

## Possible Orbital Ordering in a Spin-Singlet Ground State: $^{51}\text{V}$ NMR and NQR study of $\text{BaVS}_3$

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$^{51}\text{V}$  NMR and NQR measurements of the  $S = 1/2$  system,  $\text{BaVS}_3$ , which show a metal-insulator transition at  $T_{\text{MI}} \cong 70$  K, revealed a nonmagnetic ground state, presence of a huge and extraordinary asymmetric electrical field gradient at V sites below  $T_X \cong 30$  K, and its motional fadeout at  $T_X$ . The temperature dependences of the  $^{51}\text{V}$  Knight shift and relaxation time indicate the presence of a spin gap ( $\Delta \cong 250$  K) below  $T_{\text{MI}}$ . These characteristic features may be interpreted as orbital ordering in a spin-singlet state. The possible existence of low-lying collective excitations of ordered orbitals is also argued. [S0031-9007(97)04475-X]

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Energy gap formation in low-energy spin excitations is actively investigated for a number of low-dimensional magnetic systems, e.g., spin-Peierls, Haldane, spin-ladder, etc. [1]. On the other hand, orbital degrees of freedom are now widely recognized as an important factor in describing physical phenomena of transition metal compounds. Recently, Pen *et al.* [2] theoretically treated the orbital ordering in a two-dimensional (2D) triangular lattice and discussed the possibility of orbital ordering in a spin-singlet ground state. They proposed an interesting scenario to explain anomalous properties of exchange-frustrated lattices with orbital degeneracies.

$\text{BaVS}_3$ , which exhibits a metal-insulator (MI) transition at  $T_{\text{MI}} \cong 70$  K, forms a hexagonal  $P6_3/mmc$  structure above  $T_S \cong 240$  K and shows orthorhombic structural deformation below  $T_S$  [3–5]. V atoms are surrounded by face sharing S octahedra and form linear chains along the  $c$  axis. The magnetic susceptibility,  $\chi$ , above  $T_{\text{MI}}$  shows Curier–Weiss-like behavior and gives an effective magnetic moment corresponding to  $S = 1/2$ . Since the intrachain V–V distance ( $\cong 2.8$  Å) is much smaller than the interchain V–V separation ( $\cong 6.7$  Å),  $\text{BaVS}_3$  has been considered as a prototype for the quasi-one-dimensional (1D)  $S = 1/2$  ( $3d^1$ ) system. However, it should be noted here that the V chains form a triangular lattice. Below  $T_S$ , crystal distortion develops mainly in the hexagonal basal plane, resulting in a slightly zigzag configuration of V atoms along the chain. Below  $T_{\text{MI}}$ , the susceptibility rapidly drops down to about 30 K and increases again at lower temperatures, although the low- $T$  upturn is strongly dependent on samples. To say nothing of the origin of the MI transition, the ground-state magnetism of  $\text{BaVS}_3$  is even still controversial. Although the  $\chi$ - $T$  curve looks like that of an antiferromagnet [4], a precise neutron diffraction experiment failed to detect long-range magnetic ordering [6], whereas earlier inelastic spin-flip neutron scattering [7] and nuclear magnetic resonance (NMR) [8] measurements suggested a transition at 31 K, which was interpreted as antiferromagnetic long-range ordering. Especially, zero-field nuclear resonance

observed at about 100 MHz and its external field dependence indicated the presence of static hyperfine fields of antiferromagnetic type. However, at about 30 K, no sign of a phase transition has been detected in thermodynamic properties such as specific heat [9] and thermal expansion [10]. We should also note the fact that the  $\text{BaVS}_3$  physical properties are extremely sensitive to stoichiometry [5], which makes it difficult to identify intrinsic properties. The purpose of this study is to determine the real ground state and to characterize the anomaly detected by only neutron spin-flip scattering and NMR experiments. Although the physical properties, especially the origin of the MI transition, have been discussed based on the quasi-1D picture [11], we pay attention to the 2D character as a triangular lattice. In this Letter, we report the results of  $^{51}\text{V}$  nuclear resonance measurements below the MI transition of stoichiometric  $\text{BaVS}_3$  and propose orbital ordering in a nonmagnetic spin-singlet ground state.

Sample preparation procedures have been described in Ref. [9]. The susceptibility measured for our sample exhibits almost no upturn at low temperatures, indicating the extraneousness of the upturn and good quality of our sample. For nuclear resonance measurements, a fine powder of a polycrystalline sample was soaked and fixed in paraffin as particles were randomly oriented. Spin-echo measurements were carried out by using a home-made phase-coherent-type pulsed spectrometer at  $T > 1.4$  K. We prepared pickup coils using silver wire instead of copper, in order to avoid the overlapping of metallic copper signals in the field-swept measurements. The nuclear spin-lattice relaxation time  $T_1$  was measured by the conventional saturation-recovery method. The crystallographic site of V atoms in  $\text{BaVS}_3$  is unique in all of the states (above and below  $T_S$ ) and, in principle, feels the finite electrical field gradient (EFG) of the lattice, which is expected to be small since the nearly octahedral configuration of the nearest-neighbor S atoms.

Although we tried to find zero-field antiferromagnetic nuclear resonance around 100 MHz reported in Ref. [8], we could not detect such a signal around the frequency by

either zero-field or field-swept measurement. Instead, we observed weak zero-field resonances near 15.5, 21.0, and 22.8 MHz at 1.4 K, which are shown in Fig. 1. The intensity ratios among resonances are not reliable due to different experimental conditions. These resonances can be assigned to  $^{51}\text{V}$  nuclear quadrupole resonances (NQR) as follows: In zero-field and in finite EFG, energy eigenvalues are obtained by solving a secular equation including the asymmetry parameter of EFG,  $\eta$ , as a parameter [12]. The energy level scheme for the nuclear spin  $I = 7/2$  (for  $^{51}\text{V}$ ) is calculated against  $\eta$  in the inset of Fig. 1. The experimental resonance frequencies are explained with the pure quadrupole frequency  $\nu_Q = 8.37 \pm 0.01$  MHz and  $\eta = 0.916 \pm 0.001$ . The resonances around 15.5, 21.0, and 22.8 MHz are assigned to transitions  $m = \pm 3/2 \leftrightarrow \pm 5/2$ ,  $m = \pm 1/2 \leftrightarrow \pm 3/2$ , and  $m = \pm 5/2 \leftrightarrow \pm 7/2$ , respectively (although  $m$  is no longer a good quantum number). The  $\eta$  value close to unity indicates the extraordinary asymmetric EFG at the V site, leading the marked shift of the  $m = \pm 1/2 \leftrightarrow \pm 3/2$  transitions from  $\nu_Q$  for  $\eta = 0$ . A field-swept spectrum measured at 1.4 K and at an operating frequency of 70.5 MHz is shown in Fig. 2(a), together with calculated patterns. The spectrum was observed around the zero Knight shift. The line is, at first sight, considerably broadened but has steplike structures at both high- and low-field sides. The basic feature of the line can be reproduced by a tentative calculation of the powder pattern using the quadrupole parameters estimated above (the Knight shift was neglected). Since the observation of NQR proves no hyperfine field, we conclude that the ground state of  $\text{BaVS}_3$  is nonmagnetic.

We have followed the temperature variation of the field-swept spectrum. Figure 2(b) shows field-swept spectra at several temperatures, which were measured in the same experimental conditions except temperature (an operating frequency 70.5 MHz, pulse separation

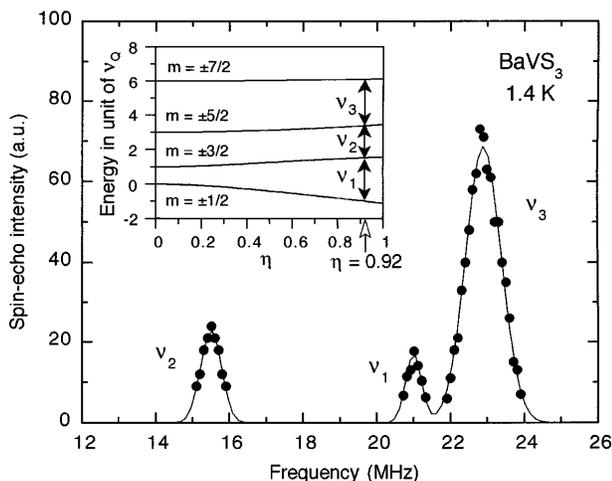


FIG. 1. The  $^{51}\text{V}$  NQR spectrum for  $\text{BaVS}_3$  measured at 1.4 K. The inset shows nuclear spin energies for  $I = 7/2$  in nonaxial EFG as a function of  $\eta$ . The analysis gives  $\nu_Q = 8.37 \pm 0.01$  MHz and  $\eta = 0.916 \pm 0.001$ .

$\tau = 10 \mu\text{s}$ ). With increasing temperature, the signal rapidly reduced its amplitude and disappeared around 30 K (which will be denoted as  $T_X$ ). The quadrupole frequency  $\nu_Q$  seems to decrease rapidly on approaching temperature to  $T_X$ . Above  $T_X$ , we observed another type of signal which is much sharper than that below  $T_X$  and exhibits a typical line shape for the axial Knight shift (see the inset in Fig. 4 below). For  $T_X < T < T_{\text{MI}}$ , we observed a distinct modulation of spin-echo decay with a period of about  $5.8 \mu\text{s}$ , which is almost  $T$  independent. The echo modulation above  $T_X$  is ascribed to the presence of small EFG ( $\nu_Q \cong 0.17$  MHz) [13]. These results indicate that the large EFG observed below  $T_X$  turns out to be very small above  $T_X$ . Figure 3 shows the  $T$  dependence of the integrated intensities of the spectra measured in the same experimental conditions. In the figure, intensities multiplied by  $T$ , which should be  $T$  independent in the case of no anomalies, are plotted. Thus it is clear that a “change” of states occurs at  $T_X \cong 30$  K from the viewpoint of nuclear resonances. It should be noted, however, that there is no sign of long-range phase transition around  $T_X$  in most of the thermodynamic properties. It is also interesting to note that the  $T_X$  anomaly is characterized by an enhancement of the nuclear spin-spin relaxation rate,  $1/T_2$ , as was already pointed out in Ref. [8]. We have observed a  $T$  dependence of  $T_2$  just as that of the intensities (Fig. 3), although quantitative estimation of  $T_2$  was difficult due to very short  $T_2$  around  $T_X$  ( $T_2 < 6 \mu\text{s}$  at  $20 < T < 32$  K). Instead, we discuss the integrated intensities of field-swept spectra (Fig. 3), since they give information on  $T_2$

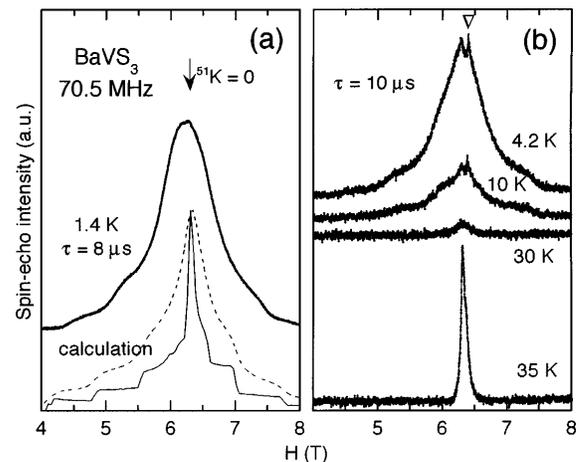


FIG. 2. (a) Field-swept  $^{51}\text{V}$  NMR spectra of  $\text{BaVS}_3$  measured at 1.4 K (at an operating frequency of 70.5 MHz and pulse separation  $\tau = 8 \mu\text{s}$ ). Impurity signal seen in spectra in (b) was subtracted. Calculated powder patterns using parameters  $\nu_Q = 8.37$  MHz and  $\eta = 0.916$  are also shown. (The Knight shift was neglected.) The Lorentzian with full width of 0.2 T was convoluted to obtain the dashed curve. (b) Field-swept spectra (at 4.2, 10, 30, and 35 K) measured in the same experimental conditions (70.5 MHz and  $\tau = 10 \mu\text{s}$ ). The sharp and small signal indicated by an open triangle is attributed to impurity phases.

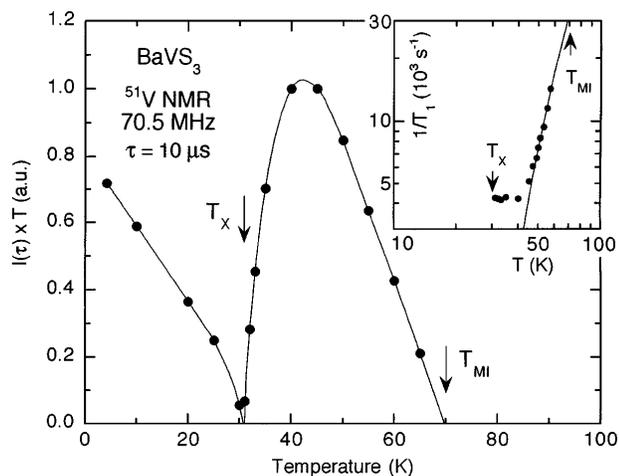


FIG. 3. The temperature dependence of  $^{51}\text{V}$  field-swept NMR integrated intensity of  $\text{BaVS}_3$  (70.5 MHz and  $\tau = 10 \mu\text{s}$ ) multiplied by temperature. The inset shows  $1/T_1$  measured using field-swept NMR (see text).

via a relation  $I(\tau) = I(0)\exp(-\tau/T_2)$ , where  $I(\tau)$  is the intensity at a pulse separation  $\tau$  and  $I(0) \propto T^{-1}$  due to the nuclear-spin Curier law. (In experiments for Fig. 3, we arbitrarily selected  $\tau = 10 \mu\text{s}$ .) Strong reduction of intensities around  $T_X$ , i.e., the enhancement of  $1/T_2$ , is not attributable to the so-called  $T_1$  process but to the nuclear spin-spin relaxation mechanism itself, since  $1/T_1$  is almost  $T$  independent just above  $T_X$  (see the inset in Fig. 3). This fact suggests that the  $T_X$  anomaly is not due to long-range ordering of the electronic system, which is consistent with no anomalies in the thermodynamic properties. Heidemann and Takano [7] observed slight energy broadening of neutron spin-flip scattering spectra below  $T_X$ , and interpreted the result as the appearance of static hyperfine fields associated with magnetic ordering. It is likely that the energy broadening can be consistently explained in terms of the appearance of huge nuclear quadrupole splittings rather than hyperfine splittings.

The above experimental results are summarized as follows: The ground state is nonmagnetic, i.e., a spin gap is formed below  $T_{\text{MI}}$  (the nature of the spin gap will be described in a subsequent part). At the ground state, there certainly exists huge and markedly asymmetric EFG at V sites. The EFG is suddenly reduced to nearly zero at  $T_X = 30 \text{ K}$ , accompanied by the enhancement of  $1/T_2$ . This result implies that asymmetric charge distribution of  $3d$  wave functions turns out to be spherical above  $T_X$ . If we believe the quasi-1D picture along the  $c$  axis, the charge asymmetry calls to mind the spin-Peierls transition along the  $c$  axis. In this case, the dimerization, which has not been detected so far, should be associated with the MI transition, i.e., at  $T_{\text{MI}}$ . However, the quasi-1D characteristics along the  $c$  axis seem to be doubtful because (1) the  $\chi$ - $T$  behavior is far from that of the 1D system [14]; (2) the crystal distortion below  $T_{\text{MI}}$  is observed mainly in the  $ab$  plane, not on the  $c$  axis [10]; (3)  $T_{\text{MI}}$  does not depend

on a field up to 5 T [15], which is not the case for the typical spin-Peierls system [16]; (4) optical conductivity measured for a single crystal is not so anisotropic [17]; (5) the spherical charge distribution above  $T_X$  is unlikely to be in accordance with the 1D picture, etc. Furthermore, a recent band calculation of  $\text{BaVS}_3$  indicates only faint 1D characteristics [18]. Alternative interpretation is based on its possible 2D characteristics. Recently, Pen *et al.* [2] proposed a fascinating scenario to explain the anomalous properties of a triangular lattice, i.e., orbital ordering in a spin-singlet state. Large hopping integrals between nearest-neighbor magnetic ions realize the orbital ordering. For the  $d^1$  ( $S = 1/2$ ) system, they proposed 1D chains of orbitals within the 2D plane as the most probable case. Although there has been no reliable argument on the magnetic coupling between neighboring V atoms in  $\text{BaVS}_3$ , if we assume strong uniaxial magnetic anisotropy along the  $c$  axis, and strong antiferromagnetic interchain coupling probably mediated by the superexchange interaction via S ions, the system is reduced to a 2D triangular lattice. This corresponds to the situation considered by Pen *et al.* It is expected that an ordered orbital (probably a certain nondegenerate orbital defined as a linear combination of  $t_{2g}$  states) produces large intra-atomic charge asymmetry in the ground state. Pen *et al.* also suggested the presence of collective modes of excitations of ordered orbitals. If thermal excitation of ordered orbitals, i.e., mixing among nearly degenerate orbitals, is induced, an intra-atomic charge redistribution is expected. Mixing among three independent  $t_{2g}$  orbitals gives rise to an average-out of the intra-atomic EFG seen from the V nucleus. A critical change of  $\nu_Q$  is expected when (tunneling) frequencies between different orbitals exceed the NMR operating frequency. In this case, excessive broadening of the linewidth, i.e., the enhancement of  $1/T_2$ , is generally expected [19]. This motional fade-out of the EFG successfully explains the  $T_X$  anomaly. Although the model proposed by Pen *et al.* (especially the substantial description of ordered orbitals) may be too simple, we believe that it gives a hint on how to understand the interesting properties of  $\text{BaVS}_3$ . Measurements of a single crystal, which can determine each component of the EFG tensor, will give a conclusive argument. If the above scenario is applicable to  $\text{BaVS}_3$ , the long-range ordering of orbitals should already be established below  $T_{\text{MI}}$ , since the  $\lambda$ -type anomaly of specific heat [9] and additional crystal distortion [10] were observed at  $T_{\text{MI}}$ . The  $T$ -linear term of low- $T$  specific heat in the insulating state [9] suggests the presence of corrective excitations of ordered orbitals. Preliminary measurements of NQR- $T_1$  suggests a  $T^n$  dependence of  $1/T_1$  with small  $n$  ( $\sim 1.5$ ), which may support this interpretation.

It is of interest to discuss spin excitations in the spin-singlet state. The Knight shift gives such information via the relation  $K = A_{\text{spin}}\chi_{\text{spin}} + A_{\text{orb}}\chi_{\text{orb}}$ , where  $\chi_{\text{spin}}$  ( $\chi_{\text{orb}}$ ) and  $A_{\text{spin}}$  ( $A_{\text{orb}}$ ) are the spin (orbital) susceptibility and the spin (orbital) components of the hyperfine

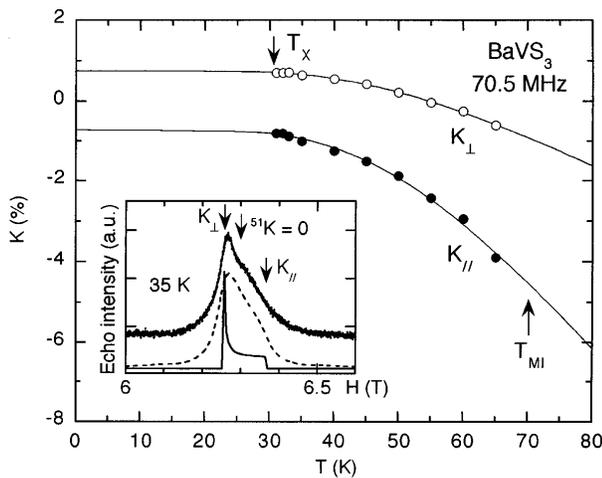


FIG. 4. Temperature dependences of parallel and vertical components of the Knight shift for  $\text{BaVS}_3$  at  $31 < T < 65$  K (see text). The inset shows a spectrum at 35 K, together with calculated curves assuming the axial Knight shift. The Lorentzian curve with full width of  $0.04$  T was convoluted to obtain the dashed curve.

coupling constant, respectively. Since  $^{51}\text{V}$  NMR spectra exhibit axial Knight shift patterns at  $T_X < T < T_{\text{MI}}$ , we estimated parallel and vertical components of the Knight shift,  $K_{\parallel}$  and  $K_{\perp}$ , which are shown in Fig. 4. The anisotropy of the shift may be ascribed to that of  $\chi_{\text{orb}}$ . To estimate  $\chi_{\text{spin}}$ , we neglected, as usual, the thermal variation of  $\chi_{\text{orb}}$ , which is possibly present in this compound around the ordering point of orbitals. Fitting both components ( $K_{\parallel}$  and  $K_{\perp}$ ) to  $\chi_{\text{spin}} \propto T^{1/2} \exp(-\Delta_S/T)$  [20] (solid curves in Fig. 4) formally gives  $\Delta_S = 240$  K. The relaxation time also gives information on the spin excitations. The  $T$  dependence of  $1/T_1$  measured using field-swept NMR (at 70.5 MHz) above  $T_X$  is shown in the inset of Fig. 3. Below  $T_{\text{MI}}$ ,  $1/T_1$  drops very rapidly with decreasing temperature and becomes almost constant below about 40 K down to  $T_X$ . A deviation from the gap-type behavior around  $T_X$  suggests an appearance of another relaxation mechanism, i.e., excitations of orbitals. A tentative fit of  $1/T_1$  above 50 K to  $1/T_1 \propto \exp(-\Delta_R/T)$  (the solid curve in the inset of Fig. 3) gives a crude value of the gap parameter  $\Delta_R = 260$  K, which is slightly larger than  $\Delta_S$ .

In summary,  $^{51}\text{V}$  nuclear resonance experiments of  $\text{BaVS}_3$  have suggested the presence of orbital ordering in a spin-singlet ground state (with a spin gap  $\Delta \cong 250$  K). We speculate that the  $T$ -linear term of low- $T$  specific heat in the insulating phase [9] points to the presence

of collective excitations of ordered orbitals and that the motional fade-out of EFG at  $T_X \cong 30$  K indicates its low-energy nature. We would like to emphasize that  $\text{BaVS}_3$  may provide an opportunity to study the orbital dynamics since spin excitations, which usually mask the orbital dynamics, are quenched at low temperatures.

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