Frustrated spin-1/2 square lattice in the layered perovskite PbVO$_3$

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We report on the magnetic properties of the layered perovskite PbVO$_3$. 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$_3$ 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$_3$ 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.

PACS numbers: 75.47.Pq, 75.30.Et

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.$^1$ 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. RVB ground state).$^{2,3,4}$

Most of the compounds realizing $S = 1/2$ square lattice are well described with HSL since NNN interactions are usually negligible. Recently two new systems with $\alpha \gg 1$ (Li$_2$VOXO$_4$, X = Si, Ge) were a subject of extensive studies and revealed columnar antiferromagnetic order.$^5,6,7,8$ 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$_3$, that reveals $S = 1/2$ 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$_3$ adopts a layered perovskite-type structure (space group $P4mm$, $a = 3.8001$ Å, $c = 4.6703$ Å) shown in Fig. 1. This structure combines the absence of an inversion center with a magnetic $V^{4+}$ cation, therefore PbVO$_3$ attracts considerable attention as a possible multiferroic.$^{9,10,11,12,13,14}$ Magnetic properties of PbVO$_3$ have not been reported so far.

Polycrystalline samples of PbVO$_3$ were prepared by a high-temperature high-pressure technique in a belt-type apparatus. Stoichiometric mixtures of PbO and VO$_2$ were placed into gold capsules and treated at 950 °C for 2 hours under a pressure of 5 GPa. The phase composition of the prepared samples was checked by XRD.

The magnetic susceptibility of PbVO$_3$ was measured between 1.8 and 400 K in the fields $\mu_0H$ of 0.1, 1, and 5 T using a Quantum Design SQUID magnetometer. The specific heat was studied in the temperature range from 1.8 to 270 K with a commercial PPMS.

The study of the magnetic properties of PbVO$_3$ 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 PbVO$_3$O$_{11}$ and VO$_2$ respectively,$^{15}$ although these impurities were not necessarily visible in XRD patterns. Fig. 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$_2$. The features of this curve are typical for all PbVO$_3$ samples within a variation of the temperature-independent background from sample to sample due to different amount of VO$_2$. These features

![FIG. 1: (Color online) Perspective view (left panel) of the crystal structure of PbVO$_3$ and projection along the [001] direction (right panel). VO$_3$ square pyramids share common corners, lead atoms are indicated by large spheres](image-url)
are: i) a very broad maximum near 190 – 200 K; ii) the difference between the zfc and fc curves below about 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 to decide unambiguously whether the anomaly at 50 K is intrinsic to 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 PbVO$_3$ in this temperature range. The conclusion is supported by thermal expansions and resistivity data. Finally, a neutron diffraction study at 1.5 K shows the absence of long-range magnetic ordering. 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 non-degenerate $d_{xy}$ ground state for V$^{4+}$ (see Refs. 5,17). The $d_{xy}$ orbitals lie parallel to the V–O layers, therefore one may expect that PbVO$_3$ is a 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 ascribed 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 VO$_2$ prevents us from using the data above 300 K. Thus, only the narrow region between the maximum ($T_{\text{max}} = 190 – 200$ K) and 300 K is appropriate for the fitting. Since the leading exchange integral $J$ is comparable to $T_{\text{max}}$, high-temperature series expansions (HTSE) are applicable in this region.

We use two types of HTSE corresponding to HSL and FSL models, respectively. A temperature-independent contribution was added to the series as an adjustable parameter ($\chi_0$) in order to account for the contribution of 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 $\chi_0 \approx 2.5 \cdot 10^{-4}$ emu/mol. We find $J = 190$ K for HSL and $J_1 = 203$ K, $\alpha = J_2/J_1 = 0.38$ 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 or FSL.

Specific heat data may provide additional quantitative information about the spin system of 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 PbVO$_3$ is about 200 K therefore the magnetic contribution does not fall to zero even at high temperatures and can not 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 PbTiO$_3$ as a non-magnetic reference. The crystal structures of PbVO$_3$ and PbTiO$_3$ look similar but vanadium and titanium adopt different coordination (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 non-magnetic compound with layered perovskite-type structure perfectly matching that of PbVO$_3$. Therefore, presently we can not estimate the magnetic contribution to the specific heat of PbVO$_3$.

Experimental data provide rather limited information about the magnetic properties of PbVO$_3$, therefore we turn to computational techniques. Band structure calculations are known as a useful tool for esti-

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**FIG. 2:** (Color online) Magnetic susceptibility of 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.

**FIG. 3:** (Color online) Specific heat of PbVO$_3$. The inset shows the comparison with the diamagnetic reference compound PbTiO$_3$. 
FIG. 4: (Color online) LDA band structure of PbVO$_3$ near the Fermi level. Dots show the contribution of V 3$d_{xy}$ states, thick solid line presents the fit of the tight-binding model. The inset shows the density of states for PbVO$_3$ near the Fermi level.

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

We start with the LDA band structure (Fig. 4). The highest occupied band reveals a significant contribution of V $d_{xy}$ orbital consistent with the square-pyramidal coordination of V$^{4+}$ (see Refs. 3-17). 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 inter-layer hopping is also extremely small ($t_{\perp} = 0.0012$ eV) suggesting a strongly two-dimensional spin system in PbVO$_3$. The $t$ values are used to estimate antiferromagnetic contributions to exchange integrals as $J_1^{\text{AFM}} = 4t_1^2/U_{\text{eff}}$ ($U_{\text{eff}}$ is an effective on-site Coulomb repulsion). Assuming $U_{\text{eff}} = 4$ eV we find $J_1 = 203$ K, $J_1 \approx 0.01$ K, $\alpha = t_2^2/t_1^2 = 0.34$ 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 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 ferromagnetic contributions to the exchange integrals. LSDA calculations for several simple spin states have been reported and we list these results in the first line of Table 1.

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 vanadium 3$d$ shell. The most simple way to introduce such correlation within DFT is provided by LSDA+$U$ technique. 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.

| $U_d$ (eV) | A-AFM | C-AFM | G-AFM |
|-----------|-------|-------|-------|
| 0         | +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 order.

| $U_d$ (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              |

Additional evidence for the frustration in 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 inter-layer coupling (for instance, Néel temperatures $T_N$ of undoped high-$T_c$ superconductors have the order of hundreds of K, see Ref. 22. If $J_1$ in PbVO$_3$ is as small as 0.01 K (tight-binding result) $T_N \approx 0.2J_1 \approx 40$ K. The phase transition at 40 K can
is formed. Unfortunately, we can not give a more precise value for PbVO$_3$ ordering at 1.5 K. Anyway, the frustration in PbVO$_3$ square lattice is a crucial feature of PbVO$_3$ in thin film as compared to bulk solid. The resistivity curve reported in Ref. 9 shows an anomaly at 90 K. We assign this anomaly to ferromagnetic ordering of PbV$_6$O$_{11}$ impurity, see Ref. 3 for details.

Summarizing, this study provides strong evidence that PbVO$_3$ is the first example of $S = 1/2$ 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 PbVO$_3$. The recent study of epitaxial thin films of PbVO$_3$ 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 PbVO$_3$ reveals significant frustration of the square lattice that prevents this compound from long-range spin ordering down to 1.8 K. 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 $S = 1/2$ square lattice.

Acknowledgments

Financial support of RFBR (07-03-00890), GIF (I-811-257.14/03), Alfred Toepfer Foundation, and the Emmy Noether Program is acknowledged.

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