axis. To clarify this question, it is additionally necessary to perform electronic structure calculations in order to identify the real spatial orientation of the vanadium  $3d$  magnetic orbitals in the crystal structure of  $\beta$ - $\text{TeVO}_4$ .

The main feature of the three  $\chi(T)$  curves for the  $a$ ,  $b$ ,  $c$  axes is the presence of a maximum at  $T_{\chi_{\text{max}}} = 14.0 \pm 0.1$  K (a temperature at which  $d\chi/dT = 0$ ), which is characteristic for low-dimensional spin systems. Note, the magnetic susceptibility of a uniform antiferromagnetic Heisenberg spin- $\frac{1}{2}$  chain is characterized by a maximum in  $\chi$  at a temperature  $T_{\chi_{\text{max}}} = 0.640851 \cdot |J_{1D}|/k_B$  with a value  $\chi_{\text{max}} = 0.146926 \cdot N g^2 \mu_B^2 / |J_{1D}|$ .<sup>15,16</sup> By using these relations, we can easily estimate an expected AF exchange coupling as  $|J_{1D}|/k_B = 21.8$  K and an axial  $g$ -tensor with  $g = (2.188, 2.285, 2.196)$ , which is a little bit larger than expected for the  $\text{V}^{4+}$  ions. From high-temperature series expansion of  $\chi(T)$ , a negative AF Curie-Weiss temperature  $\theta_{1D} = -\frac{1}{2}|J_{1D}|/k_B \approx -10.9$  K in the Curie-Weiss law  $\chi(T) = C/(T - \theta_{1D})$  is expected.

Additional details of the high-temperature behavior become more visible in the plot of  $\chi(T)T$  vs  $T$  presented in Fig. 5. A closer look at the product  $\chi(T)T$  gives an indication of the presence of the weak ferromagnetic spin-spin correlations down to  $T_{\text{Cros}} = 130$  K: The value of  $\chi(T)T$  continuously increases on cooling to reach a broad maximum at  $T_{\text{Cros}} = 130$  K and then rapidly decreases when the temperature is lowered, which is the typical nature of significant antiferromagnetic exchange interactions between the magnetic centers. A broad crossover at  $T_{\text{Cros}}$  separates two different magnetic regimes with predominantly ferro- and antiferromagnetic correlations above and below this temperature. Note, such a scenario is possible only for the complex topology of the exchange pathways in low-dimensional spin systems. In addition, there are two features at 315 K ( $H \perp b$ ) and at 380 K ( $H \parallel b$ ) marked by vertical arrows in the insert of Fig. 5, which might be due to other magnetic instabilities and require a further investigation.

### 1. Magnetization

Magnetization curves measured in the temperature range 2–50 K in the applied fields along three crystallographic axes were well proportional to the applied magnetic field, which implies that a significant spin gap is not present in this system. No remanent magnetization at  $H = 0$  is detected. Figure 6 shows the magnetization  $M(H)$  vs  $H$  along the  $b$  axis at varying temperatures from 2 to 50 K.

From isothermal magnetization measurements in magnetic fields of 0–5 T at varying temperatures, we have extracted the values for the differential magnetic susceptibilities  $(\frac{dM(T)}{dH})_{H \rightarrow 0}$ , which can be compared with magnetic data presented in Fig. 4. The collapse of the susceptibility data is absolute. Figure 6 shows a perfectly linear regime of the magnetization  $M(H)$ , at least above 5 K.

### 2. Low-temperature behavior of magnetic susceptibility (below 5 K)

The low-temperature behavior of magnetic susceptibility  $\chi(T)$  of single-crystal  $\beta$ - $\text{TeVO}_4$ , measured in a magnetic field along the  $a$ ,  $b$ , and  $c$  axes, is presented in Fig. 7. This is an enlarged low-temperature part of data set shown in the main panel of Fig. 4. Below 5 K, three different magnetic features at  $T = 2.26, 3.28,$  and  $4.65$  K are observed. The

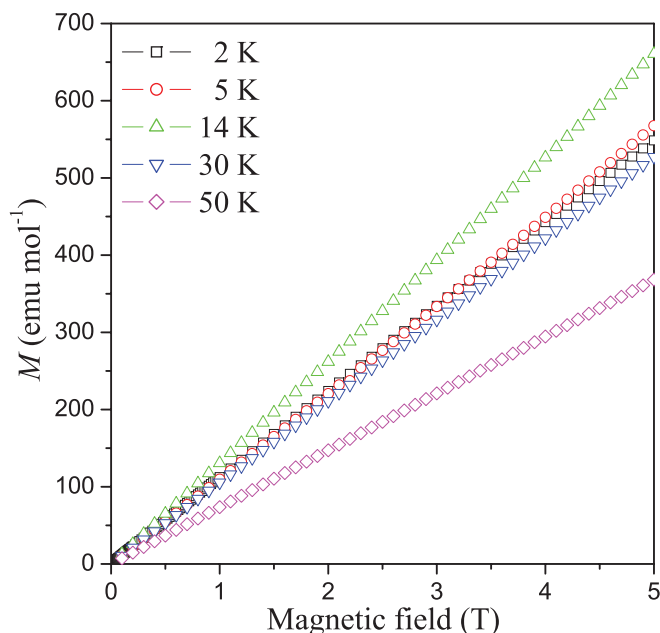


FIG. 6. (Color online) Isothermal magnetization measurements in DC fields from 0 to 5 T along the  $b$  axis at varying temperatures as indicated in the figure.

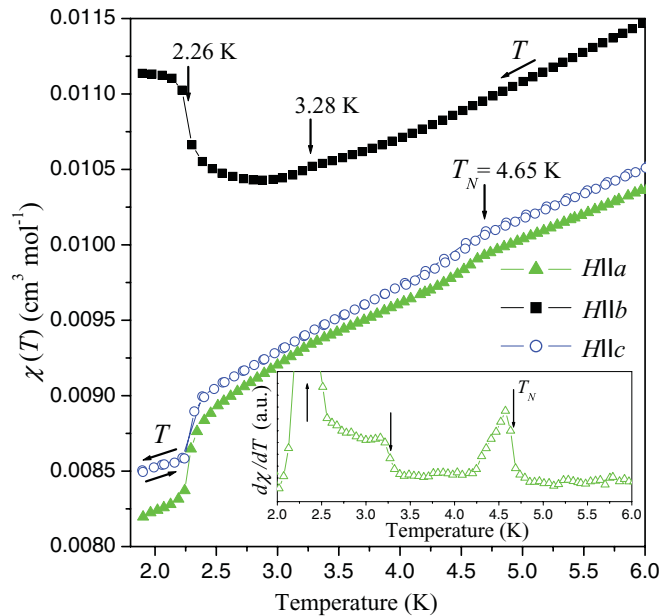


FIG. 7. (Color online) Low-temperature behavior of magnetic susceptibility  $\chi(T)$  of single-crystal  $\beta$ -TeVO<sub>4</sub> measured in a magnetic field  $H = 0.02$  T applied along three crystallographic axes. The vertical arrows indicate three observed magnetic features. The insert shows  $d\chi/dT$  vs  $T$  for  $H||a$ .

first two, at 3.28 and 4.65 K, look like a kink on  $\chi(T)$ . The high-temperature kink is more highly visible for  $H\perp b$ , while the low-temperature kink is more pronounced for  $H||b$ . A closer look at the derivative  $d\chi/dT$  vs  $T$  (see inset in Fig. 7) gives us a proof that both of these features simultaneously exist for any orientation of measured field. The third feature at 2.26 K looks like a jump (with a step-like shape) on  $\chi(T)$  and has much stronger amplitude than the previous two. Note, there is a “sign” change in the susceptibility jump from “−” to “+” for directions perpendicular and along the  $b$  axis. All three features do not show any significant hysteresis behavior upon cooling and warming up (see, for instance, the curve for  $H||c$ ). All three features might be interpreted as a series of magnetic phase transitions in a low-dimensional spin system. However, the nature of each phase transformation is unknown. Taking into account the predominant character of antiferromagnetic correlations below 130 K, we can assume that the compound at  $T_N = 4.65$  K undergoes a magnetic phase transition into a long-range-ordered AF magnetic state, and the next two features are due to further modifications of the antiferromagnetic ordered phase. Such a scenario containing a series of a few phase transitions pointing to a complex multistage rearrangement of the spin structure was reported for the quasi-one-dimensional helimagnetic systems LiCu<sub>2</sub>O<sub>2</sub><sup>17</sup> and NaCu<sub>2</sub>O<sub>2</sub><sup>12</sup>. Specific heat measurements are better suited to unambiguously identify  $T_N$  and the nature of other two features in  $\beta$ -TeVO<sub>4</sub> and are in progress.

Note, the absence of any characteristic upturns of  $\chi(T)$  in the low-temperature range (below 2.2 K) indicates that the Curie tail is very weak in  $\beta$ -TeVO<sub>4</sub> and provides testimony to the high quality of the single crystal without any impurity or defects.

### 3. Analysis

The analysis of the magnetic properties of  $\beta$ -TeVO<sub>4</sub> was performed in the following three steps. First, in the high-temperature range 150–400 K, we used a Curie-Weiss law to obtain preliminary information on the sign and average magnitude of the exchange correlations between the V<sup>4+</sup> ( $S = \frac{1}{2}$ ) ions. Then, we made an attempt to analyze the obtained experimental data within the framework of a few microscopic models with a uniform exchange coupling constant (FM or AF) between nearest-neighbor spins into the chain. In a third step, we considered several 1D models that are “exotic” for a given case. The main purpose of this analysis was to find a magnetic model yielding a good qualitative and quantitative agreement with experimental data in the wide temperature range (above the long-range ordering  $T_N$ ).

(a) *High-temperature range.* In a first attempt at setting up a simple model capable of describing the main features of the magnetic susceptibility of  $\beta$ -TeVO<sub>4</sub> at high temperatures above 130 K, magnetic behavior can be assigned to Curie-Weiss-like temperature dependence  $\chi(T) = C/(T - \theta)$  with a Curie constant  $C$  and a Curie-Weiss temperature  $\theta$ . A Curie-Weiss fit of magnetic susceptibility in the temperature range 150 K  $< T < 400$  K yields a Curie constant  $C_b = 0.3852$  cm<sup>3</sup> mol<sup>−1</sup> K and a positive Curie-Weiss temperature of  $\theta_b = +4.418$  K for a magnetic field applied along the  $b$  axis. For magnetic fields applied within the  $ac$  plane ( $H\perp b$ ), we find  $C_a = 0.3609$  cm<sup>3</sup> mol<sup>−1</sup> K and  $\theta_a = +1.598$  K (along the  $a$  axis) and  $C_c = 0.3623$  cm<sup>3</sup> mol<sup>−1</sup> K and  $\theta_c = +1.658$  K (along the  $c$  axis), respectively. The results are summarized in Table I. The obtained Curie constant is consistent with the presence of one V<sup>4+</sup> ion ( $S = \frac{1}{2}$ ) per formula unit yielding a spin-only value of  $C_{\text{theory}} = 0.3751$  cm<sup>3</sup> mol<sup>−1</sup> K. The latter number is based on a spectroscopic  $g$ -value of 2.0. It should be noted that the  $g$ -tensor extracted from the obtained Curie constant ( $C = \frac{N\mu_B^2 g^2 S(S+1)}{3k_B}$ , where  $N$  is Avogadro’s number,  $\mu_B$  is the Bohr magneton,  $k_B$  is the Boltzmann constant,  $S = \frac{1}{2}$ , and the  $g$ -value is for the V<sup>4+</sup> ions) has an axial anisotropy, and its components ( $g_{\perp}$ ,  $g_{\parallel}$ ) are in satisfactory agreement to the expected ones from the literature (see Table I). The expected range of the spectroscopic  $g$ -values for the V<sup>4+</sup> ions within a square-pyramidal oxygen environment is 1.94–1.98.<sup>14</sup> Note, such anisotropy supposes that the magnetic orbitals of the V<sup>4+</sup> ions with a square-pyramidal environment are orthogonal to a very short vanadyl bond V–O<sub>ap</sub> (and to a zigzag chain direction too). The positive Curie-Weiss temperatures indicate a possible predominant ferromagnetic character of the interactions with quite small amplitudes (or a sum of AF and FM interactions with almost similar exchange strength). It is possible to discuss a small axial anisotropy for these effective ferromagnetic interactions, which follows from the different Curie-Weiss temperatures of the system along and perpendicular to the  $b$  axis.

At a first glance, the fit by using a simple Curie-Weiss law agrees quite well with the experimental data in the high-temperature region (see the dashed lines in inset of Figs. 4 and 5). However, it should be noted that a simple Curie-Weiss law can not explain the strong decrease in  $\chi(T)T$  below  $T_{\text{Cros}} = 130$  K, which is clearly indicative of the dominant antiferromagnetic interactions in this compound. Thus,

for a low-temperature range, the search for an appropriate microscopic magnetic model would be desirable.

(b) *Uniform exchange coupling model.* The uniform Heisenberg spin- $\frac{1}{2}$  chain with FM or AF coupling is a magnetic model that is frequently realized in low-dimensional solids. The isotropic AF spin- $\frac{1}{2}$  Heisenberg chain was first diagonalized by Bethe.<sup>18</sup> The spin Hamiltonian of the uniform Heisenberg spin- $\frac{1}{2}$  chain  $H = -J \sum_i \vec{S}_i \cdot \vec{S}_{i+1}$  (for  $J > 0$  and  $J < 0$ ) was examined by Bonner and Fisher (1964).<sup>16</sup> Following these works, many important properties with the highest accuracy for this model have been obtained by several authors.<sup>15,19</sup>

Taking into account only the structural data and without additional knowledge about the studied system, it is difficult to predict the exact relationship and the signs of all exchange integrals  $\{J_1, J_2, J_3, J_4\}$  in the zigzag chain of  $\beta$ -TeVO<sub>4</sub>. Let's discuss a  $J_1$ - $J_2$  model ( $J_1, J_2 \gg J_3, J_4$ ), where  $J_1$  and  $J_2$ , for instance, are the NN (V–O–V) and NNN (V–O–O–V) exchange paths (see Fig. 3). The presence of a broad crossover may provide a different sign for two these interactions. Under the conditions  $|J_1| \gg |J_2|$  or  $|J_1| \ll |J_2|$ , the zigzag chain has the main properties of a uniform FM or AF spin- $\frac{1}{2}$  Heisenberg chain with the smallest exchange as a model extension. It should be noted that the model of a uniform FM spin chain coupled with a weak AF interaction (FM  $|J_1| \gg$  AF  $|J_2|$ ) cannot be applied for our case because, for this model, the maximum of ferromagnetic susceptibility  $\chi_{\max}$  and its temperature position  $T_{\chi_{\max}}$  may have a strong field dependence, as expected.<sup>16</sup> In contrast to this, our experimental data do not show any field dependence on the magnetic susceptibility of  $\beta$ -TeVO<sub>4</sub>. Thus, we will try to assume that the sign of dominant exchange is presumably AF, while the next one is probably FM (FM  $|J_1| \ll$  AF  $|J_2|$ ). This assumption, as well as taking into account the possible influence of other weak interactions  $J_3, J_4$ , and  $J_{\perp}$ , suggests that the magnetic interactions are frustrated, and the magnetic model is close to a system of weakly coupled antiferromagnetic chains ( $|J_2| \gg |J_1|, |J_3|, |J_4|, |J_{\perp}|$ ). Thus, we will try to estimate two effective magnetic parameters: the dominant intrachain exchange coupling  $J$  ( $J \equiv J_2$ ) and the interchain interaction  $J'$ , which is the result of some combination of all weak interactions  $\{J_1, J_3, J_4, J_{\perp}\}$  and leads to the long-range magnetic order at low temperatures.

To determine the dominant antiferromagnetic exchange parameter  $J$ , we fit our magnetic susceptibility measurements with an expression of the form:

$$\chi(T) = \chi_{1D}(T) + \chi_{\text{TIP}}. \quad (1)$$

$\chi_{1D}(T)$  is the contribution of the spin  $S = \frac{1}{2}$  Heisenberg antiferromagnetic chains, which is known with a high precision over the whole measured temperature range.<sup>15</sup> We took the polynomial approximation of Bonner and Fisher (a well-known Bonner-Fisher model):

$$\chi_{1D}(T) = \frac{Ng^2\mu_B^2}{k_B T} \frac{0.25 + 0.074975x + 0.075236x^2}{1 + 0.9931x + 0.172135x^2 + 0.757825x^3}, \quad (2)$$

where  $x = |J|/k_B T$ . The presence of weak ferromagnetic correlations at the high temperatures was accounted for by

TABLE II. Magnetic parameters extracted using Bonner-Fisher model in the temperature range 5–400 K.

Field direction	$J/k_B$ (K)	$g$	$\chi_{\text{TIP}}$ ( $\times 10^{-4}$ cm <sup>3</sup> mol <sup>-1</sup> )
$H  b$	21.20	2.280	-2.5
$H  a$ ( $H \perp b$ )	21.41	2.185	-2.5
$H  c$ ( $H \perp b$ )	21.56	2.200	-2.5

using an additional temperature-independent parameter  $\chi_{\text{TIP}}$  with a small negative value. The chosen value of  $\chi_{\text{TIP}}$  is comparable in amplitude with the estimated value of the diamagnetic contribution for  $\beta$ -TeVO<sub>4</sub>. One can note that the proposed AF uniform exchange coupling model provides a good fit to the measured curves in the wide temperature range 5–400 K (see solid lines, mostly hidden by the experimental data, in Fig. 4). The best least-squares fit parameters are summarized in Table II. The most important conclusions that emerge from this analysis are the following: (i) The compound  $\beta$ -TeVO<sub>4</sub> exhibits a rather pronounced  $S = \frac{1}{2}$  quasi-1D antiferromagnetic behavior over a wide temperature range; and (ii) the value of the single antiferromagnetic *intrachain* exchange constant can be evaluated as  $J/k_B = 21.4 \pm 0.2$  K, quite independently of the choice of principal crystallographic direction. There is only one open question: The obtained  $g$ -values (2.18–2.28) are much bigger than expected ones (1.94–1.98) from the literature and those estimated from high-temperature analysis.

In the next step of analysis, we can introduce the further conjunction between the AF spin chains, which is due to the effective interchain interaction  $J'$  ( $J' \ll J$ ). The magnetic behavior of weakly coupled chains in a quasi-one-dimensional spin system can be described by a chain mean-field theory developed by Schulz.<sup>20</sup> This theory gives the relations among the ordered magnetic moment  $m_0$ , the ordering temperature  $T_N$ , the main antiferromagnetic exchange coupling  $J$ , and the average of interchain interactions  $|J'|$  in a quasi-one-dimensional spin system. One of these relations allows an estimate for  $|J'|$ :

$$|J'| = \frac{T_N}{4 \cdot 0.32 (\ln(5.8J/T_N))^{1/2}}. \quad (3)$$

In our case, where  $T_N = 4.65$  K and  $J/k_B = 21.4$  K, this gives  $|J'|/k_B = 2.00$  K. The real value for  $|J'|$  may be even somewhat higher because quantum fluctuations are not fully accounted for in the chain mean-field theory. Thus, the ratio between interchain and intrachain coupling is  $9.3 \times 10^{-2}$ , showing that this compound is a quasi-one-dimensional spin-system.

In order to estimate the average amplitude and the sign of the possible interchain interaction  $J'$ , we will try to reanalyze the experimental data in the temperature range 5–400 K by using the following mean-field approximation for magnetic susceptibility:

$$\chi_{MF}(T) = \frac{\chi_{1D}}{1 + (2zJ'/Ng^2\mu_B^2)\chi_{1D}}, \quad (4)$$

where  $z$  is the number of nearest neighbors. The important conclusions from this analysis are: (i) the sign of the average *interchain* interaction  $J'$  is negative, which is in favor of weak ferromagnetic interchain correlations; (ii) the best fit gives a parameter  $z|J'|/k_B$  of ferromagnetic coupling of the order of 0.3–0.9 K; and (iii) the presence of the weak *interchain* interactions does not affect the value of the main antiferromagnetic *intrachain* coupling ( $J \gg J'$ ) and does not bring a significant improvement to the description accuracy of the experimental data set as a whole. Note, as it is demonstrated in Fig. 5, the description using an isolated and weakly coupled chain model is in quite good agreement with the experimental data at low temperatures and is not perfect above  $T_{\text{Cros}} = 130$  K (see, for example, the solid and dot-dashed lines as the best fits for  $\mathbf{H} \parallel b$ ).

As one of the last possible extensions of the uniform Heisenberg spin- $\frac{1}{2}$  chain model, we can try to introduce an alternation of the AF interactions into a chain, which leads to the formation of a spin gap at low temperatures. The accurate theory for spin- $\frac{1}{2}$  AF alternating-exchange Heisenberg chains was developed by D.C. Johnston and coauthors.<sup>15</sup> The best fits with the alternation parameter  $\alpha \geq 0.99$  gave similarly good accuracy for the experimental description as in two previous cases. From this analysis, we can conclude that we are not able to detect experimentally the presence of a spin gap in the 1D system if the exchange alternating parameter  $\alpha \geq 0.92$  (for given AF exchange of 21.4 K). It should be noted that even below the ordering temperature  $T_N = 4.65$  K, the deviations of the experimental susceptibility data from the theoretical predictions for a uniform Heisenberg spin- $\frac{1}{2}$  chain are quite small and keep the tendency of the temperature evolution of a nonordered phase.

(c) *Nonuniform exchange coupling models.* In a third step, we considered several additional 1D models that might be realized in the studied system with the small amplitudes of exchange interactions: alternating chain with FM and AF interactions<sup>21</sup> and Bleaney-Bowers AF dimer.<sup>22</sup> Note, all these models yield no satisfactory agreement with the observed experimental data, especially around a maximum.

To summarize, we have found that an AF uniform exchange coupling model for spin  $S = \frac{1}{2}$  chain (see solid lines in Fig. 4), even without the possible model extensions such as weakly coupled AF chains or an alternating-exchange AF spin- $\frac{1}{2}$  chain, is capable of satisfactorily reproducing the magnetic behavior of the studied compound. The fact that only a *single* parameter such as an *intrachain* AF coupling can cover the main properties of the low-dimensional system with the complex topology of the exchange interactions is not surprising. As was demonstrated for a quasi-one-dimensional helimagnet  $\text{NaCu}_2\text{O}_2$ ,<sup>12</sup> the magnetic behavior of the helix model with four exchange parameters  $\{J_1, J_2, J_3, J_4\}$  coincides surprisingly

good with the susceptibility of the 1D AF Heisenberg chain the under condition that the single AF coupling is dominant.

#### IV. CONCLUSIONS

To summarize, we have presented the magnetic susceptibility and magnetization of a quasi-one-dimensional spin- $\frac{1}{2}$  chain system,  $\beta\text{-TeVO}_4$ . Magnetic data for three crystallographic axes show an axial anisotropy of magnetic properties with respect to the  $b$  axis, which can be due to a small anisotropy of the  $g$ -tensor for the  $\text{V}^{4+}$  ions. A Curie-Weiss fit of the magnetic susceptibility above 130 K yields a positive Curie-Weiss temperature, indicating predominant small ferromagnetic correlations. At  $T_{\text{Cros}} = 130 \pm 5$  K, the product  $\chi(T)T$  shows the presence of a broad crossover, indicating a change in the character of exchange interactions. The low-temperature magnetic behavior of  $\beta\text{-TeVO}_4$  below 130 K clearly demonstrates the presence of predominant antiferromagnetic correlations in a 1D spin system. In the low-temperature behavior of magnetic susceptibility  $\chi(T)$ , the observed three features at  $T = 2.28, 3.28,$  and  $4.65$  K can be interpreted as phase transitions of the studied quasi-one-dimensional spin system: to a long-range-ordered AF state at  $T_N = 4.65$  K and further modifications of antiferromagnetic ordered phase (2.28, 3.28 K).

A fit of the magnetic susceptibility in the frame of a few low-dimensional spin- $\frac{1}{2}$  models was performed. The best qualitative agreement with the experiment in the wide temperature range  $5 < T < 400$  K was obtained for an AF uniform exchange coupling model for spin- $\frac{1}{2}$  chain with the *single* intrachain antiferromagnetic coupling constant  $J/k_B = 21.4 \pm 0.2$  K. The use of possible extensions of the 1D spin model shows that the strength of other exchange integrals (AF or FM nature) does not exceed a few Kelvin for this quasi-one-dimensional antiferromagnet. Although knowledge of the magnetic data is not enough to definitely determine all model parameters, we believe that the compound  $\beta\text{-TeVO}_4$  is a promising candidate to study the particularities of a weak-coupled  $J_1$ - $J_2$  model, especially from the side of one-dimensional helimagnets. Further investigations, such as inelastic neutron scattering, would be helpful in determining the weak coupling parameters, magnetic ground state, and the nature of the observed phase transformations. Given the lack of inorganic materials exhibiting these physical properties so far, the low-temperature properties of this system are likely to attract a lot of attention in the future.

#### ACKNOWLEDGMENTS

This work was supported by the Ukrainian Fundamental Research State Fund (F4-11). We thank A.A. Zvyagin for important discussions.

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