Distribution of internal transverse magnetic fields in a Mn$_{12}$-based single molecule magnet

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A distribution of internal transverse magnetic fields has been observed in single molecule magnet Mn$_{12}$-BrAc in the pure magnetic quantum tunneling (MQT) regime. Magnetic relaxation experiments at 0.4 K are used to produce a hole in the distribution of transverse fields whose angle and depth depend on the orientation and amplitude of an applied transverse "digging field." The presence of such transverse magnetic fields can explain the main features of resonant MQT in this material, including the tunneling rates, the form of the relaxation and the absence of tunneling selection rules. We propose a model in which the transverse fields originate from a distribution of tilts of the molecular magnetic easy axes.

Quantum effects in single molecule magnets (SMMs) have been the subject of intense research since their discovery in the 1990s.[1–12] SMMs consist of a core of transition metal ions that are strongly exchange coupled with a high-spin ferrimagnetic ground state ($S=4$–13) and uniaxial magnetic anisotropy. The latter leads to a preference for the net spin to orient parallel or antiparallel to this axis (taken to be the z axis). A number of phenomena have been clearly observed in these materials, including resonant magnetic quantum tunneling (MQT) between projections of the spin,[1–3] Berry phase effects[13] and the crossover between thermally assisted and pure MQT,[6] to name a few. SMMs have also led experimentalists to develop more advanced magnetic and spectroscopic techniques to probe the subtleties of MQT. This includes techniques to examine the distribution of internal axial dipolar or nuclear hyperfine fields, molecular microenvironments[11] as well as high-field single-crystal EPR methods.[7,8,12] The field has also benefited greatly from recently synthesized variations of the original SMM, Mn$_{12}$-Ac, which are enabling comparative studies of MQT.[17] Critical to understanding MQT are methods that provide access to transverse interactions that break the axial symmetry and thus lead to quantum transitions between spin projections.

This can be seen from the form of the effective spin Hamiltonian for SMMs

$$\mathcal{H}=-DS_z^2-BS_z^4-g\mu_B\mathbf{H}\cdot\mathbf{S}. \tag{1}$$

The first two terms are the uniaxial magnetic anisotropy of the molecule (positive D and B). The third term is the Zeeman interaction of the spin and the magnetic field. The $2S+1$ allowed projections of the spin, labeled by m, are split by the uniaxial magnetic anisotropy. A longitudinal field H_z shifts the energy levels favoring the projections of the magnetization aligned with the field. At well-defined longitudinal fields (resonance fields) the levels m and m' with antiparallel projections on the z axis are nearly degenerate, $H_k \sim kD/g\mu_B$ ($k=m+m'$). At these resonances MQT is turned on by interactions that break the axial symmetry and mix the levels m and m', lifting the degeneracy by a small energy Δ_k known as the tunnel splitting. These transverse interactions

can be due to transverse magnetic anisotropies (associated with spin-orbit interactions) and/or a transverse magnetic field H_T.

Mn$_{12}$-BrAc is shorthand for the molecule $[\mathrm{Mn_{12}O_{12}(O_2CCH_2Br)_{16}(H_2O)_4}]$-8CH$_2Cl_2$.[15] The core of the molecule is same as that of Mn$_{12}$-Ac and the molecule has a $S=10$ ground state. Mn$_{12}$-BrAc molecules have tetragonal (S_4-site) symmetry. Hence the lowest-order transverse anisotropy term allowed by symmetry is fourth order, $C(S_+^4+S_-^4)$, and would lead to the tunneling selection rule $m-m'=4i$, with i an integer. Thus pure MQT, tunneling without thermal activation, is only allowed for resonances $k=4i$. However, in this and all other known Mn$_{12}$-based SMMs, all tunneling resonances are observed. Further, the tunneling probability increases monotonically with resonance number k. While this means that transverse magnetic fields are present, up to now there has been no direct experimental evidence for such fields.

In this Rapid Communication, we show clear experimental evidence for a distribution of internal transverse magnetic fields in Mn$_{12}$BrAc that can explain the MQT phenomena, including the absence of tunneling selection rules and the nonexponential form of the magnetic relaxation. Such transverse fields are likely to be present and important in other SMMs, including Mn$_{12}$-Ac. However, Mn$_{12}$BrAc is an ideal material to study the effect of transverse fields because it has small transverse anisotropies, likely because of the nature of the solvent microenvironment around the Mn$_{12}$ core.[16] In fact, we find that the relaxation rate is insensitive to the orientation of a small external transverse field.

We have used a high sensitivity micro-Hall effect magnetometer in a low-temperature helium 3 system to measure the magnetization of a Mn$_{12}$-BrAc single crystal in the pure quantum regime ($T=0.4$ K) where magnetic relaxation is in the pure quantum tunneling regime. The crossover to pure quantum tunneling occurs at ~1 K for resonance $k=6$, similar to the crossover temperature found in Mn$_{12}$-Ac.[6] Single crystals were removed from the mother liquor just prior to measurement and immediately placed in grease to minimize solvent loss. Further, x-ray diffraction results at 100 K on the same crystal used in these experiments show

that the crystal is both chemically and crystallographically the same as that reported previously,[15] but that the solvent (CH_2Cl_2) content in the current crystal is double what was previously found. A high-field superconducting vector magnet was used to apply magnetic fields at arbitrary directions with respect to the crystallographic axes of the sample. To study MQT rates we sweep the applied z-axis field at a constant rate ($\nu = dH_z/dt$) through a resonance n times. The normalized change in sample magnetization at a resonance, $(M_{before} - M_{after})/(M_{before} - M_{eq})$ (where $M_{eq} = M_s$), is the MQT probability P.[13] For a monodisperse system of molecules this probability for resonance k is related to the tunnel splitting by the Landau-Zener formula, $P_{LZ} = 1 - \exp(-\pi\Delta^2 n/2\nu_0\nu)$, where $\nu_0 = g\mu_B(2S-k)$ and $\nu_0\nu$ is the energy sweep rate. However, for a system with a distribution of tunnel splittings (i.e., due to a distribution of transverse anisotropy parameters or transverse fields) each molecule in the initial state $m = 10$ prior to crossing a resonance has a different tunneling probability. Therefore, it is possible to study different parts of the distribution of tunnel splittings in the crystal by appropriate preparation of the initial magnetization state.

We have used a method similar to that of Ref. 14 to produce a hole in the distribution of transverse fields. The dependence of the tunnel splitting of a molecule at a resonance k on the transverse field can be approximated by a power law, $\Delta_k = a_k H_T^{b_k}$, where a_k and b_k are constants that depend on parameters in the spin Hamiltonian.[18] Consequently, a distribution of transverse field generates a distribution of tunnel splittings. In the presence of an external transverse field a molecule sensing a given magnitude and orientation of the internal transverse field will behave in a manner that depends on the magnitude of the vector sum of these fields. With this procedure we prepare the initial magnetization state of the system $M_{ini} = -M_s$. Then we sweep the longitudinal field from 0 T to 3.25 T at $\nu = 0.4$ T/min and go back to 0 T crossing resonance $k = 6$ twice in the presence of a digging transverse field H_{dig} applied at a digging angle ϕ_{dig} in the x-y plane (steps 1 and 2 in Fig. 1). The molecules with highest splitting values have the greatest probability to relax by MQT. In the next step (step 3 in Fig. 1) we sweep the longitudinal field across the same resonance in the presence of a transverse field H_T applied in a direction ϕ. In this crossing only those molecules that remain in the metastable well during the digging process can tunnel across the barrier and contribute to the MQT probability. We repeat this procedure for different values of ϕ from $\phi = \phi_{dig} - 180°$ to $\phi = \phi_{dig} + 180°$. In Fig. 1 we show results for two different digging fields, $H_{dig} = 0$ (dashed line) and 0.2 T (solid line), applied along $\phi_{dig} = 0$ during steps 1 and 2. The measurement in step 3 was done with a transverse field $H_T = 0.2$ T applied along $\phi = 0$ and 180° in both cases. The shift of the center of the resonance to higher fields with step number is associated with changes in sample internal field during relaxation (see Fig. 1 in Ref. 6).

We have carried out hole digging experiments in two different forms. (a) In the first case the values of the transverse digging field and the transverse field used in the measure-
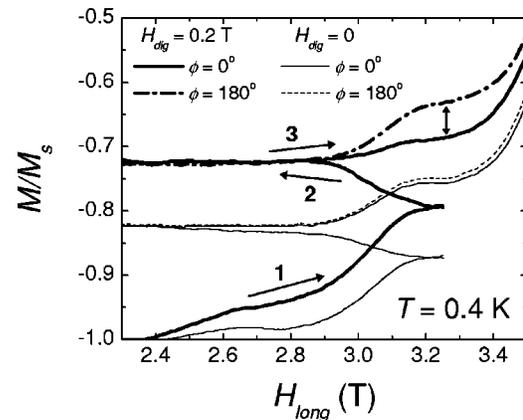

FIG. 1. Hole digging method. Magnetization vs applied longitudinal field. Steps 1 and 2: a transverse digging field, $H_{dig} = 0$ (thin lines) $H_{dig} = 0.2$ T (thick lines), is applied along $\phi_{dig} = 0$ during the crossing of resonance $k = 6$ back and forth. Step 3: resonance $k = 6$ is crossed after the hole digging process in the presence of a transverse field, $H_T = 0.2$ T applied along $\phi = 0$ and 180° for both cases.

ment of the MQT probability are equal, $H_{dig} = H_T$. In Fig. 2(a) we show the results obtained with the digging transverse field applied along $\phi_{dig} = 0$ for different values of $H_{dig} = H_T = 0.2$, 0.25, 0.35, and 0.37 T. (b) In the second case we used a constant value of the transverse "measurement" field, $H_T = 0.2$ T, while we produce the hole with different transverse digging fields, $H_{dig} = 0$, 0.025, 0.1, 0.2, and 0.4 T, applied along $\phi_{dig} = 0$. The results are shown in Fig. 3(a). The MQT probability clearly shows a hole at the same angle at which the transverse digging field was applied, $\phi = 0$.[19] This observation unambiguously establishes the existence of a distribution of transverse fields.

These figures show that: (1) the hole width and depth increase with the magnitude of the digging field, (2) the probability far from the hole (i.e., $\pm 180°$) in Fig. 3(a) first increases with the digging field (from $H_{dig} = 0$ to 0.2 T) and then decreases, and (3) the flat response (within the noise) of the curve of $H_{dig} = 0$ [Fig. 3(a)] is indicative of the absence of second- and fourth-order anisotropy terms in the Hamiltonian, which would lead to two-fold and four-fold patterns of maxima, respectively.[20] This can also be seen in the pink data of Fig. 2(a), which are insensitive to the orientation of the transverse magnetic field.[22] These data have been obtained without using the hole digging process, so in this case all the molecules contribute to the MQT probability at resonance $k = 6$. Observation (2), the fact that $P_{k=6}(\pm 180°)$ first increases then decreases with digging field, implies that there are significant transverse fields present in the sample (~ 0.2 T), as will be discussed below.

To study the behavior of different parts of the distribution of quantum splittings as a function of an external transverse field we have measured the MQT probability in Landau-Zener multicrossing measurements of resonance $k = 6$ at a sweep rate, $\nu = 0.6$ T/min, in the presence of different transverse fields, $H_T = 0$, 0.1, 0.2, 0.3, and 0.5 T (see Ref. 10 for details on the procedure). The results are shown in Fig. 4 starting from a saturated sample. The fact that relaxation is
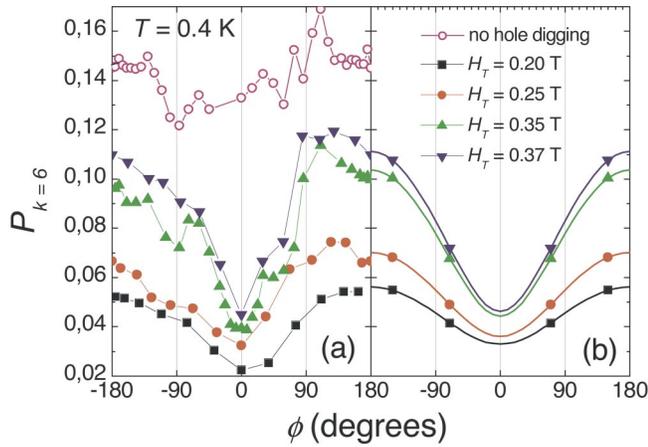
FIG. 2. (Color online) Hole digging measurements. (a) Measured MQT probability for $k=6$ as a function of the angle and magnitude of the transverse field and (b) calculation of MQT probability of resonance $k=6$ for different transverse fields $H_T=H_{dig}$ at $\nu=0.4$ T/min, as described in the text.

broad on a logarithm scale confirms the presence of a distribution of tunnel splittings in the crystal. An interesting result is that the relaxation curves are rather insensitive to small values of the applied transverse field ($H_T<0.2$ T).

We can model these data assuming a distribution of internal transverse fields of a Gaussian form, $f(H_{Tint},\beta)dH_{Tint}d\beta=\exp(-H_{Tint}^2/2\sigma^2)dH_{Tint}d\beta$, where σ is the standard deviation, H_{Tint} is the magnitude of the internal transverse field and β is the direction of the transverse field in the x-y plane (we assume the distribution is isotropic in the x-y plane). When an external transverse field H_T is applied at an angle ϕ the total transverse field felt by a molecule is the vector sum of both internal and external fields, $\vec{h}_T=\vec{H}_{Tint}+\vec{H}_T$. As mentioned above the dependence of the tunnel splitting on the transverse field can be approximated by $\Delta_k=a_k h_T^{b_k}$. This approximation is valid for transverse fields below 1 T. The solution of the Hamil-
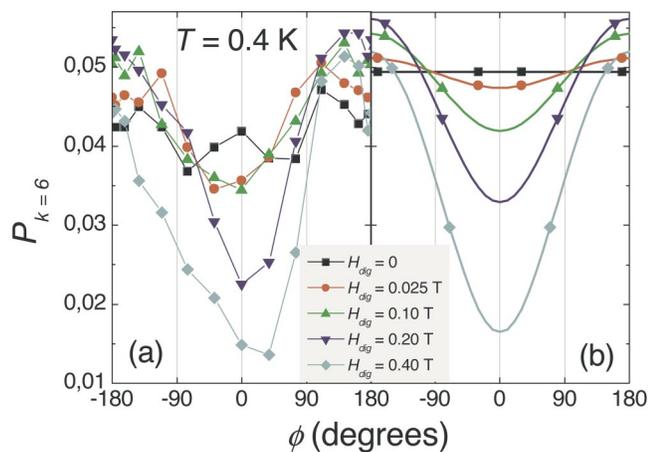

FIG. 3. (Color online) Hole digging measurements. (a) Measured MQT probability for $k=6$ as a function of the angle of the transverse field ($H_T=0.2$ T) and magnitude of the digging field H_{dig} and (b) calculation of the probability as described in the text.
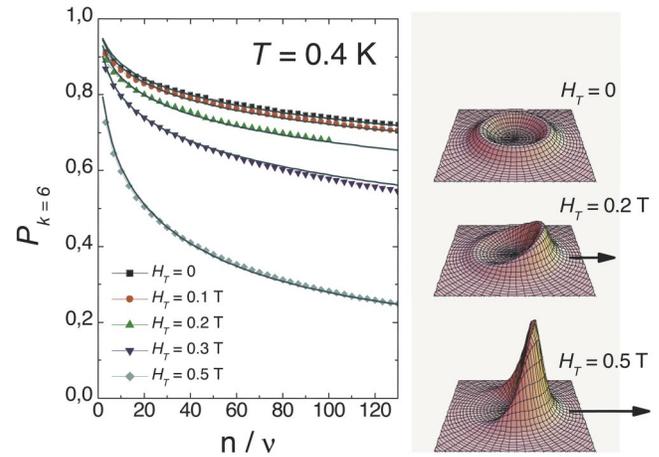

FIG. 4. (Color online) Multicrossing relaxation curves of resonance $k=6$ for different applied transverse fields. The illustrations represent the portion of $f(H_{Tint})$ that relaxes at $n=1$.

tonian of Eq. (1) using $D=0.63$ K, $B=1.0$ mK, and $C=0.023$ mK (these parameters are from EPR studies[21]) gives $a_6=1.55\times10^{-5}$ K/T and $b_6=2.06$. To calculate the MQT probability we have integrated the Landau-Zener probability over the distribution of tilts, where a_k, b_k, and σ have been used as fit parameters. The results of this calculation are shown in Fig. 4 (continuous lines). The fit has been obtained with $a_k=1.5\times10^{-6}$ K, $b_k=3.3$, and $\sigma=0.38$ T. The values of a_k and b_k are similar to those obtained by diagonalization of the Hamiltonian. Note that $f(H_{Tint})$ must be broad to explain the slow increase in the relaxation as a function of external transverse field H_T observed in Fig. 4. A small change in the width of the distribution (i.e., ±0.01 T) leads to a lower quality fit to the data.

On the right-hand margin of Fig. 4 we show three-dimensional plots that illustrate the portion of molecules within $f(H_{Tint})$ that relaxes in the first crossing of resonance $k=6$ in the presence of several external transverse fields. In Figs. 2(b) and 3(b) we show the model calculations corresponding to the situation in the experiments in Figs. 2(a) and 3(a), respectively, using the parameters obtained from fitting of the multicrossing relaxation curves. The calculations reproduce the behavior of the MQT probability close and far from the hole in the distribution. As in the experiment, one can see in Fig. 3(b) how the probability far from the hole (i.e., $\pm180°$) first increases with the digging field (from $H_{dig}=0$ to 0.2 T) and then decreases. This can be understood from the illustrations in Fig. 4. For low fields the portion of molecules relaxing that have internal transverse fields antiparallel to the digging field is significant and consequently the MQT probability far from the hole becomes smaller because some molecules with this internal transverse field direction relax during the digging procedure. As the digging field is increased, the portion of such molecules decreases and therefore the MQT probability for 180° increases. The field at which the probability $P_{k=6}(\pm180°)$ begins to decrease with increasing digging field is the characteristic field scale of $f(H_{Tint})$.

We now consider possible origins of internal fields per-

pendicular to the easy axis of the molecules. A natural explanation is that there are tilts of the molecular easy axes. Molecules with different tilts, α, experience different transverse magnetic fields, $H_{Tint} = H_L \sin \alpha$. Small tilts generate large transverse fields due to the high longitudinal fields used in the experiments. The distribution of transverse fields used to model our data would result from a Gaussian distribution of tilt angles with a standard deviation of $\sigma = 7.3°$. This standard deviation appears large, but would be reduced when other sources of disorder are included (i.e., D and/or g strain[23]). We also note that tilts of the magnetic easy axis were first shown to occur due to crystal dislocations.[24] In addition, small tilts were shown to result from solvent disorder in Mn_{12}-Ac.[9] Further, large tilts have been observed in a low anisotropy barrier form of Mn_{12} and associated with an unusual Jahn-Teller distortion at a Mn(III) ion.[26] We also note that tilts were assumed to explain the longitudinal field EPR line shapes.[25]

Our results constrain models of the origin of $f(H_{Tint})$. While there are large transverse fields (~ 0.4 T), *there is not a broad distribution of longitudinal fields* in the sample, as the latter would completely smooth out the resonances in the magnetic hysteresis loops. This excludes any source of magnetic fields that are randomly oriented (i.e., dipolar or hyperfine fields). Also, the magnitude of the observed transverse fields precludes dipolar and hyperfine fields (≤ 0.05 T). Exchange interactions between molecules is a possible source of internal ''bias'' fields. There is, however, no evidence of longitudinal fields associated with intermolecular exchange; we have not observed exchange biasing or shifts of the $k = 0$ resonance from zero longitudinal field in experiments conducted below the blocking temperature $T_B \sim 3.2$ K. While the basic interactions at the origin of these internal transverse fields is not known, these experiments show that transverse fields are important to MQT in this SMM.

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[1] J.R. Friedman, M.P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

[2] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).

[3] J.M. Hernandez, X.X. Zhang, F. Luis, J. Bartolome, J. Tejada, and R. Ziolo, Europhys. Lett. **35**, 301 (1996).

[4] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).

[5] A.L. Barra, D. Gatteschi, and R. Sessoli, Phys. Rev. B **56**, 8192 (1997).

[6] L. Bokacheva, A.D. Kent, and M.A. Walters, Phys. Rev. Lett. **85**, 4803 (2000).

[7] S. Hill, J.A.A.J. Perenboom, N.S. Dalal, T. Hathaway, T. Stalcup, and J.S. Brooks, Phys. Rev. Lett. **80**, 2453 (1998).

[8] E. del Barco, J.M. Hernandez, J. Tejada, N. Biskup, R. Achey, I. Rutel, N. Dalal, and J. Brooks, Phys. Rev. B **62**, 3018 (2000).

[9] A. Cornia, R. Sessoli, L. Sorace, D. Gatteschi, A.L. Barra, and C. Daiguebonne, Phys. Rev. Lett. **89**, 257201 (2002).

[10] E. del Barco, A.D. Kent, E.M. Rumberger, D.N. Hendrickson, and G. Christou, Europhys. Lett. **60**, 768 (2002).

[11] E. del Barco, A.D. Kent, E.M. Rumberger, D.N. Hendrickson, and G. Christou, Phys. Rev. Lett. **91**, 047203 (2003).

[12] S. Hill, R.S. Edwards, S.I. Jones, J.M. North, and N.S. Dalal, Phys. Rev. Lett. **90**, 217204 (2003).

[13] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).

[14] W. Wernsdorfer, R. Sessoli, and D. Gatteschi, Europhys. Lett. **47**, 254 (1999).

[15] J. An, Z.D. Chen, X.X. Zhang, H.G. Raubenheimer, C. Esterhuysen, S. Gao, and G.X. Xu, J. Chem. Soc. Dalton Trans. **22**, 3352 (2001).

[16] In Mn_{12}-Ac there are on average two acetic acid (CH_3COOH) solvents per molecule and four possible solvent positions around the molecule. Disorder in the position of these solvents lowers the molecule symmetry and leads to a strong second-order transverse anisotropy (Refs. 11 and 12). In Mn_{12}-BrAc there are $8CH_2Cl_2$ solvents/mol. and weaker solvent/molecule hydrogen bonding interactions and no apparent second-order transverse anisotropy (Ref. 21).

[17] G. Christou, D. Gatteschi, D.N. Hendrickson, and R. Sessoli, MRS Bull. **25**, 66 (2000).

[18] D.A. Garanin and E.M. Chudnovsky, Phys. Rev. B **56**, 11102 (1997).

[19] We have done hole digging experiments by applying the digging transverse field at an angle, $\phi_{dig} = 200°$. The result showed a hole centered at $\phi = 200°$. This is evidence that the hole orientation depends on the orientation of the digging field and supports our assumption of an isotropic distribution of tilts in the x-y plane.

[20] For the amplitudes of the transverse magnetic fields applied in these experiments (≤ 0.4 T) the expected change in tunneling probability with angle ϕ is negligible on the scale of the plots in Figs. 2 and 3 (Ref. 10). However, the four-fold rotation symmetry in the x-y plane has been seen in recent EPR experiments in which larger transverse magnetic fields (~ 4 T) are employed (Ref. 21).

[21] S. Hill (private communication).

[22] The minimum and the maximum observed at $\phi = \pm 90°$ in the pink curve of Fig. 2(a) are due to small nonlinearities in the Hall magnetometer when there is a (~ 0.3 T) magnetic field applied perpendicular to the plane of the sensor. This also leads to the fluctuations seen in the other curves in Figs. 2(a) and 3(a).

[23] K. Park, M.A. Novotny, N.S. Dalal, S. Hill, and P.A. Rikvold, Phys. Rev. B **65**, 014426 (2002); S. Hill, S. Maccagnano, K. Park, R.M. Achey, J.M. North, and N.S. Dalal, *ibid.* **65**, 224410 (2002).

[24] E.M. Chudnovsky and D.A. Garanin, Phys. Rev. Lett. **87**, 187203 (2001).

[25] K. Park, N.S. Dalal, and P.A. Rikvold, J. Chem. Phys. **117**, 11 292 (2002).

[26] K. Takeda, K. Awaga, T. Inabe, A. Yamaguchi, H. Ishimoto, T. Tomita, H. Mitamura, T. Goto, N. Mori, and H. Nojiri, Phys. Rev. B **65**, 094424 (2002).