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Magnetic phase boundary of BaVS$_3$ clarified with high-pressure $\mu^{+}$SR

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The magnetic nature of the quasi-one-dimensional BaVS$_3$ has been studied as a function of temperature down to 0.25 K and pressure up to 1.97 GPa on a powder sample using the positive muon spin rotation and relaxation ($\mu^{+}$SR) technique. At ambient pressure, BaVS$_3$ enters an incommensurate antiferromagnetic ordered state below the Néel temperature ($T_N$) 31 K. $T_N$ is almost constant as the pressure ($p$) increases from ambient pressure to 1.4 GPa, then $T_N$ decreases rapidly for $p > 1.4$ GPa, and finally disappears at $p \sim 1.8$ GPa, above which a metallic phase is stabilized. Hence, $T_N$ is found to be equivalent to the pressure-induced metal-insulator transition temperature ($T_{\text{MI}}$) at $p > 1.4$ GPa.

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I. INTRODUCTION

The magnetic ground state of the two-dimensional triangular lattice with $S = \frac{1}{2}$ is expected to vary with the external pressure ($p$), mainly due to a change in the interactions between the nearest-neighboring magnetic ions [1]. Particularly for the quasi-one-dimensional (Q1D) compound BaVS$_3$ (see Fig. 1) [2–6], in which the 1D ferromagnetic (FM) interaction along the $c$ axis is stronger than the two-dimensional (2D) antiferromagnetic (AF) interaction along the $a$ axis [7], a metal-insulator transition occurs at $T_{\text{MI}} = 70$ K at ambient pressure. However, as $p$ increases, $T_{\text{MI}}$ is found to vanish at a critical pressure ($p_{c}$) $\sim 1.8$ GPa, based on resistivity, infrared, and x-ray diffraction (XRD) measurements [8–11]. The metal-insulator transition is thought to be induced by the formation of a commensurate charge-density wave (CDW) Peierls ground state below $T_{\text{MI}}$ with the doubling of the $c$-axis length. Interestingly, such second-order Peierls transition disappears at $p \sim 1.5$ GPa, and a commensurate-incommensurate (C-IC) first-order structural transition occurs instead. Finally, a metallic ground state is stabilized at $p \geq 1.8$ GPa, implying the presence of a quantum critical transition (QCT) in BaVS$_3$ [12].

Despite the drastic changes in structural and electrical properties at $T_{\text{MI}}$ mentioned above, a magnetic transition is found to occur at 30 K and not at $T_{\text{MI}}$. That is, even though the magnetization-vs-temperature [$M(T)$] curve exhibits a sharp maximum at $T_{\text{MI}}$ [3–5], past NMR [14,15] and neutron diffraction work [16] clarified that BaVS$_3$ undergoes a magnetic transition from a high-$T$ paramagnetic state to a low-$T$ IC-AF ordered state below $T_N = 30$ K at ambient pressure. The IC magnetic modulation vector was assigned to (0 0 2 2 6 0) in a hexagonal setting and the ordered magnetic moment was estimated as $\sim 0.5 \mu_B$ at 4 K [16]. The details of the IC-AF state are still unknown, but either a linear or a cycloidal spin density wave (SDW) order state was proposed as a ground state. In addition, since at present there is no available data on the pressure dependence of $T_N$, the following three scenarios were proposed for the $T - p$ phase diagram of BaVS$_3$ [17]:

1. $T_N$ is suppressed to zero at $p < p_{c}$,
2. $T_N$ is suppressed to zero at $p = p_{c}$, or
3. $T_N$ is suppressed to zero at $p > p_{c}$.

Based on magnetoresistance measurements under high pressures, scenario 3 was thought to be suitable for BaVS$_3$ [17,18]. Note that, besides scenario 2, the IC-AF order is assumed to be independent of the structural modification caused by the CDW formation. Such independence is consistent with the fact that $T_{\text{MI}} = 70$ K, whereas $T_N = 30$ K at ambient pressure.

To understand the correlation between the crystal structure and the magnetic order, an essential first step would be to clarify the pressure dependence of $T_N$ in BaVS$_3$ with direct magnetic measurements. A positive muon spin rotation and relaxation ($\mu^{+}$SR) experiment has therefore been performed under pressures up to 2 GPa. The $\mu^{+}$SR technique is one of the most powerful tools for studying internal magnetic fields in solids [19,20] including the Q1D compounds [21–24], and,
in this paper, it demonstrates that scenario 2 is realized in BaVS₃.

II. EXPERIMENTAL

A powder sample of BaVS₃ was prepared by a conventional solid-state-reaction technique reported in Ref. [5]. That is, a mixture of BaS (99.9%±), V (99.9%), and S (99.9999%) was heated in an evacuated quartz tube at 1223 K for four days. The reaction mixture was ground and then heated at 923 K with excess sulfur in an evacuated quartz tube for three days to avoid sulfur deficiency. After the synthesis, the powdered sample was characterized by XRD. Later, the sample was sealed in a quartz tube together with S and transferred to the Paul Sherrer Institute (PSI) in Switzerland. Immediately before the μ⁺SR measurements, the sample was removed from the quartz tube.

The μ⁺SR spectra of BaVS₃ were recorded using both the General Purpose Spectrometer (GPS) at the surface muon beam-line pIM3 and the General Purpose Decay-Channel Spectrometer (GPD) at the decay beam line muE4 of the Laboratory for muon spin spectroscopy (LMU) of the PSI in Switzerland. On the GPS, approximately 200 mg of powder sample was placed in an envelope with 1 × 1 cm² area, made of Al-coated Mylar tape with 0.05 mm thickness to minimize the signal from the envelope. The envelope was attached to a fork-type low-background sample holder and inserted in a liquid-He flow-type cryostat for measurements in a temperature range between 2 and 40 K.

On the GPD, three pelletized discs of the powder sample with 6-mm diameter and 15-mm total height (5 mm each) were stacked in a piston-cylinder-type pressure cell made of MP35 alloy. To apply hydrostatic pressure to the sample, Daphne oil was used as a pressure-transmitting medium. The actual pressure at low temperatures was estimated by measuring the superconducting transition temperature of an indium wire placed at the bottom of the sample space, by AC susceptibility. The accuracy of the pressure determined by such measurement is estimated as ±0.01 GPa [25]. A Janis ⁴He flow cryostat and a Quantum ⁴He cryostat with a ³He insert were used to reach temperatures as low as 2 K and 0.25 K, respectively.

The experimental techniques are described in more detail elsewhere [19,20,26,27]. The obtained μ⁺SR data was analyzed with the MUSRFIT software suite [28].

The muon sites in the BaVS₃ lattice were predicted by density-functional theory (DFT) calculations for the total electron energy with the VASP code package [29]. Such predictions reveal that there are two possible muon sites in the lattice. That is, (2/3, 1/3, 3/4) and (1/3, 1/3, 1/2) (see Fig. 1).

III. RESULTS AND DISCUSSION

In this section, the microscopic magnetic nature of BaVS₃ under ambient pressure is described in the first two subsections (Secs. III A and III B). Pressure-dependent results, the main part of this paper, are reported in the last two subsections (Secs. III C and III D).
FIG. 3. (a) The Fourier transform power frequency spectrum of BaVS₃ obtained from the $\mu^+\mu$SR time spectra recorded at 2 K and the internal magnetic field at the two muon sites predicted by DIPOL-Calc [30] for (b) the linear IC-SDW order and (c) the cycloidal IC-SDW order with the modulation vector (0.226, 0.226, 0). In (a), arrows show the three frequencies to provide the best fit for the time spectra recorded at 2 K and the field distributions for both orders are almost the same as those for $\xi = 0$, i.e., (b) and (c). (a) is the same as the top spectrum in Fig. 2(b).

a Kubo-Toyabe-like behavior even at 2 K due to a random internal magnetic field was reported. This is most likely caused by either lower sample quality or sample degradation problems in past work (see Sec. IV).

Since the AF order in BaVS₃ is incommensurate to the lattice [16], each muon feels a slightly different internal magnetic field. Thus, the ZF-$\mu$SR spectrum exhibits a rapidly damped oscillation with multiple frequencies. In fact, the frequency spectrum, i.e., the Fourier transform of the time spectrum, indicates the presence of at least three frequencies, $\sim$8 MHz, $\sim$11 MHz, and $\sim$21 MHz with large field distribution widths [Fig. 3(a)]. The comparison of the measured internal fields with the predicted internal magnetic fields at the two muon sites, i.e., (2/3,1/3,3/4) and (1/3,1/3,1/2), for the linear and the cycloidal IC-SDW order indicates that the linear IC-SDW is most probably realized in BaVS₃ below $T_N$ [Figs. 3(b) and 3(c)]. Note that for the linear IC-SDW, the direction of the magnetic moment is fixed and its magnitude is modulated between positive and negative values. For the cycloidal IC-SDW, the propagation vector is in the same ab plane as the rotating moments. Furthermore, recent resonant soft XRD measurements suggested the presence of two magnetically different V ions in the lattice [34], leading to a more complex IC-AF structure than that simulated in Fig. 3. However, at present it is difficult to calculate the internal magnetic field of such IC-AF order due to the absence of data concerning the direction and the magnitude of the ordered magnetic moments of the V ions. Moreover, although $\mu^+\mu$SR sometimes provides essential information to select the most reasonable magnetic structure among multiple proposed candidates [35,36], $\mu^+\mu$SR itself is a local probe and not a suitable tool to identify a magnetic structure, if one is based only on the $\mu^+\mu$SR data. Therefore, precise neutron diffraction experiments using a single-crystal sample is highly required to obtain information on the AF spin structure in BaVS₃.

Considering the field distribution shown in Fig. 3(b), the $\mu^+\mu$SR spectrum was fitted by a combination of a Gaussian relaxing Bessel function, contribution from the muons at site (1/3,1/3,1/2); two Gaussian relaxing cosine functions, contribution from the muons at site (2/3,1/3,3/4); an exponentially relaxing nonoscillatory signal for a 1/3 tail signal in a powder sample from the muons at both sites [19,20]; and a time-independent background signal from the muons stopped in nonmagnetic impurity phases in the sample and at surroundings of the sample,

$$A_0 P_{\text{ZF}}(t) = A_{\text{AF1}} J_0(2\pi f_{\text{AF1}} t) \exp \left(-\frac{\sigma_{\text{AF1}}^2 t^2}{2}\right) + A_{\text{AF2}} \cos(2\pi f_{\text{AF2}} t + \phi_{\text{AF2}}) \exp \left(-\frac{\sigma_{\text{AF2}}^2 t^2}{2}\right) + A_{\text{AF3}} \cos(2\pi f_{\text{AF3}} t + \phi_{\text{AF3}}) \exp \left(-\frac{\sigma_{\text{AF3}}^2 t^2}{2}\right) + A_{\text{tail}} \exp(-\lambda_{\text{tail}} t) + A_{\text{BG}},$$

where $A_0$ is the initial asymmetry, $A_{\text{AF1}}, A_{\text{AF2}}, A_{\text{AF3}}, A_{\text{tail}},$ and $A_{\text{BG}}$ are the asymmetries associated with the five signals, $J_0(2\pi f t)$ is a zeroth-order Bessel function of the first kind that describes the muon polarization evolution in an incommensurate field distribution [19,20,37]. Here, $f_{\text{AF1}}$ and $f_{\text{AF2}}$ represent higher cutoff frequencies, while $f_{\text{AF3}}$ represents a lower cutoff frequency, i.e., $f_{\text{AF1}} > f_{\text{AF2}} > f_{\text{AF3}}$. More precisely, both field distributions for the muons at site (1/3,1/3,1/2) and site (2/3,1/3,3/4) in Fig. 3(b) are characteristic for an IC-AF order. The former single-peak distribution drawn by a red line is well reproduced by $J_0$, while the latter double-peaked distribution drawn by a black line is better fitted with two cosines than with a combination of $J_0$ and cosine [37]. This is because $J_0$ is nonzero even at 0 MHz. The AF3 signal, which corresponds to the lower peak in the double-peaked distribution, is well fitted with a cosine, since such distribution is thought as a delta function in the frequency domain. Furthermore, based on the weak transverse field (wTF) measurements described in Sec. III B, $A_0 = 0.25$, $A_{\text{BG}} = 0.025$, and we assume $\sum_{i=1} A_{\text{AFi}} = \frac{f}{4}(A_0 - A_{\text{BG}})$ and $A_{\text{tail}} = \frac{1}{4}(A_0 - A_{\text{BG}})$ at temperatures below 25 K.

Figure 4 shows the temperature dependencies of the $\mu^+\mu$SR parameters in Eq. (1). Each of the three precession frequencies ($f_{\text{AFi}}$) decreases with increasing temperature and disappears at $T_N$. Below the vicinity of $T_N$, i.e., at temperatures above 28 K, the AF2 signal merges to the AF3 signal, as seen in
FIG. 4. The temperature dependencies of the ZF-μ+SR parameters in BaVS$_3$ at ambient pressure. (a) The three muon spin precession frequencies (f$_{AF1}$, f$_{AF2}$, and f$_{AF3}$), (b) the normalized asymmetries (A$_{AF1}/A_0$, A$_{AF2}/A_0$, and A$_{AF3}/A_0$), and (c) the Gaussian relaxation rates of AF signals ($\sigma$$_{AF1}$, $\sigma$$_{AF2}$, and $\sigma$$_{AF3}$), (d) the delay of the initial phase ($\phi$$_{AF2}$ and $\phi$$_{AF3}$), and (e) the exponential relaxation rate of the tail signal ($\lambda$$_{tail}$). The data were obtained by fitting the ZF-μ+SR spectrum with Eq. (1). Vertical broken lines show the Néel temperature determined by weak transverse field measurements (see Fig. 6); that is, T$_N$ = 31.55(6) K. In (a) and (b), error bars are smaller than the data point symbols.

Fig. 2(b). Using the fitted values of f$_{AF1}$, f$_{AF2}$, and f$_{AF3}$ at 2 K and the linear IC-SDW model, the ordered V moment ($\mu$$_{ord}$) is estimated as 1.20(7) $\mu_B$ (Fig. 5). However, the past neutron work using a powder sample reported that $\mu$$_{ord}$ ~ 0.5 $\mu_B$ at 4 K, under the assumption that the ordering occurred with a constant magnitude within the ab plane [16]. This could be a reason for the underestimation of $\mu$$_{ord}$ with neutron diffraction. To clarify the reason for such discrepancy between $\mu$$_{ord}$ estimated with μ+SR and that with neutron, it is highly preferable to perform neutron diffraction experiments using a high-quality single crystal sample. In fact, for Nd$_2$Fe$_{14}$B magnets, the neutron work using a powder sample reported that the ordered Nd moment ($\mu$$_{Nd}$) is ≲ 1 $\mu_B$ [38] or 1.5 $\mu_B$ [39], while the neutron study using a single-crystal sample revealed that $\mu$$_{ord}$ = 3.2 $\mu_B$ [40]. On the contrary, μ+SR on a powder sample showed that $\mu$$_{ord}$ = 3.31 $\mu_B$ [41].

Back to Fig. 4(b), as temperature increases from 2 K, each asymmetry is roughly temperature independent up to around 15 K. Then A$_{AF2}$ increases up to ~0.1 at around 22 K, instead of the decreases in A$_{AF1}$. Then, A$_{AF2}$ decreases with further increasing temperature and merges into A$_{AF3}$ at ~29 K, whereas A$_{AF1}$ increases monotonically with temperature. Such oscillatory components become 0 at T$_N$, while A$_{tail}$ increases with further increasing temperature and approaches the maximum value above T$_N$.

As seen in Fig. 4(c), the relaxation rates, $\sigma$$_{AF3}$ ranges below 10 $\mu$s$^{-1}$ and almost temperature independent up to about 25 K, i.e., in the vicinity of T$_N$. σ$_{AF1}$, on the other hand, increases ~16 $\mu$s$^{-1}$ at the lowest temperature measured (2 K). At higher temperatures, it decreases with increasing temperature up to 22 K, and starts increasing again toward T$_N$ like a critical behavior. On the contrary, $\sigma$$_{AF2}$ ~ 10 $\mu$s$^{-1}$ at 2 K and increases with temperature up to 20 K, then it decreases again and merges into $\sigma$$_{AF3}$ at ~29 K.

For a field distribution at the muon site created by an IC magnetic structure, a cosine fit of the internal magnetic field [38] is known to provide a large delay of the initial phase (φ$_{AF}$) [19,20,37]. Indeed, both $\phi$$_{AF2}$ and $\phi$$_{AF3}$ range between $-7$ and $-50^\circ$ even at 2 K due to the wide field distribution at the muon sites [Fig. 4(d)].

For the tail signal, which corresponds to the parallel component of the internal magnetic fields to the initial muon spin polarization, $\lambda$$_{tail}$ is very small compared with $\lambda$$_{AF}$ at temperatures below T$_N$, and decreases with decreasing temperature [Fig. 4(e)], as expected.

Overall, the μ+SR parameters obtained by fitting with Eq. (1) vary continuously with temperature. However, as seen in Fig. 2(b), the Fourier transform spectrum at 2 K looks slightly different from those above 2 K. Such difference is explained by the increase in $\sigma$$_{AF2}$ with temperature below 20 K, leading to a reduction of the height of the central peak in Fig. 5. The relationship between the measured internal magnetic field ([f$_{AF}/(\gamma\mu/2\pi)$]) at 2 K and the simulated internal magnetic field for the linear SDW. Here, $\gamma\mu/2\pi$ is the muon gyromagnetic constant (13.554 kHz/Oe). Since the magnetic order is AF, we assumed that the internal magnetic field is equivalent to the dipole field. A solid line represents a linear fit, which provides $\mu$$_{ord}$ = 1.20(7) $\mu_B$ at 2 K. Error bars are smaller than the data point symbol.

FIG. 5. The relationship between the measured internal magnetic field ([f$_{AF}/(\gamma\mu/2\pi)$]) at 2 K and the simulated internal magnetic field for the linear SDW. Here, $\gamma\mu/2\pi$ is the muon gyromagnetic constant (13.554 kHz/Oe). Since the magnetic order is AF, we assumed that the internal magnetic field is equivalent to the dipole field. A solid line represents a linear fit, which provides $\mu$$_{ord}$ = 1.20(7) $\mu_B$ at 2 K. Error bars are smaller than the data point symbol.
oscillatory signal rapidly decreases, but a slowly relaxing background signal increases, which corresponds to the tail signal in the ZF spectrum. Hence, considering Eq. (1), the wTF-μSR spectrum was fitted by a combination of an exponentially relaxing cosine oscillation due to wTF and two exponentially relaxing nonscillatory signals caused by the AF oscillations and tail components,

$$A_0 P_{TF}(t) = A_{TF} \cos(2\pi f_{TF} t + \phi_{TF}) \exp(-\lambda_{TF} t) + A_{AF} \exp\left(-\frac{\sigma_{AF}^2}{2}\right) + A_{tail} \exp(-\lambda_{tail} t),$$

where \( f_{TF} \) is the muon spin precession frequency due to wTF and is given by \( f_{TF} = \gamma_0 / 2\pi \times 50 \text{ Oe} \times 13.554 \text{ kHz/Oe} \times 50 \text{ Oe} \approx 0.68 \text{ MHz} \). The \( A_{AF} \) signal corresponds to the first three terms in Eq. (1), which are predominant in an early time domain below 0.5 μs. However, since we need to focus on the \( A_{TF} \) oscillatory signal up to 10 μs in the wTF-μSR spectrum, the sum of the first three terms in Eq. (1) is simplified as one exponentially relaxing \( A_{AF} \) signal in Eq. (2).

Figure 6(b) shows the temperature dependencies of the three normalized asymmetries (\( A_{AF}/A_0 \), \( A_{AP}/A_0 \), and \( A_{tail}/A_0 \)). The magnitude of wTF was 50 Oe. In (a), solid lines represent the best fits with Eq. (2). In (b), a solid line represents the best fit with a sigmoid function, and error bars are smaller than the data point symbols.

in Fig. 2(b) above 2 K. This also implies a small change in the field distribution formed by the IC-AF order, for the details are unknown at present. To clarify this, neutron diffraction work on a high-quality single-crystal sample is desirable, as already mentioned.

Finally, it should be noted that, besides the discrepancy between the estimated \( \mu_0^V_{ord} \) from μ+SR and neutron diffraction, the temperature dependencies of the \( \mu^+ \)SR parameters are consistent with the NMR [14,15] and neutron diffraction [16] results, i.e., the static AF order appears below \( \sim 31 \) K.

C. wTF-μSR at high pressures

Figure 7 shows the wTF-μSR spectrum above and below \( T_N \). Since the pressure cell is paramagnetic even at the lowest temperature achievable on the GPD, the muons stopped in the pressure cell provide (similar to a nonmagnetic impurity phase in the sample) an oscillatory signal due to wTF regardless of temperature. More correctly, a nonmagnetic impurity phase in the sample also provides a temperature-independent wTF oscillatory signal.

At temperatures above \( T_N \), the muons stopped in the BaVS₃ phase also give an oscillatory signal due to wTF. The wTF-μSR spectrum thus exhibits the wTF oscillation with a full asymmetry in total [Fig. 7(a)]. On the contrary, at temperatures below \( T_N \), wTF in the BaVS₃ phase is hidden by the larger AF internal field, which is given by a sum of the AF oscillatory signals and 1/3 tail signal [Eq. (1)], leading to the loss of the wTF asymmetry from the BaVS₃ phase. In this case, about 40% of the implanted muons stop in the BaVS₃ phase and the rest 60% in the pressure cell [Fig. 7(b)] (more correctly, about 4% in the nonmagnetic impurity phase in the sample and 56% in the cell). Therefore, by measuring the wTF-μSR spectrum as a function of temperature, \( T_N \) of BaVS₃ is clearly determined even in the pressure cell. The wTF-μSR spectrum at high pressures was also fitted by Eq. (2).

Figure 8(a) shows the normalized \( A_{TF}(T) [A_{TF}(T)/A_0] \) curves at several pressures. At ambient pressure, as \( T \) decreases from 45 K, the \( A_{TF}(T)/A_0 \) curve exhibits a sharp drop.

FIG. 6. (a) wTF-μSR spectra for BaVS₃ recorded at selected temperatures and (b) the temperature dependencies of the three normalized asymmetries, \( A_{TF}/A_0 \), \( A_{AP}/A_0 \), and \( A_{tail}/A_0 \). The magnitude of wTF was 50 Oe. In (a), solid lines represent the best fits with Eq. (2). In (b), a solid line represents the best fit with a sigmoid function, and error bars are smaller than the data point symbols.
FIG. 7. The wTF-μ+SR spectrum for the BaVS₃ sample in the pressure cell (a) above $T_N$ (45.0 K) and (b) below $T_N$ (4.9 K) at ambient pressure. The applied wTF was 50 Oe. In (a), both the sample and cell are paramagnetic, while in (b) only the cell is paramagnetic. From the wTF-μ+SR spectrum in (b), the volume fraction of the cell is estimated as about 60%.

at 30 K, as in the case without pressure cell [Fig. 6(b)]. As mentioned above, since about 60% of the implanted muons stop in the pressure cell, which is paramagnetic even at the lowest temperature measured, $A_{TF}/A_0$ is $\sim 0.6$ below $T_N$ [compare with Fig. 6(b) for the case without pressure cell]. From the middle point of the steplike change in the $A_{TF}(T)/A_0$ curve, $T_N$ is estimated as 30.2(3) K at ambient pressure, which is roughly equivalent to the value estimated from the wTF data obtained without pressure cell. The discrepancy between the GPD and GPS is probably caused by an indirect temperature measurement in the GPS, particularly for the fork-type folder, to which the sample is suspended by a Mylar tape. As pressure increases from ambient pressure, the transition temperature slightly shifts toward a lower temperature with pressure up to around 1.42 GPa. The transition temperature decreases rapidly at even higher pressures until finally it is completely suppressed at $p \geq 1.86$ GPa.

Using these $A_{TF}(T)/A_0$ curves, the estimated $T_N$ is plotted as a function of pressure together with the reported structural phase boundaries [11] in Fig. 8(b). $T_N$ is almost pressure independent until the structural phase boundary at $p \sim 1.4 - 1.5$ GPa, suggesting that the magnetic phase boundary corresponds to the structural phase boundary at $p \geq 1.4$ GPa. Moreover, the magnetic order is completely suppressed at $p \geq 1.86$ GPa, where a high-pressure metallic phase is stabilized as a ground state. Therefore, among the proposed three scenarios [17], the second one, in which $T_N$ is suppressed to zero at $p = P_{cr}$, is correct for BaVS₃.

The magnitude of $A_{TF}/A_0$ at the lowest temperature is found to slightly increase with pressure, meaning the decrease in the volume fraction of the sample with pressure. This is probably due to the compression of the pressed powder sample with pressure, which reduces the height of the sample discs and decreases the number of the muons stopped in the sample. Alternatively, the pressure medium, i.e., Daphne oil, could be compressed with pressure, leading to the increase in the density of the pressure medium. This would also reduce the number of the muons stopped in the sample. Since recent high-pressure $\mu^+\text{SR}$ measurements on $K_2\text{Cr}_8\text{O}_{16}$ using the same setup as this work also show a similar decrease in $A_{TF}/A_0$ with pressure [27], such decrease is most unlikely caused by an intrinsic change in the BaVS₃ sample.

D. ZF-μ+SR at high pressures

To study the magnetic ground state at high pressures, the ZF-μ+SR spectrum was also measured at the lowest temperature (see Fig. 9). It is very clear that the ZF-μ+SR spectrum recorded at $p = 1.42$ and 1.68 GPa is essentially the same.
as that recorded at ambient pressure, while the spectrum at $p = 1.74$ GPa is slightly different from those at $p \leq 1.68$ GPa. In the IC structure phase appearing in the high-$p$ and low-$T$ region, that is $p \geq 1.4$ GPa and $T \leq 30$ K [see Fig. 8(b)], the deviation from $1/2c^*$ is estimated as 0.015–0.024, whereas no change in $a^*$ and $b^*$ was observed [11]. Such a small structural modification along the $c$ axis is unlikely to drastically alter the internal magnetic field caused by the IC-AF order in the $ab$ plane, because the intrachain 1D interaction along the $c$ axis is FM-ordered 1D chains without 2D-AF order at high pressures, i.e., such a FM-ordered 1D chain behaves as a localized moment [22]. However, the ZF-$\mu^+$ SR result. On the other hand, the ZF-$\mu^+$ SR confirms the absence of magnetic order down to 0.25 K, when $p = 1.95$ GPa.

In the BaVS$_3$ lattice, the intrachain 1D FM interaction is known to be stronger than the interchain 2D AF interaction [7]. This could raise a question on the presence of a phase formed by either long or short FM-ordered 1D chains without the 2D-AF order at high pressures, i.e., such a FM-ordered 1D chain behaves as a localized moment [22]. However, the ZF-$\mu^+$ SR spectrum recorded at $T = 0.25$ K with $p = 1.95$ GPa demonstrates the absence of magnetic order. This suggests that both 1D-FM and 2D-AF interactions are suppressed by pressure, particularly at $p > 1.4$ GPa, and any magnetic order entirely vanishes at $p > p_c$. Therefore, we can exclude a contribution of magnetic order to the origin of a non-Fermi-liquid behavior observed by resistivity measurements at $p > p_c$ and $T < 40$ K [9].

To obtain $H_{\text{int}}$ in BaVS$_3$ at high pressures, we have attempted to extract the ZF-$\mu^+$ SR spectrum for BaVS$_3$, particularly in a slow time domain, from the spectrum recorded using a pressure cell. Such a spectrum is naturally represented as

$$A_0 P_{ZF}(p, T, t) = A_C P_{ZF,C}(p, T, t) + A_S P_{ZF,S}(p, T, t),$$  \hspace{1cm} (3)

where $A_C$ and $A_S$ are the asymmetries from the pressure cell and sample, and $P_{ZF,C}(p, T, t)$ and $P_{ZF,S}(p, T, t)$ are their respective depolarization function. $P_{ZF,C}(p, T, t)$ is known to be almost independent of $p$ and $T$ above 1.5 K [26]. Thus, if we ignore the small variations in $A_C$ and $A_S$ with $p$, $P_{ZF,S}(p, T, t)$ is roughly given by

$$A_S P_{ZF,S}(p, T, t) = A_0 P_{ZF}(p, T, t) - A_0 P_{ZF}(0.1\text{MPa}, T, t) + A_S P_{ZF,S}(0.1\text{MPa}, T, t).$$  \hspace{1cm} (4)

The ZF-$\mu^+$ SR measurements without pressure cell provide information about $P_{ZF,S}(0.1\text{MPa}, T, t)$ and $A_S \sim 0.42$ ($A_C \sim 0.58$) is obtained from Fig. 8(a). As a result, $P_{ZF,S}(p, T, t)$ at $p = 1.97$ GPa and $T = 2$ K is estimated as shown in Fig. 10(a), in which $P_{ZF,S}(0.1\text{MPa}, T, t)$ at $T = 40$ K is also plotted for comparison. Considering the fact that $A_{BG}/A_0 = 0.1$ from the wTF measurements without pressure cell [see Fig. 6(b)], the maximum value of $P_{ZF}$ for the BaVS$_3$ phase is fixed at 0.9.

In the paramagnetic state at $p = 0.1$ MPa and $T = 40$ K, the ZF-$\mu^+$ SR spectrum is fitted by a static Kubo-Toyabe function, $\frac{1}{2} + \frac{1}{2}(1 - \Delta^2/\tau^2)\exp(-\Delta^2/\tau^2)$, with the field distribution width $\Delta = 0.060(2)$ $\mu$T$^{-1}$ [corresponding to 0.70(2) Oe], which indicates that each muon feels only a nuclear magnetic field, i.e., the absence of localized V moments above $T_S$. On the other hand, in the pressure induced paramagnetic state at $p = 1.97$ GPa and $T = 2$ K, the time spectrum is fitted by an exponential relaxation function, $\exp(-\lambda t)$, with $\lambda = 0.185(6)$ $\mu$s$^{-1}$. This means that a slowly fluctuating $H_{\text{int}}$ caused by V moments are present even in a metallic state. Such slowly fluctuating $H_{\text{int}}$ is most likely the origin of a non-Fermi-liquid behavior [9] around QCT. To demonstrate the reliability of such extracted spectrum, Fig. 10(b) shows the comparison of the two normalized ZF-$\mu^+$ SR spectra in the AF state; that is, $P_{ZF,S}(p, T, t)$ at

![FIG. 9. The ZF-$\mu^+$ SR spectrum at the lowest temperature measured under five different pressures. Each spectrum is shifted upward by 0.03 for clarity of display.](image_url)

![FIG. 10. Comparison of the two normalized ZF-$\mu^+$ SR spectra for BaVS$_3$ recorded in (a) the paramagnetic states and (b) the antiferromagnetic state. In (a), black symbol shows the spectrum at 0.1 MPa and 40 K, while red symbols shows that at 1.97 GPa and 2 K. In (b), black symbol shows the spectrum at 0.1 MPa and 2 K, while red symbols shows that at 1.68 GPa and 2 K. The spectra shown by red symbols were extracted from three ZF-$\mu^+$ SR spectra using Eq. (4). In (a), a green solid line represents the best fit using a Kubo-Toyabe function, while a blue solid line represents the best fit using an exponential relaxation function. In (b), solid lines represent the best fit using an exponential relaxation function.](image_url)
$p = 1.68 \text{ GPa and } T = 2 \text{ K and } P_\text{ZF-S}(0.1 \text{ MPa}, T, t) \text{ at } T = 2 \text{ K}, \text{ which was recorded without pressure cell. Besides the oscillatory signal in an early time domain, both spectra exhibit the } 1/3 \text{ tail signal in the AF ordered state. A fit using an exponential relaxation function, } (A_{\text{tail}}/A_0) \exp(-\lambda_{\text{tail}}t), \text{ in the time domain between 0.5 and 9.7 } \mu s \text{ provides that } (A_{\text{tail}}/A_0) = 0.329(12) \text{ and } \lambda_{\text{tail}} = 0.038(7) \mu s^{-1} \text{ for the time spectrum under pressure, while } (A_{\text{tail}}/A_0) = 0.304(6) \text{ and } \lambda_{\text{tail}} = 0.044(4) \mu s^{-1} \text{ for the time spectrum at ambient pressure. Considering the small variations in } A_C \text{ and } A_S \text{ with } p, \text{ such extraction is found to give a reasonable } ZF-\mu^+\text{SR spectrum for the sample in a pressure cell.}

### IV. SUMMARY

We have investigated the microscopic magnetic nature of BaVS$_3$ at ambient and high pressures with $\mu$+$\text{SR using a powder sample. The } \mu^+\text{SR measurements in a zero magnetic field (ZF) at ambient pressure clarified the appearance of a clear oscillatory signal below } T_N = 31 \text{ K, which evidenced the formation of static AF order. The analysis of an internal magnetic field supported an incommensurate linear spin density wave order as a magnetic ground state of BaVS$_3$.}

The $\mu^+\text{SR measurements in a wTF at high pressures showed that } T_N \text{ is almost pressure } (p) \text{ independent up to } 1.4 \text{ GPa, then } T_N \text{ decreases rapidly with } p \text{ for } p > 1.4 \text{ GPa and finally disappears at } p_{\text{cr}} \sim 1.8 \text{ GPa, above which a paramagnetic phase is stabilized. This suggested that the AF order is coupled with a metal-insulator transition caused by the formation of long-range structural order. According to the } ZF-\mu^+\text{SR measurements at the lowest temperature measured, it was found that the internal AF field is almost } p \text{ independent up to } p_{\text{cr}} \text{ and vanishes above } p_{\text{cr}}, \text{ but a slowly fluctuating internal magnetic field appears instead.}

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## APPENDIX

The magnetic properties of BaVS$_3$ are known to be sensitive to sulfur deficiency, which induces FM order below about $T_C \leq 15 \text{ K}$. To study the effect of sulfur deficiency on the local magnetic environments, we have also measured the $\mu^+\text{SR spectrum for BaVS}_{2.8} \text{ at 0.1 MPa and } 2.44 \text{ GPa. The BaVS}_{2.8} \text{ sample was prepared by a solid-state reaction technique between BaS, V, and S, as well as BaVS$_1$, but without postheating with S}. [5,44] \text{ Note that the amount of S is a nominal composition. Figure 11 shows the } ZF-\mu^+\text{SR time spectrum recorded at } 2 \text{ K without pressure cell, i.e., at } 0.1 \text{ MPa. The } ZF-\mu^+\text{SR spectrum is found to exhibit a strongly damped oscillation compared with that of BaVS$_1$ [see Fig. 2(a)]. Such spectrum is reasonably fitted with} [33]

$$A_0 P_{\text{ZF}}(t) = A_1 \cos(2\pi f_1 t) \exp\left(-\frac{\sigma^2 t^2}{2}\right) + \frac{1}{2} A_1 \exp(-\lambda t).$$

The fit provided with $A_1 = 0.1631(10)$, $f_1 = 7.4(2)$ MHz, which roughly corresponds to $H_{\text{int}} = 550(13)$ Oe, and $\sigma = 36.1(1.3) \mu s^{-1}$, $\lambda = 0.021(2) \mu s^{-1}$, and $\gamma = 693(20)$ Oe, where $\omega = 2\pi f_1$.

Figure 12 shows the temperature dependencies of the normalized wTF asymmetry ($A_{\text{TF}}/A_0$) for the BaVS$_{2.8}$ sample in the pressure cell recorded at 0.1 MPa and 2.44 GPa. Since the $A_{\text{TF}}(T)/A_0$ curve at 0.1 MPa shows two steplike changes at 29.98(2) K and 13.92(2) K, the BaVS$_{2.8}$ sample is found to consist of two phases. Namely, one is the BaVS$_3$ phase with $T_N \sim 30 \text{ K and the other is the BaVS}_{3-\delta}$ phase with

![FIG. 11. The $ZF-\mu^+\text{SR}$ time spectrum for BaVS$_{2.8}$ recorded at 2 K. A solid line represents a best fit with Eq. (A1).](image-url)

![FIG. 12. The temperature dependence of the normalized $A_{\text{TF}}$ for the BaVS$_{2.8}$ sample in the pressure cell recorded at 0.1 MPa and 2.44 GPa.](image-url)
$T_C \sim 14$ K. The volume fraction of each phase is about 50%. The wTF measurements without pressure cell also supported above estimations.

On the contrary, the $A_{TF}(T)/A_0$ curve at 2.44 GPa exhibits one step-like change at $T_C = 16.04(6)$ K, revealing that the BaVS$_{3-\delta}$ phase is still in a FM state. This is because BaVS$_3$ enters into a paramagnetic phase above 1.8 GPa (see Fig. 8). Furthermore, since $T_C$ is slightly increasing with $p$, the BaVS$_{3-\delta}$ phase with $T_C \sim 14$ K does not correspond to the focused material in this paper. This also demonstrates the importance of stoichiometry in the BaVS$_3$ sample for clarifying the magnetic nature.

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