Journal of the Physical Society of Japan
Vol. 71, No. 10, October, 2002, pp. 2361–2364

Muon Spin Relaxation Study of Magnetism of a Triangular Lattice $BaVS_3$

Wataru HIGEMOTO, Akihiro KODA, Goro MARUTA*, Kusuo NISHIYAMA,
Hiroyuki NAKAMURA[1], Saurav GIRI[1†] and Masayuki SHIGA[1]

Meson Science Laboratory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801
[1]*Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501*

(Received March 26, 2002)

We performed muon spin relaxation (μSR) experiments on a $S = \frac{1}{2}$ triangular lattice system, $BaVS_3$. Fast muon spin relaxation was observed below $T_X \simeq 30$ K, indicating magnetic ordering. The hyperfine field at the muon site is about 500 G at 2.2 K, which agrees with the spin structure proposed from recent low-energy neutron diffraction results. No fast fluctuation of local fields was observed below T_X, which restricts the interpretation of nuclear resonance data.

KEYWORDS: $BaVS_3$, μSR, magnetic ordering
DOI: 10.1143/JPSJ.71.2361

A triangular-lattice vanadium sulfide $BaVS_3$ (a spin-$\frac{1}{2}$ system) exhibits a metal-insulator transition at $T_{MI} \simeq 70$ K.[1)] Related to the Mott transition and the frustration of spin, charge and orbital degrees of freedom, the origin of the transition at T_{MI} has attracted considerable attention. In addition, although the susceptibility shows a typical antiferromagnetic-like drop below T_{MI},[2–4)] the nature of magnetic states below T_{MI} is not simple but is a matter of interest.

$BaVS_3$ forms a hexagonal perovskite type structure (space group: $P6_3/mmc$) at high temperatures,[1)] in which V atoms (at the 2*a* site) form one-dimensional chains along the *c*-axis with a small interatomic distance ($\simeq$2.8 Å) and a triangular lattice in the *c*-plane with a large interchain distance ($\simeq$6.7 Å). Below $T_S \simeq 240$ K, $BaVS_3$ shows a small orthorhombic structural deformation.[5)] Since a V atom is surrounded by an almost regular octahedral configuration of S atoms even below T_S, we expect nearly degenerate $3d$–t_{2g} orbitals. In early neutron diffraction studies,[6,7)] no extra diffraction was observed at low temperatures, which ruled out simple long-range magnetic ordering at the ground state. In earlier studies, the possibility of short-range ordering or a specific type of magnetic ordering was discussed by several authors.[6,8,9)] On the other hand, Nakamura *et al.*[10)] found zero-field (ZF) nuclear resonances in a relatively low frequency range of <24 MHz in a temperature range below $T_X \simeq 30$ K, interpreted them as ^{51}V nuclear quadrupole resonance (NQR), i.e., the appearance of a large and asymmetric electric field gradient at V sites, and proposed an orbital-ordered spin-singlet state as the ground state, referring to the absence of the magnetic Bragg reflections[6)] and a theoretical work by Pen *et al.*[11)] Nakamura *et al.*[12)] also performed positive muon spin relaxation (μSR) measurements at the KEK-MSL, Tsukuba, Japan and determined a marked muon-spin depolarization below T_X without appreciable critical divergence. Considering the spin-singlet ground state, the possibility of muonium formation in the insulating state was discussed rather than electron spin freezing. Nakamura *et al.*[13)] carried out low-energy neutron diffraction experiments of a powder sample using a cold neutron beam and found unexpected magnetic reflections in contrast to the previous results.[6,7)] The new result revealed clearly the occurrence of *long-range* magnetic ordering with the incommensurate propagation vector (0.226 0.226 0) (in the hexagonal index) with averaged ordered moment $\sim$0.5 μ_B/V below T_X. However, the details of the nature of the magnetic state, such as the spin structure, have not yet been clarified and the nuclear resonance data remains to be interpreted consistently. Interestingly, the static magnetic reflections disappear above T_X, not at T_{MI} with the susceptibility peak. At $T_X < T < T_{MI}$, magnetic scattering was found at a finite but small energy transfer near the magnetic Bragg points, which was interpreted to be the formation of a spin-liquid-like state. Recently, Mihály *et al.*[14)] suggested spin and orbital short-range ordering from their single crystalline data and calculations. Thus, the nature of the magnetic states below T_{MI} and the driving force of the transitions at T_{MI} and T_X are still controversial. These anomalous features may be caused by the charge or orbital instability and/or characteristic spin dynamics of geometrically frustrated triangular lattice chains. We believe that understanding the magnetic states below T_{MI} will lead to elucidation of the origin of this exotic metal-insulator transition in $BaVS_3$. In this letter, we report new muon spin relaxation measurements in a powder sample of $BaVS_3$. Since a measurable time scale of μSR is intermediate between neutron diffraction and NMR, μSR possesses a considerable advantage in this study. In the previous μSR measurement,[12)] a pulsed muon beam was used. Since the time scale of muon spin relaxation in $BaVS_3$ below T_X is faster than the time resolution of the pulse muon beam, the beginning part of μSR spectra was unobservable. In the present study, we used a continuous muon beam to perform new μSR experiments with a better time resolution and carried out a detailed investigation of the magnetism of $BaVS_3$.

A powder sample of $BaVS_3$ was prepared by the same procedures[15)] as those used in the previous μSR study.[12)] Since the deficiency of S enhances the ferromagnetic interaction,[16)] the sample quality was checked by measuring the temperature dependence of the susceptibility. For μSR experiments, powder with a mass of approximately 5 g was

*Present address: Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810.
†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.

pressed into 1-mm-thick disks. The present μSR experiments were performed using the M9B decay muon channel at TRIUMF, Vancouver, Canada. The standard μSR technique was applied. We implanted spin polarized muons with the momentum of $\sim$50 MeV/c into the polycrystalline sample of $BaVS_3$. The sample was cooled in helium gas for thermal exchange.

Figures 1(a) and 1(b) show typical ZF-μSR spectra in $BaVS_3$ at various temperatures. Above 30 K ($\sim T_X$), slow muon spin relaxation was observed, which originates from the nuclear dipolar moment of ^{51}V and is consistent with previous results.[12] Below T_X, fast muon spin relaxation appears, indicating magnetic ordering. As shown in Fig. 1(a), the fraction of the fast Gaussian type muon spin relaxation and its relaxation rate increase with decreasing temperature. In a typical antiferromagnetic or ferromagnetic state, a homogeneous local field appears at each muon site and a spontaneous muon spin precession is observable. In the present case, absence of such a spontaneous precession in ZF suggests randomness or disorder of local magnetic fields at muon sites. We note that there was no muonium formation in $BaVS_3$ discussed in the previous paper.[12] Figure 1(b) demonstrates muon spin relaxation at a long time region. When static magnetic fields are present, muon spin relaxation after a long duration returns to 1/3 of the total amplitude, because 1/3 of the local fields are parallel to the direction of initial muon polarization and hence do not contribute to the muon spin relaxation. The observed slow muon spin relaxation with time suggests (1) the presence of fast fluctuating local fields or (2) the existence of two types of local magnetic states. To distinguish these two situations, we measured the longitudinal field (LF) dependence of the muon spin relaxation (LF-μSR) at the lowest temperature (2.2 K). If we tentatively assume that the ZF muon spin relaxation spectra at 2.2 K can be represented by one component of the dynamical Kubo–Toyabe function, we observe a local field fluctuates fast with the time scale of the order of 10^{-7} s. However, as shown in Figs. 2(a) and 2(b), LF dependences of the muon spin relaxation at 2.2 K are weaker than the simple expectation for the fast fluctuation [dashed curves in Fig. 2(b)], but can be roughly reproduced by the sum of the dynamic Kubo–Toyabe function with slow modulation [solid curves in Fig. 2(b), which are under LF with a dipolar field, 505 G, fluctuating with a small frequency, <0.5 MHz] and slow paramagnetic relaxation, which will be discussed later. Thus, we can conclude that the internal field of about 500 G at the muon site is not fluctuating fast at 2.2 K.

Above 2.2 K, the ZF-μSR spectra were fitted to the sum of slow relaxation $[A_s G_s(\Delta_s, t)]$ and the dynamic Gaussian Kubo–Toyabe function $[A_{dKT} G_{dKT}(\Delta, \nu, t)]$,[17]

$$P(t) = A_{dKT} G_{dKT}(\Delta, \nu, t) + A_s G_s(\Delta_s, t). \quad (1)$$

Here, $G_s(\Delta_s, t)$ corresponds the muon spin relaxation by the weak and static nuclear dipolar field of ^{51}V, which is expressed by the static Kubo–Toyabe function.[17] The

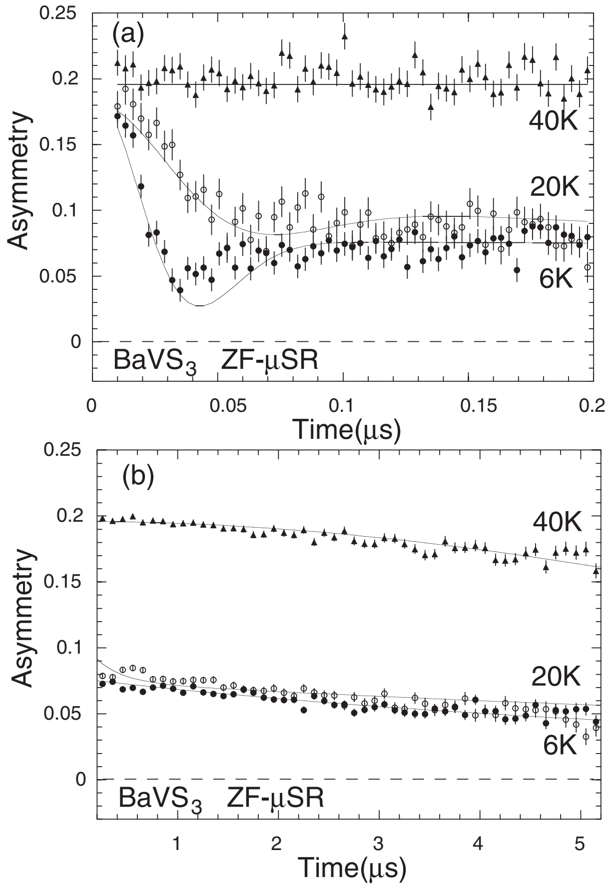

Fig. 1. Time evolution of muon spin asymmetry in zero field at various temperatures (a) 0–0.2 μs and (b) 0.2–5 μs.

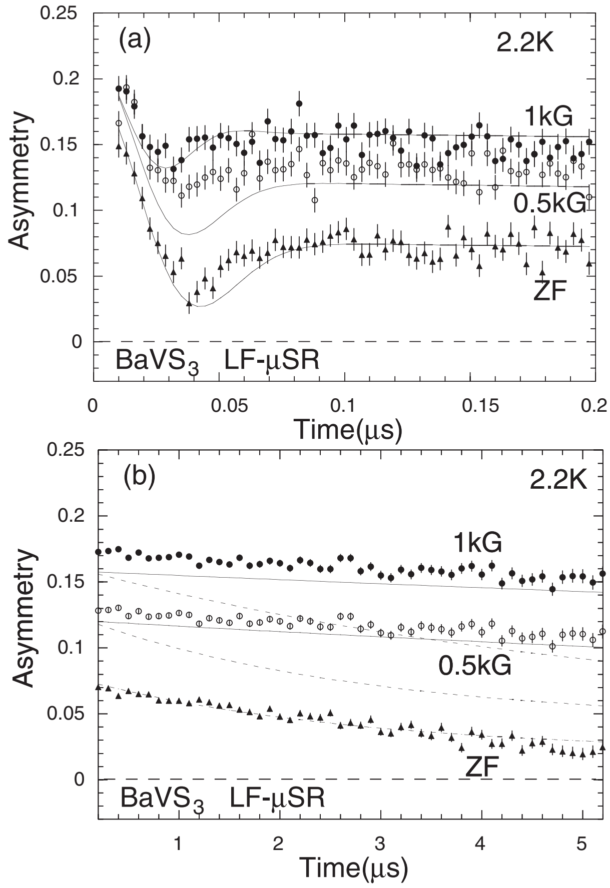

Fig. 2. Time evolution of muon spin asymmetry in a longitudinal field at various fields (a) 0–0.2 μs and (b) 0.2–5 μs. See text.

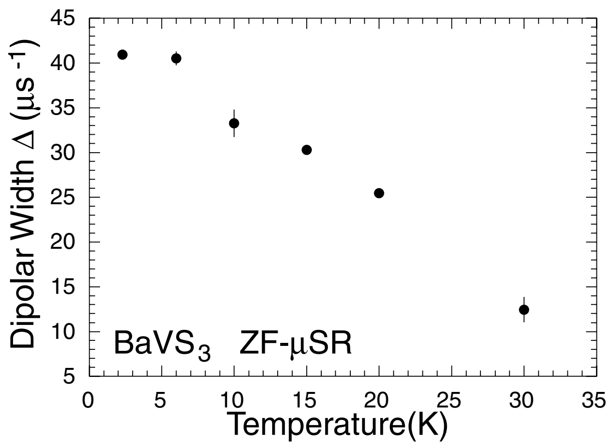

Fig. 3. Temperature dependence of dipolar width Δ $(= \gamma_\mu H_{\mathrm{loc}})$. $\Delta = 10\,\mu\mathrm{s}^{-1}$ corresponding to a dipolar field width of $\sim$118 G.

nuclear dipolar width Δ_{s} is fixed to the value $\Delta_{\mathrm{s}} = 0.098\,\mu\mathrm{s}^{-1}$ which is determined at 40 K. Figure 3 shows the temperature dependence of the dipolar width Δ in eq. (1). Δ increases with decreasing temperature below T_{X}, indicating that local fields at muon sites increase with decreasing temperature. The temperature dependence of the dipolar field H_{loc} $(= \Delta/\gamma_\mu)$ agrees well with that of the magnetic peak intensity of the neutron diffraction experiment.[13] Above 20 K, the ZF-μSR spectra cannot be reproduced without introducing fluctuation of the local field of the order of 10^{-6} s, suggesting that the local field partially dynamic even below T_{X}.

Next, we discuss a muon stopping site. In $BaVS_3$, it is likely that a muon forms a S–μ^+ bond (an analogy of S–H bonding, bond length 1.3 Å). Assuming the muon stopping site to be (0.17 0.53 0.25) (1.3 Å from a S atom), dipolar fields are estimated to be 570–590 G by assuming the modulated spin 120° structure with moments of $\sim$0.5 μ_{B}/V suggested from neutron diffraction results.[13] There are three types of dipolar fields at the muon stopping site due to three types of spin triangles of a spin 120° structure. Among the three muon stopping sites, the difference in the dipolar fields is small ($\sim$20 G). Incommensurability of the spin structure also modifies dipolar fields within 20 G. Hence, the magnitude of the observed field H_{loc} ($\sim$500 G at 2.2 K) is roughly consistent with the dipolar field produced by the helically ordered spins with the magnitude $\sim$0.5 μ_{B}/V. No spontaneous precession in the ZF spectra suggests weak randomness or disorder of the spin-ordered state.

Between T_{X} and T_{MI}, no fast relaxation was observed, indicating that spins fluctuate at high frequencies that are out of the time window of μSR measurements. This result agrees with the lack of observable magnetic Bragg reflections in this temperature range[13] and indicates that the spins are in a *paramagnetic* or spin-liquid-like state, as suggested from neutron scattering experiments.[13]

Below T_{X}, we observed a distinct feature of magnetic ordering, consistent with the recent low-energy neutron diffraction results.[13] On the other hand, below T_{X}, ZF nuclear resonances were observed at relatively low frequencies, which were interpreted as the appearance of large electric field gradient.[10] However, since the interpretation hinged on no long-range magnetic ordering evidenced from earlier neutron diffraction experiments,[6] it seems at present to be reasonable to assign the low-frequency resonances to small internal fields at ^{51}V sites (In this case, internal fields at the ^{51}V site are estimated to be at most $\sim$20 kG). Even so, however, the internal fields seem to be considerably small if we apply a typical hyperfine coupling, *e.g.*, -120 kG/μ_{B} for ^{51}V, and take into account the ordered moment $\sim$0.5 μ_{B}/V.[13] One possible explanation for this discrepancy is the dynamics of spins, that is, local fields fluctuate at the order of NMR frequency. Ground-state degeneracies due to the chirality in the 120° structure may give rise to this kind of specific spin dynamics. For example, in $CsMnBr_3$ (a d^5 system), which exhibits the 120° structure, such a possibility was argued by means of polarized neutron scattering,[18] and a reduction of the internal field at the ^{55}Mn site was discussed from NMR experiments.[19] For $CsMnBr_3$, no μSR signal was observed, probably because the local field at the muon site is beyond the observable range.[20] 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 hyperfine field may be averaged out in the time range of NMR. Since the observable time scale of μSR experiment (typically 10^{-5}–10^{-10} s) is faster than that of NMR and slower than neutron passing time, muons can detect such fluctuating local fields. However, as mentioned above, the fluctuation of the local field is slower than about 0.5 MHz at 2.2 K or in the ground state. Since the frequency is sufficiently smaller than the NMR frequency, it is unlikely that the spin dynamics is the main origin of small internal fields at the ^{51}V nuclear site. This result also denies the NQR interpretation of the nuclear resonance data. A more probable interpretation is the cancellation of the hyperfine field at the ^{51}V site. If the anisotropic hyperfine field, which originates mainly in the intra-atomic spin dipolar field and related to asphericity of *d* orbitals, is large, the isotropic field at ^{51}V site may be canceled depending on the relative direction between the spin and the local symmetry axis at the ^{51}V site. Marked anisotropic hyperfine coupling has actually been observed in some paramagnetic vanadium oxides.[21]

Recently, it was proven from X-ray diffraction experiments that the crystallographic V site separates into two different sites with equal population below T_{MI}.[22] Here, we consider the possibility of magnetic site separation (or charge ordering), for example, to 1 μ_{B} and 0 μ_{B}. With two V sites with equal population, it is likely that the hyperfine field at the muon site, which is mostly dominated by the nearest V spin, separates into large and small magnitudes with the same fraction and then the μSR spectrum exhibits two components. In the present results, we observed two components (will be denoted as *magnetic* and *nonmagnetic* phases, respectively, although the origin of the latter is not clear). However, their fractions are not the same as shown below, and in the *magnetic* part, only one component was observed. Thus, we have no explicit μSR result which points to the magnetic site separation in the V site. However, since μSR measurements usually detect the hyperfine field at interstitial sites in the crystal, difference in the hyperfine fields at the two muon sites might be too small to be distinguished in μSR spectra.

Figure 4 shows the temperature dependence of volume fraction of the *magnetic* phase determined from ZF-μSR

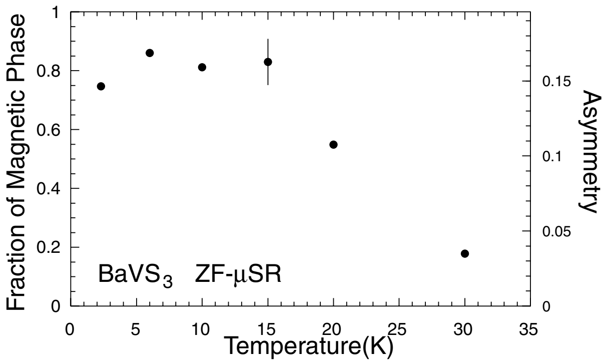

Fig. 4. Temperature dependence of fraction of the *magnetic* phase (left axis) and asymmetry (right axis).

[$A_{dKT}(T)/A_s(40\,K)$ in eq. (1)]. The remaining part is the *nonmagnetic* phase. The volume fraction of the *magnetic* phase gradually increases with decreasing temperature down to about 15 K which corresponds to $\sim 0.5\,T_X$. This result indicates that the substantial transition temperature is widely distributed from T_X to $\sim 0.5\,T_X$ probably due to randomness. It is also noted that about 20% of implanted muons are still in the *nonmagnetic* phase down to 2.2 K. Since the magnetic field at the muon sites in the *nonmagnetic* phase is less than a few Gauss, which is three orders of magnitude smaller than that in the *magnetic* phase, we roughly estimate no static spins in the region of $\sim$50 Å sphere around a muon in the *nonmagnetic* phase. From the present results, it cannot be concluded whether the *magnetic* and *nonmagnetic* phases are separated into two macro domains. One possibility is that such a separation is extrinsic. The magnetic ordering may be destroyed easily in a wide region around lattice defects as a result of a dynamic effect for strong frustration.

In conclusion, we performed muon spin relaxation experiments on the $S = \frac{1}{2}$ triangular lattice system, $BaVS_3$. Fast muon spin relaxation was observed below $T_X \simeq 30\,K$, which indicates the onset of static magnetic ordering, being consistent with the recent low-energy neutron diffraction results.[13] No fast fluctuation in the magnetic component restricts the origin of the small internal fields at the ^{51}V site observed by NMR experiments.[10]

The authors are indebted to M. Mekata and H. Imai for collaboration in the previous muon spin relaxation measurements of $BaVS_3$ and discussion, and to T. Yamasaki for assistance in analyses. We also thank X.G. Zheng and TRIUMF staff for helpful support during measurements. This work was partially supported by Grants-in-Aid for Scientific Research of the Japan Society for the Promotion of Science (11440107, 12640345) and a Grant-in-Aid on priority area "Novel Quantum Phenomena in Transition Metal Oxides" from the Ministry of Education, Culture, Sports, Science and Technology (12046243).

1) R. A. Gardner, M. Vlasse and A. Wold: Acta Crystallogr. B **25** (1969) 781.
2) M. Takano, H. Kosugi, N. Nakanishi, M. Shimada, T. Wada and M. Koizumi: J. Phys. Soc. Jpn. **43** (1977) 1101.
3) O. Massenet, R. Buder, J. J. Since, C. Schlenker, J. Mercier, J. Kelber and D. G. Stucky: Mater. Res. Bull. **13** (1978) 187.
4) O. Massenet, J. J. Since, J. Mercier, M. Avignon, R. Buder, V. D. Nguyen and J. Kelber: J. Phys. Chem. Solids **40** (1979) 573.
5) F. Sayetat, M. Ghedira, J. Chenavas and M. Marezio: J. Phys. C **15** (1982) 1627.
6) M. Ghedira, M. Anne, J. Chenavas, M. Marezio and F. Sayetat: J. Phys. C **19** (1986) 6489.
7) J. Kelber, A. T. Aldred, G. H. Lander, M. H. Mueller, O. Massenet and G. D. Stucky: J. Solid State Chem. **32** (1980) 351.
8) H. Nishihara and M. Takano: J. Phys. Soc. Jpn. **50** (1981) 426.
9) A. Heidemann and M. Takano: Phys. Status Solidi B **100** (1980) 343.
10) H. Nakamura, H. Imai and M. Shiga: Phys. Rev. Lett. **79** (1997) 3779.
11) H. F. Pen, J. van den Brink, D. I. Khomskii and G. A. Sawatzky: Phys. Rev. Lett. **78** (1997) 1323.
12) H. Nakamura, H. Imai, M. Shiga, M. Mekata, K. Nishiyama and K. Nagamine: Hyperfine Interactions **120/121** (1999) 633.
13) H. Nakamura, T. Yamasaki, S. Giri, H. Imai, M. Shiga, K. Kojima, M. Nishi, K. Kakurai and N. Metoki: J. Phys. Soc. Jpn. **69** (2000) 2763.
14) G. Mihály, I. Kézsmárki, F. Zámborszky, M. Miljak, K. Penc, P. Fazekas, H. Berger and L. Forró: Phys. Rev. B **61** (2000) R7831.
15) H. Imai, H. Wada and M. Shiga: J. Phys. Soc. Jpn. **65** (1996) 3460.
16) T. Yamasaki, H. Nakamura and M. Shiga: J. Phys. Soc. Jpn. **69** (2000) 3068.
17) R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki and R. Kubo: Phys. Rev. B **20** (1979) 850.
18) S. V. Maleyev, V. P. Plakhty, O. P. Smirnov, J. Wosnitza, D. Visser, R. K. Kremer and J. Kulda: J. Phys.: Condens. Matter **10** (1998) 951.
19) A. S. Borovik-Romanov, S. V. Petrof, A. M. Tikhonov and B. S. Dumesh: J. Exp. Theor. Phys. **86** (1998) 197 [Zh. Exsp. Teor. Fiz. **113** (1998) 352].
20) M. Mekata: unpublished result.
21) For example, T. Ohama, M. Isobe and Y. Ueda: J. Phys. Soc. Jpn. **69** (2000) 1574.
22) T. Inami, K. Ohwada, H. Kimura, M. Watanabe, Y. Noda, H. Nakamura, T. Yamasaki, M. Shiga, N. Ikeda and Y. Murakami: to be published in Phys. Rev. B.