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Incommensurate Magnetic Ordering and Spin-Liquid-Like State in a Triangular Lattice $BaVS_3$: Neutron Diffraction and Scattering Study

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We performed powder neutron diffraction and scattering experiments of the $S = \frac{1}{2}$ triangular lattice system, $BaVS_3$, and found magnetic reflections below $T_X \simeq 30\,K$. The propagation vector is determined to be incommensurate (0.226 0.226 0) in the hexagonal index. The ordered moment is roughly estimated to be $\sim 0.5\,\mu_B/V$. Although the elastic magnetic diffractions disappear above T_X, low-energy inelastic scattering, which has an $Q - \omega$ dispersion similar to that below T_X, was observed between T_X and the metal-insulator transition point $T_{MI} \simeq 70\,K$, indicating the presence of a long-range and dynamic antiferromagnetic correlation, i.e., a spin-liquid-like state, between T_X and T_{MI}.

KEYWORDS: $BaVS_3$, neutron diffraction, neutron scattering, incommensurate magnetic ordering, spin liquid

Physical properties of transition metal sulphides are usually considered analogous to oxides, but are sometimes seen to be more unique than those of oxides, probably due to the stronger covalency or charge instability. $BaVS_3$, which is considered to be a spin-$\frac{1}{2}$ system, is one such novel material. The metal-insulator transition observed at $T_{MI} \simeq 70\,K$[1] has attracted considerable attention. Although the susceptibility shows an antiferromagnetic-like drop below T_{MI},[2-4] the nature of magnetic states below T_{MI} is still controversial. In particular, the magnetic dimensionality has been a matter of interest.[5-8]

$BaVS_3$ forms a hexagonal perovskite type structure (space group: $P6_3/mmc$) at high temperatures,[1] in which V atoms (at the $2a$ site) form one-dimensional chains along the c axis with a small interatomic distance ($\simeq 2.8$ Å) and a triangular lattice in the c plane with a very large interchain distance ($\simeq 6.7$ Å). If there is antiferromagnetic coupling among the c chains, the effect of geometrical magnetic frustration on the triangular lattice[9] is expected. Below $T_S \simeq 240\,K$, $BaVS_3$ shows a small orthorhombic structural deformation, resulting in a slightly zigzag configuration of V atom chains along the c axis.[10] Since a V atom is surrounded by an almost regular octahedral configuration of S atoms even below T_S, we may expect degeneracies of $3d$-t_{2g} orbitals. It has been reported in a previous neutron diffraction study[11] that no extra diffraction is observed at low temperatures, which ruled out long-range magnetic ordering. Recently, we proposed an orbital-ordered spin-singlet state as the ground state of this compound based on ^{51}V nuclear resonance results,[12] referring to this neutron diffraction result and a theoretical work by Pen *et al.*[13] In this case, we interpreted the anomaly at $T_X = 30\,K$ as an appearance of a large and asymmetric electric field gradient at V sites, which was ascribed to the symmetry lowering of $3d$ electron wave functions due to the orbital ordering.

We have reported the results of preliminary inelastic neutron scattering experiments of a powder sample, which were performed to detect the spin gap with thermal neutrons.[14] At low temperatures, we observed clear inelastic scattering around the energy transfer $\Delta E \sim 10\,meV$ at the scattering vector $Q = 1.2\,Å^{-1}$, which disappeared above T_{MI}. We interpreted the scattering as that of a spin gap. In the same experiments, however, we also observed low-energy excitations in a low-Q range, whose origin has not been clarified. In order to investigate its origin, we carried out the present low-energy neutron scattering experiments using a cold neutron beam and obtained rather unexpected results, magnetic reflections, which were not observed in the previous neutron diffraction experiment.[11] In this Letter, we report the neutron diffraction and scattering results below T_{MI} and reveal the incommensurate long-range magnetic ordering and a spin-liquid-like state between T_X and T_{MI}.

A powder sample of $BaVS_3$ was prepared by following the procedures described elsewhere.[8] It is known that magnetic properties of $BaVS_3$ are sensitive to the sample quality, particularly, the deficiency of S, which induces

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ferromagnetism. Therefore, the sample quality was evaluated by measuring the temperature dependence of the susceptibility to confirm no upturn at low temperatures. For neutron diffraction and scattering experiments, a powder sample with a mass of approximately 10 g was packed into a vanadium tube with 15 mm diameter and 40 mm height and sealed in a helium gas atmosphere. The experiments were mainly performed using a triple-axis spectrometer ISSP-HER installed at the C1-1 cold-neutron guide of the research reactor JRR-3M at Japan Atomic Energy Research Institute (JAERI), Tokai. All the measurements were carried out at a fixed incident energy $k_{\rm i} = 1.55\,\text{Å}^{-1}$ ($E_{\rm i} = 5.0\,\text{meV}$, $\lambda_{\rm i} = 4.05\,\text{Å}$) with a collimation sequence of open-open-80′-80′ and using a Be filter situated in front of the sample. The energy resolution is estimated to be $2\Gamma \simeq 0.21\,\text{meV}$. Polarization analyses of magnetic diffractions were performed with thermal neutrons using the TAS-1 triple-axis spectrometer installed in the reactor hall JRR-3M.

Figure 1 shows the neutron diffraction pattern of $BaVS_3$ measured at 4 K. In addition to nuclear reflections, three extra peaks were observed at $Q = 0.425$, 0.74 and $1.17\,\text{Å}^{-1}$ in the Q range of $Q < 1.2\,\text{Å}^{-1}$. reflection (1 0 0) (in the hexagonal Miller index). The third reflection is split into two peaks as in the inset of Fig. 1 due to the *crystal* distortion below $T_{\rm S}$. It was confirmed that the energy widths of these reflections are resolution-limited. Polarization analyses indicate that these peaks are magnetic in origin. The Q-widths are also resolution-limited, indicating a sufficiently long-range correlation. The observation of magnetic reflections is rather unexpected and seems to be inconsistent with the previous result.[11] However, it is likely that these low-Q peaks were out of the measurement range because thermal neutrons were used for the previous measurement. It is unlikely that these magnetic reflections are due to extrinsic origins such as impurity phases because the estimated ordered moment (discussed below) is rather large.

To discuss the crude nature of the magnetic structure, we neglect the small orthorhombic distortion and use indices of the hexagonal Bravais lattice. We assume ferromagnetic coupling along the c axis, referring to the presence of the strong ferromagnetic coupling suggested from the positive Weiss temperature[5,8] and the absence of antiferromagnetic intrachain coupling suggested from results of inelastic experiments.[14] With this assumption, the modulation vector is determined to be incommensurate (0.226 0.226 0). It is not known from the present experiment whether the modulation is of a helical- or spin-density type. To estimate the magnitude of the ordered moment, we assume that magnetic moments with a constant magnitude lie in the c plane, by taking into account the fact that the susceptibility along the c axis is larger than that in the c plane at low temperature.[15] Further, we assume a helical structure derived from the so-called 120° structure (the propagation vector is $(\frac{1}{3}\,\frac{1}{3}\,0)$). With these assumptions, the ordered moment is estimated to be $\sim 0.5\,\mu_{\rm B}/\text{V}$. This value is smaller than the full moment of $S = \frac{1}{2}$ but is sufficiently large to conclude that most V atoms have comparatively large ordered moments. Similar modulated 120° structures were found in ionic crystals with the same crystal structure as $RbFeCl_3$ at finite temperatures[16] and $CsFeCl_3$ under applied fields.[17]

The intensity of the first magnetic peak is plotted as a function of temperature in Fig. 2. As seen in the figure, the static magnetic reflections disappear above $T_{\rm X} \simeq 30\,\text{K}$. The magnetic intensity measured near the Bragg point and with a small energy transfer exhibits typical critical scattering at $T_{\rm X}$. These results indicate that static and long-range antiferromagnetic correlation is established at $T_{\rm X}$, not at $T_{\rm MI}$ where the susceptibility shows the antiferromagnetic-like drop. Previously, we interpreted that the $T_{\rm X}$-anomaly is not a phase transition but a crossover because no appreciable anomaly has been found at $T_{\rm X}$ in thermodynamic properties such as specific heat[8] and thermal expansion[10] and only dynamic probes such as NMR detected an anomaly.[12,18] However, the present neutron diffraction result clearly indicates symmetry lowering at $T_{\rm X}$. Recently, it was found that the susceptibility measured for a single crystal shows a clear anomaly at $T_{\rm X}$,[15] which is consistent with the present neutron diffraction results. Below $T_{\rm X}$, magnetic scattering was also observed at finite energy transfer (see Fig. 3(a)), and shows a continuous $Q - \omega$

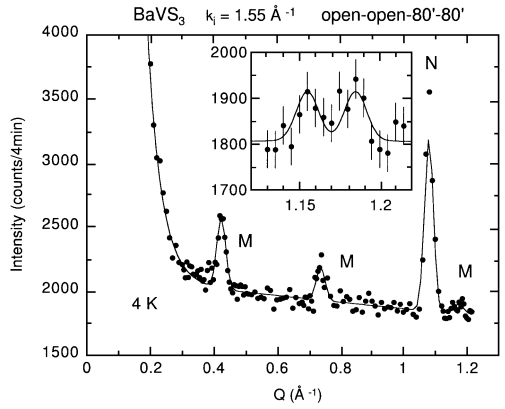

Fig. 1. Neutron diffraction pattern of $BaVS_3$ measured at 4 K. N and M denote nuclear and magnetic reflections, respectively. The inset shows the magnification at $Q \simeq 1.17\,\text{Å}^{-1}$.

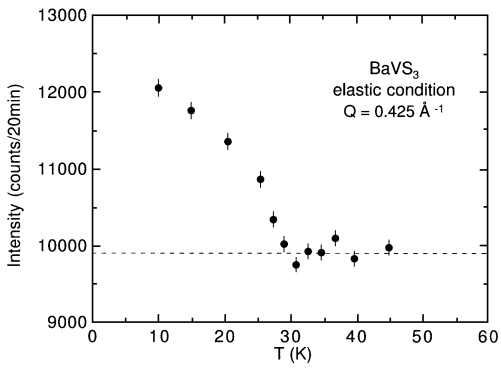

Fig. 2. Temperature dependencies of the magnetic intensity measured under elastic conditions (the magnetic Bragg peak at $Q = 0.425\,\text{Å}^{-1}$). The broken curve indicates the background.

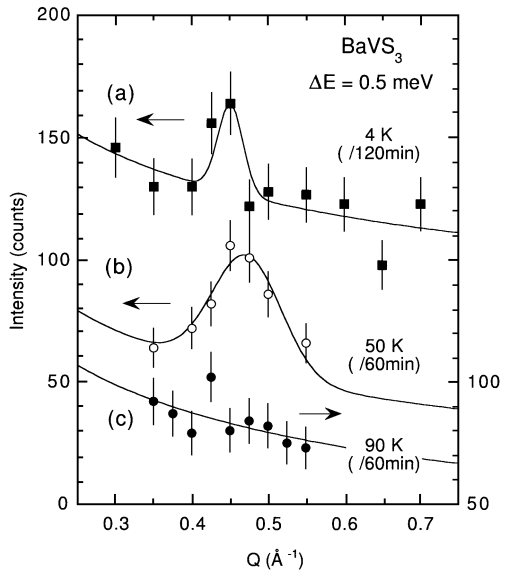

Fig. 3. Q-scan spectra measured at $\Delta E = 0.5\,\mathrm{meV}$ at 4 (a), 50 (b) and 90 K (c).

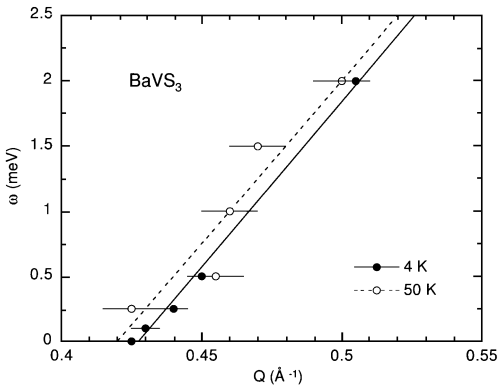

Fig. 4. $Q-\omega$ dispersion curves of the magnetic scattering measured at 4 K (closed circles) and 50 K (open circles). Solid and broken lines are guides for the eye.

dispersion as in Fig. 4, suggesting spin-wave-like collective excitations although the present powder experiment is not sufficient to discuss the details of the mode.

It should be noted that, although the macroscopic susceptibility starts to decrease from T_{MI}, neutron diffraction data indicate no static antiferromagnetism between T_{MI} and T_{X}. Interestingly, however, we observed the magnetic scattering at finite but small energy transfer near the magnetic Bragg point in the temperature range of $T_{\mathrm{X}} < T < T_{\mathrm{MI}}$. Figure 3(b) shows an example of inelastic Q-scan spectra measured at 50 K and at $\Delta E = 0.5\,\mathrm{meV}$. The scattering shows a continuous $Q-\omega$ dependence similar to that below T_{X} as shown in Fig. 4, and disappears above T_{MI}, as in Fig. 3(c). Although it is difficult to discuss the behavior at $\Delta E \sim 0$ due to the strong V incoherent scattering, we may conclude that there exists a very small spin excitation gap of the order of 0.1 meV, referring to NMR and μ-SR results,[12, 19] which clearly indicate no static internal field. These results indicate that, at $T_{\mathrm{X}} < T < T_{\mathrm{MI}}$, spins fluctuate dynamically and maintain almost the same antiferromagnetic correlation as in below T_{X}. That is, a spin-liquid-like state, which reduces the macroscopic susceptibility on average, is formed below T_{MI} and slows down below T_{X}. The Q-widths of the inelastic scattering are narrow and comparable to those below T_{X}, suggesting a rather long correlation length. In a previous neutron scattering experiment, we observed inelastic scattering at $\Delta E \sim 10\,\mathrm{meV}$ (with broad maxima at $Q \sim (\frac{1}{2}\,0\,0)$ and $(\frac{1}{2}\,1\,0)$),[14] which may correspond to single-particle excitations of antiferromagnetic coupling. Recently, from variational calculations of clusters, taking into account orbital-dependent hopping matrix elements and spin-orbit coupling, Mihály *et al.*[15] proposed the formation of a spin-singlet pair liquid, which shows no static pairing over a broad temperature interval below T_{MI} and exhibits long-range static ordering only at T_{X}. They suggested that the transition at T_{X} is not accompanied by a considerable entropy change because of the pre-existing short-range ordering, which may explain why there is no appreciable anomaly in specific heat and thermal expansion.

In the previous paper,[12] we reported the results of nuclear resonance experiments of $BaVS_3$ at low temperatures. The zero-field resonances found in a frequency range of <24 MHz and at 1.4 K were interpreted as ^{51}V NQR. Field-swept spectra measured at the same temperature were consistently explained by this interpretation. These results imply no static spins even at low temperatures. The detection of magnetic reflections is inconsistent with this interpretation if we apply the same hyperfine coupling constant estimated from the Knight shift in the paramagnetic state, $A_{\mathrm{hf}} \simeq -120\,\mathrm{kOe}/\mu_{\mathrm{B}}$;[20, 21] we expect antiferromagnetic nuclear resonances at ∼70 MHz for the ordered moment of $\sim 0.5\,\mu_{\mathrm{B}}$/V. On the other hand, muon spin relaxation experiments detected the appearance of static hyperfine fields at muon sites below T_{X},[19] which is in accordance with the neutron observation. Some possible interpretations of these contradictory results are discussed. First, a kind of charge ordering in V sites, which gives rise to a separation of V sites into magnetic and nonmagnetic sites, should be considered. The nonmagnetic (or spin-singlet) sites give low-frequency signals and magnetic atoms give another high-frequency signal, which has not been observed in our sample for various reasons. Such charge ordering has been found in some vanadium oxides.[22] Almost two decades ago, Heidemann and Takano[23] proposed, on the basis of the intensity analysis of neutron inelastic intensity, that only about half of the V sites are magnetic and the other half remain nonmagnetic. Nishihara and Takano[20] observed a zero-field signal at around 100 MHz for their sample. However, we did not detect such a signal in our sample. Instead, for S-deficient samples, we observed ferromagnetic nuclear resonance signals at >130 MHz;[24] the frequency exactly corresponds to the full moment of $S = \frac{1}{2}$ $(1\,\mu_{\mathrm{B}})$. Nevertheless, we cannot deny the possible coexistence of the high-frequency signal in pure $BaVS_3$, which has not been observed due to certain reasons such as a short relaxation time. To check the possibility of charge ordering, we need explicit

evidence of the separation of the V site. Another possibility is that the antiferromagnetic sublattice fluctuates (or rotates) faster than the NMR frequency ($\sim 10^{-7}$ s) but slower than the neutron passing time ($\sim 10^{-12}$ s). In particular, ground-state degeneracies due to the chirality in the 120° structure[9] may give rise to this kind of unique spin dynamics. Discrepancy between NMR and neutron diffraction results has been found in some compounds with the same crystal structure. For example, for $CsMnI_3$, neutron diffraction revealed the 120° structure in the c plane canted to the c axis of the $S = \frac{5}{2}$ full moment.[25] Kubo *et al.*[26] argued that the ^{55}Mn hyperfine field in $CsMnI_3$ is smaller than that expected for the $S = \frac{5}{2}$ moment because the ^{55}Mn nucleus feels only an axial component due to the rapid rotation of spins around the c axis. For $CsMnBr_3$, which exhibits the 120° structure, the dynamical chirality has recently been argued by means of polarized neutron scattering.[27] In the case of $BaVS_3$, if spins are confined to the c plane and rotate around the c axis faster than the NMR frequency, the averaged hyperfine field may be zero or very small. Here, one has to keep in mind that both the above interpretations hinge on the assumption that the hyperfine coupling estimated in the paramagnetic state is also effective in the magnetically ordered state. This is usually accepted *a priori* but may not always be true. There may be a mechanism to reduce the hyperfine coupling in the magnetically ordered (or orbital-ordered) state of these kinds of compounds, which are characterized by strong covalency. A similar situation, i.e., a large discrepancy in the ordered moments estimated from neutron diffraction and NMR, has also been reported for another vanadium sulphide, V_5S_8.[28,29] Therefore, this inconsistency may be a general trend for vanadium sulphides. In order to reach a conclusion, more experimental results from various viewpoints should be accumulated.

In conclusion, we found incommensurate long-range magnetic ordering with the propagation vector (0.2260.2260) (in the hexagonal index) below $T_X \simeq 30$ K. The ordered moment is estimated to be $\sim 0.5\,\mu_B$. Between $T_{MI} \simeq 70$ K and T_X, a spin-liquid-like state is formed. These anomalous properties may be caused by the charge (or orbital) instability and/or characteristic spin dynamics of geometrically frustrated triangular lattice chains.

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