

## Frustrated spin-1/2 square lattice in the layered perovskite PbVO<sub>3</sub>

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We report on the magnetic properties of the layered perovskite PbVO<sub>3</sub>. The results of magnetic susceptibility and specific heat measurements as well as band-structure calculations consistently suggest that the  $S=1/2$  square lattice of vanadium atoms in PbVO<sub>3</sub> is strongly frustrated due to next-nearest-neighbor antiferromagnetic interactions. The ratio of next-nearest-neighbor ( $J_2$ ) to nearest-neighbor ( $J_1$ ) exchange integrals is estimated to be  $J_2/J_1 \approx 0.2-0.4$ . Thus, PbVO<sub>3</sub> is within or close to the critical region of the  $J_1-J_2$  frustrated square lattice. Supporting this, no sign of long-range magnetic ordering was found down to 1.8 K.

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The spin-1/2 square lattice provides a number of simple and important models for theoretical physics. If one uses the Heisenberg Hamiltonian and considers nearest-neighbor (NN) interactions only, a well-known Heisenberg square lattice (HSL) is formed. This model has been successfully applied to many transition-metal compounds (in particular, undoped high- $T_c$  superconductors) and much of its physics is now well understood.<sup>1</sup> A number of new phenomena appear if next-nearest-neighbor (NNN) interactions are taken into account. If both NN ( $J_1$ ) and NNN ( $J_2$ ) interactions are antiferromagnetic, the spin lattice is frustrated since  $J_1$  and  $J_2$  tend to establish different types of magnetic order. The properties of the system are controlled by the value of  $\alpha=J_2/J_1$ . If  $\alpha$  is small, Néel order is favorable and the limit of HSL is realized. If  $\alpha$  is large, columnar antiferromagnetic order is established. However, the main interest is attracted to the intermediate region that lies close to the quantum critical point at  $\alpha_c=0.5$ . The nature of the ground state in this region is still disputed. Theoretical studies suggest different spin-liquid scenarios [e.g., resonating valence bond (RVB) ground state].<sup>2-4</sup>

Most of the compounds realizing the  $S=1/2$  square lattice are well described with HSL since NNN interactions are usually negligible. Recently, two new systems with  $\alpha \gg 1$  (Li<sub>2</sub>VOXO<sub>4</sub>,  $X=Si, Ge$ ) were a subject of extensive studies and revealed columnar antiferromagnetic order.<sup>5-8</sup> However, no compounds in the critical region close to  $\alpha_c=0.5$  have been reported so far.

Below, we present magnetic properties of a novel compound, PbVO<sub>3</sub>,<sup>9,10</sup> that reveals a  $S=1/2$  frustrated square lattice (FSL). Both experimental and computational studies show that this compound lies close to the critical region of FSL and does not undergo long-range magnetic ordering down to 1.8 K.

PbVO<sub>3</sub> adopts a layered perovskite-type structure (space group  $P4mm$ ,  $a=3.8001$  Å, and  $c=4.6703$  Å) shown in Fig. 1. This structure combines the absence of an inversion center with a magnetic V<sup>4+</sup> cation; therefore, PbVO<sub>3</sub> attracts considerable attention as a possible multiferroic.<sup>11-14</sup> Magnetic properties of PbVO<sub>3</sub> have not been reported so far.

Polycrystalline samples of PbVO<sub>3</sub> were prepared by a

high-temperature high-pressure technique in a belt-type apparatus. Stoichiometric mixtures of PbO and VO<sub>2</sub> were placed into gold capsules and treated at 950 °C for 2 h under a pressure of 5 GPa. The phase composition of the prepared samples was checked by x-ray diffraction (XRD).

The magnetic susceptibility of PbVO<sub>3</sub> was measured between 1.8 and 400 K in the fields  $\mu_0 H$  of 0.1, 1, and 5 T using a Quantum Design superconducting quantum interference device magnetometer. The specific heat was studied in the temperature range from 1.8 to 270 K with a commercial physical properties measurement system.

The study of the magnetic properties of PbVO<sub>3</sub> is complicated by the presence of magnetic impurities in the samples under investigation. All of the measured susceptibility curves revealed anomalies at 90 and/or 350 K corresponding to PbV<sub>6</sub>O<sub>11</sub> and VO<sub>2</sub>, respectively,<sup>15</sup> although these impurities were not necessarily visible in XRD patterns. Figure 2 presents one of the best  $\chi(T)$  curves (no anomaly at 90 K) below 300 K since the high-temperature part is affected by VO<sub>2</sub>. The features of this curve are typical for all PbVO<sub>3</sub> samples within a variation of the temperature-independent background from sample to sample due to different amounts of VO<sub>2</sub>. These features are (i) a very broad maximum near 190–200 K and (ii) the difference between the zero field cooled and field cooled curves below about

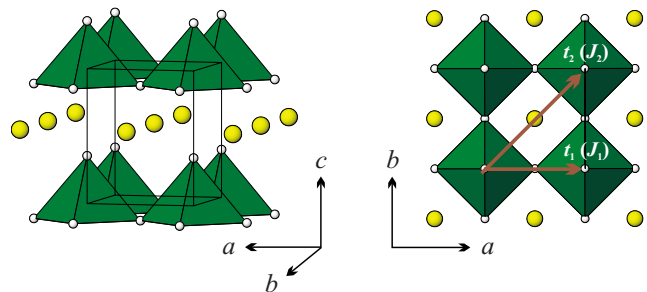


FIG. 1. (Color online) Perspective view (left panel) of the crystal structure of PbVO<sub>3</sub> and projection along the [001] direction (right panel). VO<sub>5</sub> square pyramids share common corners; lead atoms are indicated by large spheres.

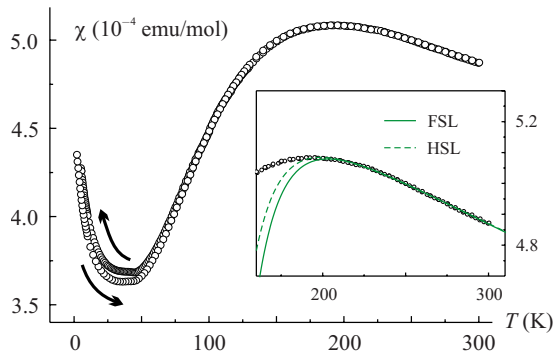


FIG. 2. (Color online) Magnetic susceptibility of  $\text{PbVO}_3$  measured at 5 T; arrows denote the curves obtained at heating and cooling. The dashed and solid curves in the inset show the fits by high-temperature series expansion for HSL model and FSL model with  $J_2/J_1=0.38$ , respectively.

50 K with small humps near 43 K (or heating-cooling hysteresis visible at Fig. 2). One should note that the anomalies at 45–50 K may appear due to the influence of trapped oxygen that undergoes condensation at about 50 K. These anomalies are especially strong if the intrinsic signal is very small (as in the case of our study). Nevertheless, the susceptibility data alone do not allow one to decide unambiguously whether the anomaly at 50 K is intrinsic to  $\text{PbVO}_3$  (e.g., indicating a phase transition) or not. Therefore, we turn to other experimental data in order to check the extrinsic nature of this anomaly.

The specific heat curve (Fig. 3) is smooth between 1.8 and 270 K and suggests the absence of phase transitions in  $\text{PbVO}_3$  in this temperature range. The conclusion is supported by thermal expansion<sup>10</sup> and resistivity<sup>9,16</sup> data. Finally, a neutron diffraction study at 1.5 K shows the absence of long-range magnetic ordering.<sup>9</sup> Thus, we conclude that the susceptibility anomaly at 50 K has extrinsic nature.

Square-pyramidal coordination of vanadium is known to give rise to a nondegenerate  $d_{xy}$  ground state for  $\text{V}^{+4}$  (see Refs. 5 and 17). The  $d_{xy}$  orbitals lie parallel to the V-O layers; therefore, one may expect that  $\text{PbVO}_3$  is a two-dimensional (2D) spin system. Indeed, the broad maximum in the susceptibility curve (Fig. 2) is typical for 2D spin systems, while the upturn at low temperatures is usually as-

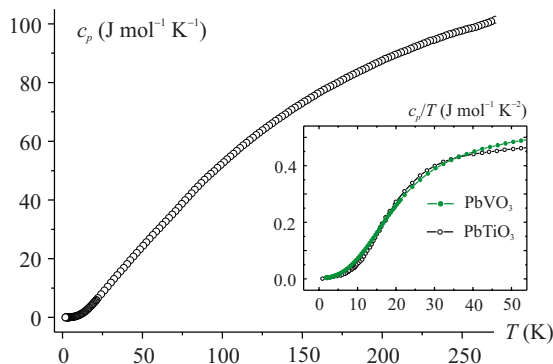


FIG. 3. (Color online) Specific heat of  $\text{PbVO}_3$ . The inset shows the comparison with the diamagnetic reference compound  $\text{PbTiO}_3$ .

cribed to the paramagnetic contribution of impurities and defects. Unfortunately, most of the regions of the curve are unsuitable for fitting since the low-temperature part is affected by impurity contributions, while the metal-insulator transition of  $\text{VO}_2$  prevents us from using the data above 300 K.<sup>18</sup> Thus, only the narrow region between the maximum ( $T_{max}=190\text{--}200$  K) and 300 K is appropriate for the fitting. Since the leading exchange integral  $J$  is comparable to  $T_{max}$ , high-temperature series expansions (HTSEs) are applicable in this region.

We use two types of HTSE corresponding to HSL and FSL models, respectively.<sup>6,19</sup> A temperature-independent contribution was added to the series as an adjustable parameter ( $\chi_0$ ) in order to account for the contribution of  $\text{VO}_2$  as well as other (diamagnetic or van Vleck) contributions of this type. Both models resulted in fits of similar quality with reasonable values of  $\chi_0 \approx 2.5 \times 10^{-4}$  emu/mol. We find  $J = 190$  K for HSL and  $J_1 = 203$  K and  $\alpha = J_2/J_1 = 0.38$  for FSL. The  $g$  value was fixed at  $g=2$  in order to get a more stable fit. Basically, we see that the susceptibility curve is consistent with both scenarios—HSL and FSL.

Specific heat data may provide additional quantitative information about the spin system of  $\text{PbVO}_3$ . However, one has to estimate and subtract the phonon part of the specific heat in order to reveal the magnetic contribution. The leading exchange integral in  $\text{PbVO}_3$  is about 200 K; therefore, the magnetic contribution does not fall to zero even at high temperatures and cannot be separated from the phonon part by a simple Debye fit. A reference diamagnetic compound has to be found in order to give a reliable estimate of the phonon contribution.

We tried to use  $\text{PbTiO}_3$  as a nonmagnetic reference. The crystal structures of  $\text{PbVO}_3$  and  $\text{PbTiO}_3$  look similar but vanadium and titanium adopt different coordinations (square pyramid and octahedron, respectively). This difference seems to be crucial: the  $c_p(T)$  curves have crossings at low temperatures (see the inset of Fig. 3), indicating quite different phonon spectra. We are not aware of any nonmagnetic compound with layered perovskite-type structure perfectly matching that of  $\text{PbVO}_3$ . Therefore, presently we cannot estimate the magnetic contribution to the specific heat of  $\text{PbVO}_3$ .

Experimental data provide rather limited information about the magnetic properties of  $\text{PbVO}_3$ ; therefore, we turn to computational techniques. Band-structure calculations are known as a useful tool for estimating exchange integrals and understanding the properties of low-dimensional spin systems. In particular, computational results were helpful in the study of FSL compounds  $\text{Li}_2\text{VOXO}_4$  and provided the first realistic estimate<sup>5</sup>  $\alpha \gg 1$  (supported by later neutron experiments, see Ref. 7) in contrast to the early experimental reports.<sup>8</sup>

Scalar relativistic band-structure calculations were performed using the full-potential local-orbital scheme (FPLO version 5.00-19)<sup>20</sup> and the parametrization of Perdew and Wang for the exchange and correlation potential.<sup>21</sup> A  $k$  mesh of 1152 points in the Brillouin zone (224 in the irreducible part) was used.

We start with the local density approximation (LDA) band structure (Fig. 4). The highest occupied band reveals a sig-

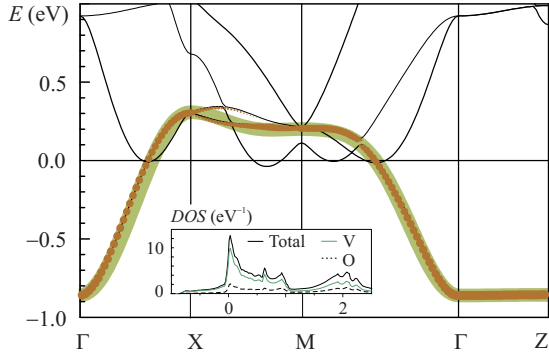


FIG. 4. (Color online) LDA band structure of  $\text{PbVO}_3$  near the Fermi level. Dots show the contribution of V  $3d_{xy}$  states; thick solid line presents the fit of the tight-binding model. The inset shows the density of states for  $\text{PbVO}_3$  near the Fermi level.

nificant contribution of V  $d_{xy}$  orbital consistent with the square-pyramidal coordination of  $\text{V}^{+4}$  (see Refs. 5 and 17). A simple one-band tight-binding model is fitted to this band. We find  $t_1=0.132$  eV and  $t_2=0.077$  eV for NN and NNN hoppings, respectively (see Fig. 1). Long-range in-layer hoppings do not exceed 0.004 eV and hence may be neglected. The interlayer hopping is also extremely small ( $t_{\perp}=0.0012$  eV), suggesting a strongly two-dimensional spin system in  $\text{PbVO}_3$ . The  $t$  values are used to estimate antiferromagnetic contributions to exchange integrals as  $J_i^{\text{AFM}}=4t_i^2/U_{\text{eff}}$  ( $U_{\text{eff}}$  is an effective on-site Coulomb repulsion). Assuming  $U_{\text{eff}}=4$  eV, we find  $J_1=203$  K,  $J_{\perp}\approx 0.01$  K, and  $\alpha=t_2^2/t_1^2=0.34$  in a perfect agreement with the FSL fit of the susceptibility data. Note that the  $\alpha$  value is a direct result of the tight-binding fit and does not depend on  $U_{\text{eff}}$ .

Thus, the tight-binding model supports the FSL scenario for  $\text{PbVO}_3$ . However, this model assumes that all the interactions in the system are antiferromagnetic. Sometimes, it is not the case and one may calculate total energies for different spin states in order to check possible ferromagnetic contributions to the exchange integrals. Local spin density approximation (LSDA) calculations for several simple spin states have been reported,<sup>11,12</sup> and we list these results in the first line of Table I.

LSDA results for transition-metal compounds are known to suffer from an unreasonable neglect of correlation effects. Below, we show that the relative values of total energy are considerably changed if one takes into account strong Coulomb correlation for the V  $3d$  shell. The most simple way to introduce such correlation within DFT is provided by

TABLE I. The total energies of different spin states of  $\text{PbVO}_3$  (the values are given in meV relative to the energy of the FM state).

$U_d$ (eV)	A-AFM	C-AFM	G-AFM
0 <sup>12</sup>	+19.4	-16.6	-16.1
4	-1.2	-19.0	-18.8
5	-1.5	-15.5	-15.3
6	-1.7	-12.6	-12.3

TABLE II.  $J_1$  and  $J_2$  values calculated via total energies of states with different spin orders.

$U_d$ (eV)	$J_1$ (K)	$J_2$ (K)	$\alpha=J_2/J_1$
4	222	30	0.14
5	182	29	0.16
6	148	28	0.19

LSDA+ $U$  technique.<sup>22</sup> We apply several physically reasonable values of  $U$  (further named  $U_d$  in order to distinguish it from  $U_{\text{eff}}$ ) and fix  $J=1$  eV.

Table I reveals quantitative rather than qualitative dependence of the LSDA+ $U$  results on the  $U_d$  value. The energy differences ( $E_{\text{A-AFM}}-E_{\text{FM}}$ ) and ( $E_{\text{C-AFM}}-E_{\text{G-AFM}}$ ) corresponding to interlayer coupling  $J_{\perp}$  are now comparable and small in contrast to the LSDA results. The sign of the interlayer interaction still is not clear but the absolute value of  $J_{\perp}$  has the order of units of kelvins. The in-layer interaction exceeds  $J_{\perp}$  at least by an order of magnitude. Thus, the spin system of  $\text{PbVO}_3$  is two-dimensional consistent with the crystal structure and the tight-binding results.

Now, we use LSDA+ $U$  to estimate in-layer interactions  $J_1$  and  $J_2$ . The results listed in Table II are in a reasonable agreement with the experimental data and the tight-binding model, although the  $\alpha$  value is somewhat lower than 0.34–0.38. Nevertheless, LSDA+ $U$  indicates considerable NNN interaction. Thus, band-structure calculations strongly support the FSL rather than the HSL scenario.

Additional evidence for the frustration in  $\text{PbVO}_3$  is found if one considers the presence of long-range magnetic ordering in this compound. The HSL tends to long-range order even at very weak interlayer coupling (for instance, Néel temperatures  $T_N$  of undoped high- $T_c$  superconductors have the order of hundreds of kelvins, see Ref. 23). If  $J_{\perp}$  in  $\text{PbVO}_3$  is as small as 0.01 K (tight-binding result),  $T_N\sim 0.2J_{\perp}\approx 40$  K.<sup>24</sup> The phase transition at 40 K can hardly be missed while analyzing experimental results. However, frustration effectively reduces  $T_N$  or even prevents the system from long-range magnetic ordering at all.

Summarizing, all the experimental data available for bulk samples of  $\text{PbVO}_3$  do not provide evidence for long-range magnetic ordering down to 1.8 K. Thermodynamic data (magnetic susceptibility, specific heat, thermal expansion, and resistivity) do not show any indications for intrinsic phase transitions, while low-temperature neutron diffraction reveals the absence of long-range spin ordering at 1.5 K.

Note that the recently reported thin films of  $\text{PbVO}_3$  (Refs. 13 and 14) show a different magnetic behavior with a possible magnetic ordering at 100–140 K. However, bulk phase and thin film may have distinct properties due to slightly different structures and strain effects. Detailed structural information for thin films of  $\text{PbVO}_3$  is not available, but the reported difference of the  $c$  parameter of the unit cell (4.67 and 5.02 Å in bulk and thin film, respectively) suggests considerable change of the structure in thin film as compared to bulk solid.<sup>25</sup>

Thus, we conclude that magnetic frustration of the square

lattice is a crucial feature of  $\text{PbVO}_3$ . If  $\alpha > \alpha_{c1}$  [ $\alpha_{c1}=0.34$  (Ref. 2) or 0.24 (Ref. 3)], long-range ordering is suppressed and some kind of spin-liquid ground state is formed. Unfortunately, we cannot give a more precise estimate of the  $\alpha$  value for  $\text{PbVO}_3$ ; hence, we cannot conclude if  $\text{PbVO}_3$  falls into the spin-liquid region or is just close to its boundary. Anyway, the frustration in  $\text{PbVO}_3$  is strong enough to suppress  $T_N$  considerably (at least by an order of magnitude as compared to the HSL estimate) or provide a disordered (spin-liquid or spin-glass) ground state.

In summary, this study provides strong evidence that  $\text{PbVO}_3$  is the first example of the  $S=1/2$  square lattice system lying within or close to the critical region of the FSL phase diagram and lacking for long-range magnetic ordering down to low temperatures ( $T_N/J < 0.01$ ). A further study of the ground state and low-temperature properties of this system is of high interest. Unfortunately, we have to point out considerable difficulties in the synthesis of bulk single-phase

samples (and, moreover, single crystals) of  $\text{PbVO}_3$ . The recent study of epitaxial thin films of  $\text{PbVO}_3$  (Refs. 13 and 14) provides an alternative route for the preparation of this interesting compound but thin films and bulk solids may have strikingly different properties as we have mentioned above.

In conclusion, we have shown that  $\text{PbVO}_3$  reveals significant frustration of the square lattice that prevents this compound from long-range spin ordering down to 1.8 K.  $\text{PbVO}_3$  lies very close to the critical region of the FSL phase diagram, and it may provide the first realization of disordered ground state for the  $S=1/2$  square lattice.

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