

Magnetism of BaVSe₃

Tomoaki YAMASAKI*, Saurav GIRI**, Hiroyuki NAKAMURA and Masayuki SHIGA

Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501

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Magnetic and transport properties of ferromagnetic BaVSe₃ (the Curie temperature $T_C \simeq 43$ K) were investigated. The resistivity shows metallic behavior. The saturation magnetization in the ferromagnetic state is homogeneously reduced to $0.34 \mu_B/\text{f.u.}$ in contrast to the large paramagnetic moment $1.42 \mu_B/\text{f.u.}$; the nearly full moment value for a local spin $1/2$. NMR experiments revealed a single magnetic V site below T_C . Although the macroscopic magnetic properties of BaVSe₃ is similar to those of sulfur-deficient BaVS_{3- δ} , BaVSe₃ is characterized by the itinerant electron magnetism in contrast to more ionic characters of the BaVS₃ system.

KEYWORDS: BaVSe₃, transition-metal chalcogenide, NMR, itinerant electron magnetism

§1. Introduction

BaVX₃ ($X = \text{S}$ and Se) form a hexagonal perovskite-type structure with a triangular lattice of V atoms in the c plane. Each V atom is in the octahedral configuration of chalcogen atoms. These substances show structural transitions from hexagonal to orthorhombic at $T_S \simeq 240$ K and 310 K for BaVS₃ and BaVSe₃, respectively.¹⁻⁵⁾ BaVS₃ is known to show a metal-insulator transition at $T_{\text{MI}} \simeq 70$ K with a sharp peak of the susceptibility at T_{MI} .³⁾ Recently long-range and incommensurate antiferromagnetic ordering was found below $T_X \simeq 30$ K by low-energy neutron diffraction experiments,⁶⁾ although the spin singlet ground state was suggested from ⁵¹V nuclear resonance experiments.⁷⁾ Note that the magnetic ordering temperature T_X is different from T_{MI} . In spite of a number of experiments, magnetic states below T_{MI} and the origin of the transitions at T_{MI} and T_X of BaVS₃ is not yet clear.

The sulfur deficient system BaVS_{3- δ} exhibits ferromagnetic behaviors in spite of the strong antiferromagnetic coupling in the stoichiometric BaVS₃.⁸⁾ Recently, we reported results of ⁵¹V NMR experiments of BaVS_{3- δ} and concluded that ferromagnetic V atoms with the moment of nearly $1 \mu_B$ and nonmagnetic ones coexist in BaVS_{3- δ} ⁹⁾ and, as a result, the averaged spontaneous magnetization becomes small, $0.34 \mu_B$ per formula unit (f.u.). It is known that the macroscopic magnetic properties of BaVSe₃ are similar to those of sulfur-deficient BaVS_{3- δ} . The detailed investigation of BaVSe₃ may give a hint to understand the unique properties of BaVS₃. In this paper, we report the magnetic and transport properties of BaVSe₃, particularly stressing on the comparison between the microscopic magnetic properties of BaVS_{3- δ} and BaVSe₃ probed by NMR.

§2. Experimental Procedures

A polycrystalline sample of BaVSe₃ was prepared by a standard solid-state reaction technique from chemicals with a molar ratio of BaSe : VSe₂ : Se = 1 : 1 : 0.1. The excess of Se was mixed to avoid Se deficiency. The mixture sealed in an evacuated quartz tube was heated at 950°C for 100 hours. A temperature dependence of the susceptibility was measured with a SQUID magnetometer from 2 to 300 K at 1 T. Magnetization curves were measured at several temperatures up to 5 T to determine spontaneous magnetizations and the Curie temperature. The resistivity was measured by the four-probe technique from 325 to 4 K. For the resistivity measurement the powder sample was pressed under 50 kgf/cm² pressure into a plate with the size $1.8 \times 6 \times 13$ mm³ and sintered at 700°C for 12 hours in an evacuated quartz tube. NMR measurements were performed at 1.4 K with a phase-coherent-type pulsed spectrometer.

§3. Results and Discussion

Figure 1 shows the temperature dependence of M/H measured at $H = 1$ T, where M and H are magnetization and external field, respectively. The magnetization increases rapidly below about 40 K due to ferromagnetic ordering. The magnetization curve measured at 2 K is shown in the inset of Fig. 2. The inverse of the susceptibility in a high temperature range is shown by open circles in Fig. 3. The susceptibility obeys the modified Curie-Weiss law, $\chi = C/(T - \Theta) + \chi_0$, with the effective moment $p_{\text{eff}} \simeq 1.42 \mu_B$, the paramagnetic Curie temperature $\Theta \simeq 44$ K and the temperature independent susceptibility $\chi_0 \simeq -1.5 \times 10^{-4}$ emu/mol. The value of p_{eff} is approximately equal to that of a local spin $S = 1/2$. The negative χ_0 seems to be unusual for this kind of metallic system (see below). Rather, the temperature dependence of Θ may be responsible for the deviation from the Curie-Weiss law. A slight jump of $d\chi/dT$ was observed at the structural transition (~ 300 K) as shown in the inset of Fig. 1. Figure 2 shows the Arrott plot

*Present address: Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501.

**Present address: Department of Solid State Physics, Indian Association for the Cultivation of Science, 2A & 2B Raja S.C. Mallik Road, Jadavpur, Kolkata 700 032, India.

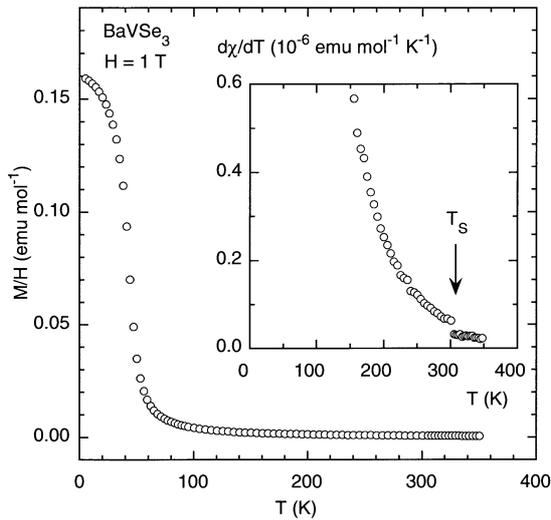


Fig. 1. The temperature dependence of M/H measured at $H = 1$ T. The inset shows the temperature dependence of $d\chi/dT$ at around the structural transition T_S .

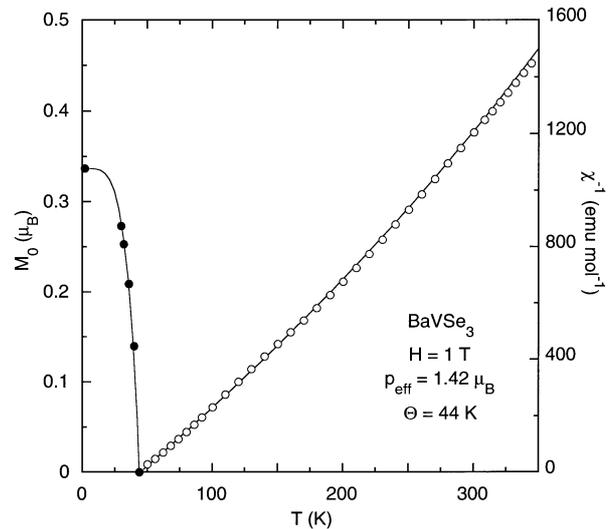


Fig. 3. The temperature dependence of the inverse susceptibility above T_C (open circles) and the spontaneous magnetization below T_C estimated from the Arrott plot (closed circles).

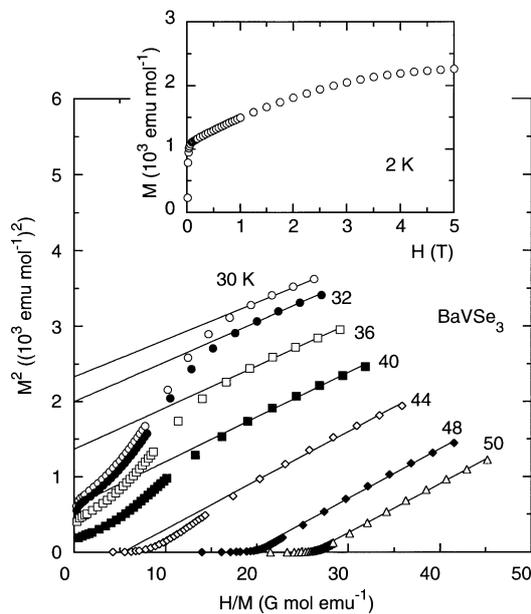


Fig. 2. The Arrott plot around T_C . The inset shows the magnetization curve at 2 K.

around the Curie temperature T_C . The linear relation between M^2 and H/M is indicated by solid lines. As the temperature where the spontaneous magnetization disappears, T_C was determined to be 43 K, which is nearly equal to Θ estimated above. The spontaneous magnetization was estimated from the extrapolation of the M^2 – H/M lines to $H = 0$. The temperature dependence of the spontaneous magnetization is shown by closed circles in Fig. 3. The value of the macroscopic magnetization at 2 K, $0.34 \mu_B/\text{f.u.}$, is much smaller than $1 \mu_B$ expected for $S = 1/2$. These results are in good accordance with the previously reported ones¹⁾ and quite similar to those of sulfur-deficient $\text{BaVS}_{3-\delta}$.⁹⁾

Figure 4 is the temperature dependence of the resistivity measured from 325 to 4 K. Since the resistivity

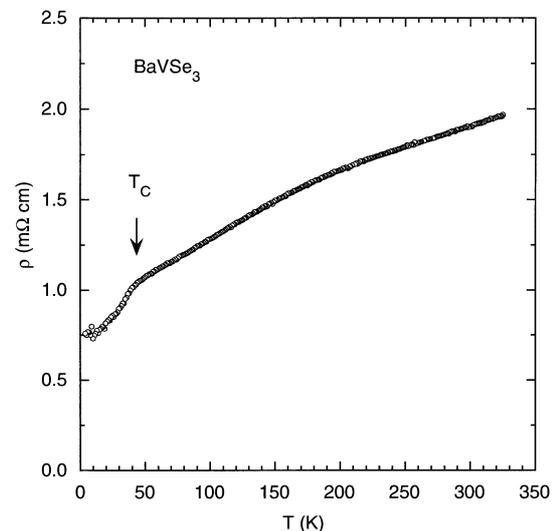


Fig. 4. The temperature dependence of the resistivity measured for fixed powder.

was measured for fixed powder, the residual resistivity is large although the absolute value may not be so reliable. In the entire temperature range the resistivity shows a metallic behavior with an anomaly at T_C . No appreciable anomaly was found at the structural transition T_S . The metallic temperature dependence is in contrast to the metal insulator transition observed for BaVS_3 ³⁾ and semiconducting behaviors of $\text{BaVS}_{3-\delta}$.⁹⁾

To obtain microscopic information we measured NMR at 1.4 K. Any signal has not been detected above T_C probably due to the fast nuclear magnetic relaxation. The frequency dependence of the spin-echo intensity measured at zero field is shown in Fig. 5. A zero-field resonance was observed at around 81.5 MHz. Figure 6 shows spin-echo field-swept spectra measured at several frequencies. Two kinds of signals were observed. Peak positions are plotted against frequency in Fig. 7. The

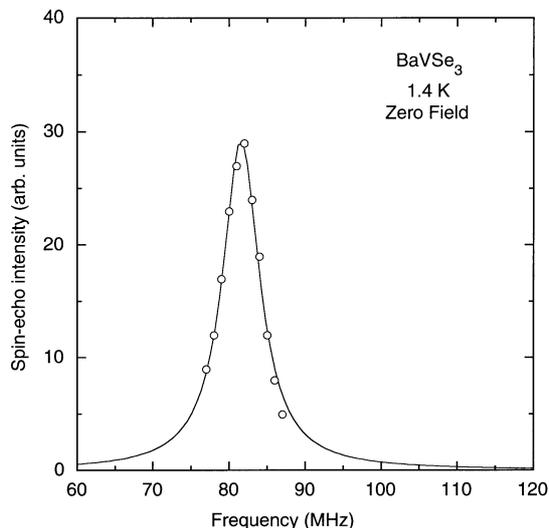


Fig. 5. The frequency dependence of the ^{51}V spin-echo intensity measured at zero field at 1.4 K.

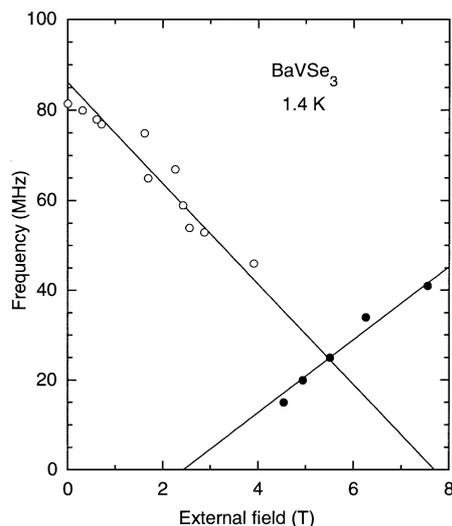


Fig. 7. The frequency dependence of the resonance field at 1.4 K. Open and closed circles are assigned to ^{51}V and ^{77}Se signals, respectively. Straight lines are drawn with the slopes of γ for corresponding nuclei.

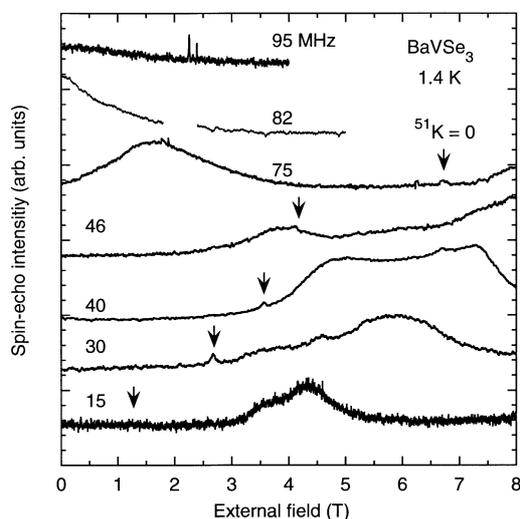


Fig. 6. Examples of field-swept NMR spectra measured at 1.4 K. The zero-Knight shift position for ^{51}V is indicated by arrows.

resonance field of one of the signals, shown by open circles in Fig. 7, decreases with increasing the operating frequency, i.e., negative hyperfine coupling, and merges to the zero-field signal at ~ 81.5 MHz. The slope is in good agreement with the gyromagnetic ratio for ^{51}V , $^{51}\gamma = 11.193$ MHz/T, indicating that the signal comes from ferromagnetic V atoms. Only a tail of the ferromagnetic signal was seen at higher frequencies than 81.5 MHz. The other signal was observed in a low-frequency and high-field range. The resonance field, shown by closed circles in Fig. 7, increases with increasing the frequency. This signal, on a linear line with a positive slope of approximately $^{77}\gamma = 8.13$ MHz/T, may be assigned to ^{77}Se . Though a weak and sharp signal was observed at around the ^{51}V zero Knight shift position (indicated by arrows in Fig. 6), this signal seems to be attributable to an extrinsic phase including paramagnetic V. The essential point is that the strong ^{51}V para-

magnetic signal as observed for sulfur-deficient $\text{BaVS}_{3-\delta}$ was not detected for BaVSe_3 ,⁹⁾ implying a single magnetic V site in BaVSe_3 in contrast to the two different magnetic sites in $\text{BaVS}_{3-\delta}$; generally it is unlikely that the paramagnetic signal is invisible due to the shorter relaxation time than that of the magnetic signal.

The resistivity result indicates that BaVSe_3 is a metallic system, which is in contrast to more ionic characters of the sulfides. This fact seems to dominate the essential difference of the magnetism between the BaVS_3 and BaVSe_3 systems. For BaVSe_3 we may expect the itinerant electron magnetism rather than localized one. The homogeneous reduction of the ordered moment in BaVSe_3 may be a characteristic of the itinerant electron magnet. On the other hand, the separation of the magnetic sites in the sulfur-deficient $\text{BaVS}_{3-\delta}$ may be reasonable since the charge separation is expected in the ionic $\text{BaVS}_{3-\delta}$. For sulfur-deficient $\text{BaVS}_{3-\delta}$, we observed the zero-field NMR signal at higher frequencies at around 137 MHz,⁹⁾ which just corresponds to the resonance frequency expected for the V magnetic moment of $1 \mu_B$, assuming the hyperfine coupling constant, $-12 \text{ T}/\mu_B$, obtained from ^{51}V Knight-shift experiments of BaVS_3 above T_S .^{10,11)} Assuming the same hyperfine coupling, the resonance frequency 81.5 MHz (the internal field 7.3 T) of BaVSe_3 corresponds to the ordered moment $0.61 \mu_B/\text{V}$, which is somewhat larger than the spontaneous magnetization $0.34 \mu_B/\text{V}$. Contrary, assuming the unique moment value $0.34 \mu_B/\text{V}$ for all V atoms, we estimate $-21 \text{ T}/\mu_B$ as the hyperfine coupling constant, which may be acceptable for the itinerant 3d electron ferromagnet if transferred fields from neighboring atoms are large and additive. We estimate the internal field at the Se site to be 2.4 T from the extrapolation of the frequency dependence of the resonance field. Then the coupling constant for ^{77}Se is estimated to be $7.2 \text{ T}/\mu_B$. This large value for ligands suggests rather large electron polarization at the Se site, indicat-

ing strong covalency or electron hybridization between V and Se. This is consistent with the itinerant character of the magnetism.

In conclusion, we measured the magnetic and transport properties of BaVSe₃. BaVSe₃ is metallic in all the temperature range. The Curie temperature, the spontaneous magnetization and the effective moment were estimated to be 43 K, 0.34 μ_B /f.u. and 1.42 μ_B /f.u., respectively. In the ferromagnetic state only an single V site was observed by the NMR measurements. The reduced ordered moment may be due to the itinerancy of 3d electrons. Although the macroscopic magnetic properties of BaVSe₃ is similar to those of sulfur-deficient BaVS_{3- δ} , the microscopic magnetism is different and BaVSe₃ is classified as the itinerant electron magnet. As a whole, the selenide BaVSe₃ has stronger covalency than the sulfide BaVS₃, discriminating the magnetism of these materials. This is in accordance with the general trend for transition-metal chalcogenides. Although the origin of the structural transition is not evident within the present study, the Jahn-Teller interaction seems to be still dominant in this itinerant electron system.

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