Magnetic Anisotropy of Paramagnetic and Ferromagnetically Ordered State of Single Crystal BaVSe$_3$

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Anisotropic magnetism of single crystal BaVSe$_3$ was studied for the first time by the combination of the susceptibility and torque methods. As reported previously for polycrystalline sample, BaVSe$_3$ undergoes ferromagnetic ordering below 43 K. Well above ferromagnetic ordering temperature, the torque measurements reveal a continuous symmetry change that influences the ordered state accordingly. We found ferromagnetic easy axis in the vanadium chain direction, i.e., along the crystallographic c-axis. The presence of two ferromagnetic domains of opposite magnetization direction signifies uniaxial symmetry of the ordered ferromagnetic state.

KEYWORDS: BaVSe$_3$, magnetic anisotropy, ferromagnetism, transition metal chalcogenide

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The compounds containing transition metal elements display a variety of interesting physical phenomena most of which are related to the existence of unpaired $d$ electrons. Depending on the dimensionality of the crystal lattice and the spin state of the $d$ electron of transition metal ion, a number of different ground states is observed in these compounds: nonmagnetic spin dimers and alternating spin chains, spin and charge density waves, colinear and noncolinear antiferromagnetic long range order, etc. BaVSe$_3$ contains vanadium $d^5$ electrons and thus belongs to the above mentioned class of compounds, just like widely studied BaVS$_3$.1–9)

BaVSe$_3$ is isostructural to BaVS$_3$.10) At high temperatures BaVX$_3$ (X = Se, S) forms a hexagonal perovskite type structure of $P6_3/mmc$ symmetry and at $T_c \approx 310$ K (240 K) BaVSe$_3$ (BaVS$_3$) exhibits a structural phase transition to orthorhombic symmetry, space group $Cmc$, shown in Fig. 1. The parameters of the orthorhombic unit cell in BaVSe$_3$ are $a = 6.992(2)$ Å, $b = 12.113(3)$ Å, and $c = 5.859(1)$ Å.11) Vanadium ions V$^{4+}$ are surrounded by six Se ions forming a distorted octahedron. VSe$_6$ octahedra form zig-zag chains along c-axis by sharing the faces of the octahedra making BaVSe$_3$ a structurally one-dimensional (1D) system. Magnetic and transport properties of polycrystalline BaVSe$_3$ were reported previously.12) Unlike BaVS$_3$ which exhibits metal-to-insulator transition (MIT) BaVSe$_3$ is metallic from room temperature down to the lowest measured temperature of 2 K.12)13) The metallic behaviour in the entire temperature range, however, is observed in BaVS$_3$ under pressure. 1D lattice fluctuations as a precursor to the MIT persist in BaVS$_3$ up to 170 K3) and at low temperatures distortion of VSe$_6$ octahedra takes place both in nonmagnetic ($T_X < T < T_{MIT}$) and magnetic phase ($T < T_X$).9) Magnetic susceptibility of BaVSe$_3$ displays paramagnetic Curie–Weiss (CW) behaviour at high temperatures and at $T_c \approx 43$ K the sample undergoes a transition to the ferromagnetically ordered state. Contrary to that, BaVS$_3$ orders antiferromagnetically below $T \approx 30$ K as evidenced from torque measurements1) and powder neutron diffraction experiment.2)

Sulfur deficient BaVS$_{3-\delta}$ also orders ferromagnetically but two different vanadium sites (magnetic and nonmagnetic) are present in those samples. NMR experiment suggests there is a single magnetic V site in BaVSe$_3$ below $T_c$.12) In BaVS$_3$ under pressure MIT is suppressed and at $p \gtrsim 2.0$ GPa BaVS$_3$ becomes metallic in the whole temperature range.14) Se ions are larger than S ions which is why the interchain orbital overlap is increased in BaVSe$_3$ making the situation similar to the one in BaVS$_3$ under pressure. The magnetic phase of BaVS$_3$ is difficult to probe under pressure, which is why a study of magnetic properties of BaVSe$_3$ is useful.

In this Letter magnetic properties of single crystals of BaVSe$_3$ are described as probed by static magnetic susceptibility and torque measurements. Magnetic anisotropy of both paramagnetic (PM) and ferromagnetic (FM) state is described.

The BaVSe$_3$ single crystals were grown by using a standard solid-state reaction technique, as described elsewhere.10) The temperature dependence of magnetic suscep-
The magnetic susceptibility in the paramagnetic regime was measured by the Faraday method in applied fields of 9 kOe. The sample used to measure the susceptibility consisted of a bunch of randomly oriented single crystals of total mass \(m = 0.004\) g. Temperature, field and angular dependence of magnetic torque were measured by the home made torque apparatus. Two samples of different masses were used due to large signal in the PM state. Mass of the sample used for measurements in the PM state was \(60\mu\)g and for the FM state \((7 \pm 2)\mu\)g. In the FM state fields of up to 500 Oe were applied, and in the PM state up to 8 kOe.

Raw susceptibility data in the paramagnetic state and corresponding CW plots are displayed in the top panel of Fig. 2. In the large temperature range susceptibility obeys the CW law \(\chi = C/(T - \Theta)\) with \(C = 0.244\) emu K/mol and positive Weiss temperature \(\Theta = +44\) K. The presence of ferromagnetic interactions. The magnetic moment obtained from CW plot amounts to \(\sim 1.4\mu\)B/\(\Omega\) which is close to the value obtained in ref. 12 for the polycrystalline sample. The single crystal orders ferromagnetically at \(T_c \approx 43\) K, as reported previously. 12) The temperature dependence of the resistivity of \(\text{BaVSe}_3\) is close to the value obtained in ref. 12 for the polycrystal.

Additional information of both PM and FM states is available from the symmetry sensitive torque measurements. In the PM state induced magnetization \(\mathbf{M}\) depends linearly on the magnetic field \(\mathbf{H}\): \(M_i = \sum_j \chi_{ij}H_j\) where \(\chi_{ij}\) is the susceptibility tensor, and \(i(j) = x, y, z\). Magnetic torque \(\mathbf{\Gamma}\) of the sample of volume \(V\) is given by the relation:

\[
\mathbf{\Gamma} = V\mathbf{M} \times \mathbf{H}
\]

Evaluation of the component of torque \(\Gamma_k\) in the case of the paramagnetic response gives:

\[
\Gamma_k = \frac{m}{2M_{\text{mol}}} - \Delta \chi_{1k}H^2 \sin(2\phi - 2\phi_0),
\]

where \(m\) is the mass of the sample, \(M_{\text{mol}}\) is the molar mass, \(\Delta \chi_{1k} = \chi_k - \chi_0\) is the susceptibility anisotropy in the plane perpendicular to the measured torque \(\Gamma_k\) which is the plane of rotation of the field \(H\) (i.e., the field plane), \(\phi\) is the field goniometer angle. The phase shift \(\phi_0\) marks the direction of the crystal magnetic axis, manifested as the zero crossing of the torque sine curve i.e., marks the coincidence of the field direction and direction of the magnetic axis. Thus, the change of underlying magnetic symmetry reflects on experimental parameter \(\phi_0\). Note that precise directions of \(a\)- and \(b\)-axes with respect to the sample morphology were not available.

The top panel of Fig. 3 displays the angular torque dependence in the PM state for the sample orientation that includes \(c\)-axis in the field plane measured at several temperatures and fields. The angle \(\phi_0\) corresponding to \(c\)-axis is marked in the figure. Measured field dependence of the torque satisfies equation (2) for \(T \geq 55\) K which means that the response of the system is paramagnetic in that...
temperature range ($M$ is linear in $H$), while the torque field dependence at $T = 54$ K (not shown) still reflects reminiscence of the short-range order. The most important result, emphasizing symmetry change, is the phase difference of almost 90° between the torque sine curves obtained at $T \leq 60$ K and $T \geq 65$ K. Detailed temperature dependence of the phase difference is shown in the inset of the bottom panel of Fig. 3. The abrupt change of the angle $\phi_0$ at 62.5 K does not correspond to a sharp transition since discontinuity in anisotropy is missing (see bottom panel of Fig. 3). At this temperature the torque amplitude becomes zero i.e., the system is fully isotropic. That is sketched in the top panel of Fig. 3 by showing the shape of the susceptibility ellipsoid (i.e., ellipse) in the field plane for temperatures above and below $T \approx 62.5$ K. Above 62.5 K the susceptibility $\chi_c$ is smaller than the susceptibility perpendicular to it in the field plane, $\chi_c < \chi_{\perp}$. At temperatures below 62.5 K $\chi_c > \chi_{\perp}$. At $T \approx 62.5$ K ellipse becomes a circle, i.e., $\chi_c = \chi_{\perp}$. Using eq. (2) evaluated anisotropy at $T = 300$ K for $ab$ plane amounts to $\Delta X_{ab}(300)$ K = $6.5 \times 10^{-7}$ emu/mol and in the plane containing $c$-axis $\Delta X_{with}(300)$ K = $2 \times 10^{-7}$ emu/mol. Regarding the known torque-method setup geometry (field direction and the orientation of the sample in the field) and rather small anisotropy in the $ab$ plane, we found that $\chi_c > \chi_{\perp}$ below 62.5 K while the system is still in the PM phase with no FM fluctuations present yet. Considering susceptibility, which follows CW law down to at least 50 K, it is surprising that the anisotropy displays a local extremum at about $T \approx 80$ K. In the case of paramagnetic susceptibility, the susceptibility anisotropy results from the temperature independent electron $g$-factor anisotropy, $\Delta X_{ijk} = (\chi) \times (g_i^2 - g_j^2)/(g_k^2)$. Figure 4 displays $\Delta \chi$ vs $\chi$ in the PM state showing no linear correlation between the two. This suggests the changes in symmetry occur in a rather wide temperature range in PM state. On the other hand, all effects of the crystal symmetry change at $T_c = 310$ K reflect only in rather small change of slope in $\Delta \chi(T)$ data (not shown).

The details of FM ordered state below $T_c = 43$ K were probed by torque measurements in fields up to 500 Oe at $T = 4.2$ K for both sample orientations as in PM state. Angular dependence is presented in Fig. 5. Note the 20 times smaller amplitude observed in the $ab$ plane compared to plane with $c$-axis. The observed torque sine curves can be described by two regular sine curves $\sim \sin(\phi - \phi_0)$ differing in phase by 180°, as shown in Fig. 5. The half period of the experimental sine curves of 180°, together with torque definition (1), proves that the torque results from field independent, i.e., spontaneous magnetization. Furthermore, the torque curve shows that the ferromagnetic easy axis is parallel to the $c$ crystallographic axis, within experimental resolution of 1°. The torque field dependence in case of spontaneous magnetization should follow linear field dependence, until the field reaches the switching value $H_s$. The field dependence of torque at two different angles is shown in Fig. 6. The top panel represents data obtained with field goniometer angle of 70° and the bottom panel with 55° (for values of torque at those angles consult Fig. 5). The bottom panel displays two linear field dependences for the same field angle away from the switching angle and the same field polarity. The only difference was that lower (negative) data was collected after the sample had some history including the switching effect that left the spontaneous magnetization oriented oppositely in respect to the
first (positive) data. The angles between $\mathbf{M}$ and $\mathbf{H}$ are shown schematically in the figure. From the series of such measurements the critical field applied in the direction opposite to the magnetization needed for reorientation of FM effects in ferromagnets are usually significant. However, in the needle shape geometry of BaVSe$_3$ with the longest dimension along $c$-axis which is also the direction of FM geometry magnetization, demagnetization effects are expected to be largely reduced.

The temperature dependence of torque measured in applied field of 400 Oe for two sample orientations is shown in Fig. 7. The torque in the plane containing $c$-axis was measured from 4.2–50 K after measuring the negative curve in the bottom panel of Fig. 6 with the same field polarity and at the same angle. For this $\mathbf{M}$ and $\mathbf{H}$ geometry magnetization should switch to opposite direction, but at low temperatures the field does not reach critical value. At higher temperatures the switching is thermally activated and torque changes sign consequently. Torque in $ab$ plane is 20 times smaller and $ab$ plane component. The torque in Fig. 7 has a characteristic order parameter temperature dependence. Assuming single-domain FM state for the fields $H > H_c$, the effective magnetic moment at 4.2 K amounts to $\mu_{\text{eff}} = (0.6 \pm 0.2)\mu_B$ from torque measurements (large value of uncertainty comes from the uncertainty of the small mass). Similar reduced value of $\mu_{\text{eff}} = 0.34$ is obtained in ref. 12 from the Arrot plot while from NMR data the same authors obtained $\mu_{\text{eff}} = 0.61\mu_B$ with assumption on equality of hyperfine interaction with BaVS$_3$.

In conclusion, single crystalline BaVSe$_3$ was studied by static magnetic susceptibility and torque measurements. Magnetic susceptibility obeys Curie–Weiss law emphasizing moderate FM interaction. From torque measurements we evaluate reduced effective magnetic moment of $\mu_{\text{eff}} = (0.6 \pm 0.2)\mu_B$ and give first evidence of the uniaxial symmetry of the ferromagnetic ordered state. We found evidence of symmetry changes in the wide temperature range of paramagnetic phase.

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