PHYSICAL REVIEW B **75**, 220408(R) (2007)

Intrinsic magnetic order in Cs_2AgF_4 detected by muon-spin relaxation

T. Lancaster,[1,*] S. J. Blundell,[1] P. J. Baker,[1] W. Hayes,[1] S. R. Giblin,[2] S. E. McLain,[2,†] F. L. Pratt,[2] Z. Salman,[1,2]
E. A. Jacobs,[3] J. F. C. Turner,[3] and T. Barnes[3]
[1]*Clarendon Laboratory, Department of Physics, Oxford University, Parks Road, Oxford, OX1 3PU, United Kingdom*
[2]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, United Kingdom*
[3]*Department of Chemistry and Neutron Sciences Consortium, University of Tennessee, Knoxville, Tennessee 37996, USA*

(Received 4 April 2007; revised manuscript received 6 June 2007; published 27 June 2007)

We present the results of a muon-spin relaxation study of the high-T_c analog material Cs_2AgF_4. We find unambiguous evidence for magnetic order, intrinsic to the material, below $T_C=13.95(3)$ K. The ratio of interplane to intraplane coupling is estimated to be $|J'/J|=1.9\times 10^{-2}$, while fits of the temperature dependence of the order parameter reveal a critical exponent $\beta=0.292(3)$, implying an intermediate character between pure two- and three-dimensional magnetism in the critical regime. Above T_C we observe a signal characteristic of dipolar interactions due to linear F-μ^+-F bonds, allowing the muon stopping sites in this compound to be characterized.

DOI: 10.1103/PhysRevB.75.220408 PACS number(s): 75.40.Cx, 74.25.Ha, 74.72.−h, 76.75.+i

Twenty years after its discovery, high-T_c superconductivity remains one of the most pressing problems in condensed-matter physics. High-T_c cuprates share a layered structure of $[CuO_2]$ planes with strong antiferromagnetic (AFM) interactions between $S=\frac{1}{2}$, $3d^9$ Cu^{2+} ions.[1,2] However, analogous materials based upon $3d$ transition-metal systems such as manganites[3] and nickelates[4] share neither the magnetic nor the superconducting properties of the high-T_c cuprates, leading to speculation that the spin-$\frac{1}{2}$ character of Cu^{2+} is unique in this context. A natural extension to this line of inquiry[5] is to explore compounds based on the $4d$ analog of Cu^{2+}, namely, $S=\frac{1}{2}$, $4d^9$ Ag^{2+}; this motivated the synthesis of the layered fluoride Cs_2AgF_4, which contains silver in the unusual divalent oxidation state.[6,7] This material possesses several structural similarities with the superconducting parent compound La_2CuO_4; it is comprised of planes of $[AgF_2]$ instead of $[CuO_2]$ separated by planes of $[CsF]$ instead of $[LaO]$ (Fig. 1).

Magnetic measurements[7] suggest that, in contrast to the antiferromagnetism of La_2CuO_4, Cs_2AgF_4 is well modeled as a two-dimensional (2D) Heisenberg ferromagnet (described by the Hamiltonian $\mathcal{H}=J\Sigma_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j$) with intralayer coupling $|J|/k_B=44.0$ K. The observation of a magnetic transition below $T_C\approx 15$ K, with no spontaneous magnetization in zero applied field (ZF) and a small saturation magnetization (~40 mT), suggests the existence of a weak, AFM interlayer coupling. This behavior is reminiscent of the 2D ferromagnet[8] K_2CuF_4, where ferromagnetic (FM) exchange results from orbital ordering driven by a Jahn-Teller distortion.[9,10] On this basis, it has been suggested that in Cs_2AgF_4 a staggered ordering of $d_{z^2-x^2}$ and $d_{z^2-y^2}$ hole-containing orbitals on the Ag^{2+} ions gives rise to the FM superexchange.[7] An alternative scenario has also been advanced on the basis of density functional calculations in which a $d_{3z^2-r^2}$-p-$d_{x^2-y^2}$ orbital interaction through the Ag-F-Ag bridges causes spin polarization of the $d_{x^2-y^2}$ band.[11]

Although inelastic neutron-scattering measurements have been carried out on this material,[7] both Cs and Ag strongly absorb neutrons, resulting in limited resolution and a poor signal-to-noise ratio. In contrast, spin-polarized muons, which are very sensitive probes of local magnetic fields, suffer no such impediments and, as we shall see, are ideally suited to investigations of the magnetism in fluoride materials. In this Rapid Communication we present the results of a ZF muon-spin relaxation (μ^+SR) investigation of Cs_2AgF_4. We confirm that the material is uniformly ordered throughout its bulk below T_C and show that the critical behavior associated with the magnetic phase transition is intermediate in character between 2D and 3D. In addition, strong coupling between the muon and F^- ions allows us to characterize the muon stopping states in this compound.

ZF μ^+SR measurements were made on the MuSR instrument at the ISIS facility, using an Oxford Instruments Variox ^{4}He cryostat. In a μ^+SR experiment spin-polarized positive muons are stopped in a target sample, where the muon usually occupies an interstitial position in the crystal. The observed property in the experiment is the time evolution of the muon-spin polarization, the behavior of which depends on the magnetic field at the muon site.[13] Polycrystalline Cs_2AgF_4 was synthesized as previously reported.[7] Due to its

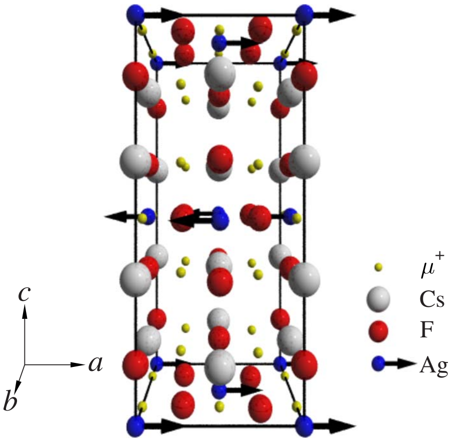

FIG. 1. (Color online) Structure of Cs_2AgF_4 showing a possible magnetic structure. Candidate muon sites occur in both the $[CsF]$ and $[AgF_2]$ planes.

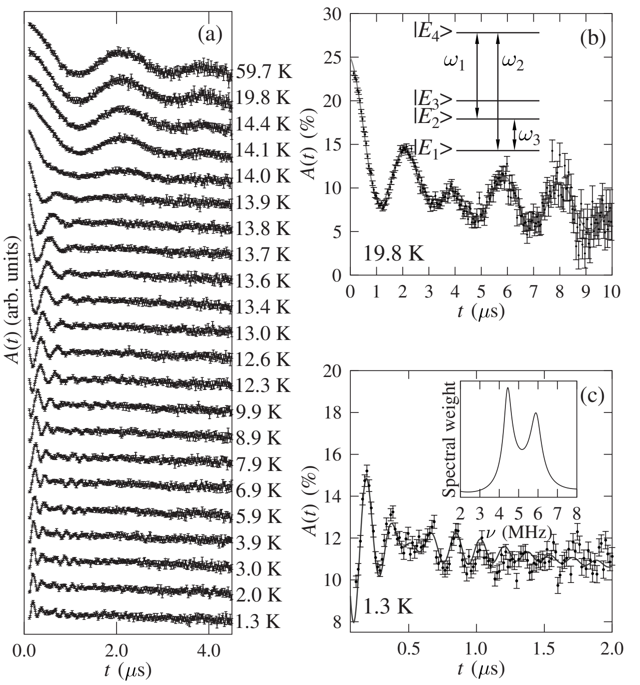

FIG. 2. (a) Temperature evolution of ZF μ^+SR spectra measured on Cs_2AgF_4 between 1.3 and 59.7 K. (b) Above T_C low-frequency oscillations are observed due to the dipole-dipole coupling of F-μ^+-F states. *Inset*: The energy level structure allows three transitions, leading to three observed frequencies. (c) Below T_C higher-frequency oscillations are observed due to quasistatic magnetic fields at the muon sites. *Inset*: Maximum entropy analysis reveals two magnetic frequencies corresponding to two magnetically inequivalent muon sites.

chemical reactivity, the sample was mounted under Ar in a gold-plated Ti sample holder with a cylindrical sample space of diameter 2.5 cm and depth 2 mm. A 25-μm-thick window was screw clamped onto a gold o-ring on the main body of the sample holder resulting in an airtight seal.

Example ZF μ^+SR spectra measured on Cs_2AgF_4 are shown in Fig. 2(a). Below T_C [Fig. 2(c)] we observe oscillations in the time dependence of the muon polarization [the "asymmetry"[12,13] $A(t)$], which are characteristic of a quasistatic local magnetic field at the muon stopping site. This local field causes a coherent precession of the spins of those muons for which a component of their spin polarization lies perpendicular to this local field (expected to be 2/3 of the total spin polarization for a powder sample). The frequency of the oscillations is given by $\nu_i=\gamma_\mu|B_i|/2\pi$, where γ_μ is the muon gyromagnetic ratio ($=2\pi\times 135.5$ MHz T^{-1}) and B_i is the average magnitude of the local magnetic field at the ith muon site. Any fluctuation in magnitude of these local fields will result in a relaxation of the oscillating signal,[14] described by relaxation rates λ_i.

Maximum entropy analysis [inset, Fig. 2(c)] reveals two separate frequencies in the spectra measured below T_C, corresponding to two magnetically inequivalent muon stopping sites in the material. The precession frequencies, which are proportional to the internal magnetic field experienced by the muon, may be viewed as an effective order parameter for these systems.[13] In order to extract the temperature dependence of the frequencies, the low-temperature data were fitted to the function

$$A(t)=\sum_{i=1}^{2}A_i\exp(-\lambda_i t)\cos(2\pi\nu_i t)+A_3\exp(-\lambda_3 t)+A_{bg}, \tag{1}$$

where A_1 and A_2 are the amplitudes of the precession signals and A_3 accounts for the contributions from muon-spin components parallel to the local magnetic field. The term A_{bg} reflects the nonrelaxing signal from those muons which stop in the sample holder or cryostat tail.

The two precession frequencies were found to have the same temperature dependence, with a ratio $\nu_2/\nu_1=0.83$, and this ratio was therefore fixed in the fitting procedure. The amplitudes A_i were found to be constant across the temperature range and were fixed at values $A_1=1.66\%$, $A_2=3.74\%$, and $A_3=5.54\%$. This shows that the probability of a muon stopping in a site that gives rise to frequency ν_1 is approximately half that of a muon stopping in a site that corresponds to ν_2. We note also that A_3 is in excess of the expected ratio of $A_3/(A_1+A_2)=1/2$. The unambiguous assignment of amplitudes is made difficult by the resolution limitations that a pulsed muon source places on the measurement. The muon pulse at ISIS[13] has FWHM $\tau_{\text{mp}}\sim 80$ ns, limiting the response for frequencies above $\sim\tau_{\text{mp}}^{-1}$. We should expect, therefore, slightly reduced amplitudes or increased relaxation (see below) for the oscillating components in our spectra for which $\nu_{1,2}\gtrsim 5$ MHz. Nevertheless, the total oscillatory amplitude is of sufficient magnitude for us to conclude that magnetic order occurs in at least the majority phase of our sample. Moreover, we find no evidence of any signal from a minority phase, whether chemical or magnetic. These observations, along with the constancy of amplitudes $A_{1,2,3}$ below T_C and the complete recovery of the total expected muon asymmetry above T_C, lead us to conclude that Cs_2AgF_4 is completely ordered throughout its bulk below T_C.

Figure 3(a) shows the evolution of the precession frequencies ν_i, allowing us to investigate the critical behavior associated with the phase transition. From fits of ν_i to the form $\nu_i(T)=\nu_i(0)(1-T/T_C)^\beta$ for $T>10$ K, we estimate $T_C=13.95(3)$ K and $\beta=0.292(3)$. In fact, good fits to $\nu_i(T)=\nu_i(0)(1-T/13.95)^{0.292}$ are achieved over the entire measured temperature range (that is, no spin-wave-related contribution was evident at low temperatures), yielding $\nu_1(0)=6.0(1)$ MHz and $\nu_2(0)=4.9(2)$ MHz corresponding to local magnetic fields at the two muon sites of $B_1=44(1)$ mT and $B_2=36(1)$ mT. A value of $\beta=0.292(3)$ is less than expected for three-dimensional models ($\beta=0.367$ for 3D Heisenberg), but larger than expected for 2D models ($\beta=0.23$ for 2D XY or $\beta=0.125$ for 2D Ising).[15,16] This suggests that in the critical regime the behavior is intermediate in character between 2D and 3D; this contrasts with the magnetic properties of K_2CuF_4, where $\beta=0.33$, typical of a 3D system, is observed in the reduced temperature region[17–19] $t_r\equiv(T_C-T)/T_C>7\times 10^{-2}$, with a crossover to more 2D-like behavior at $t_r<7\times 10^{-2}$, where $\beta=0.22$. Our measurements

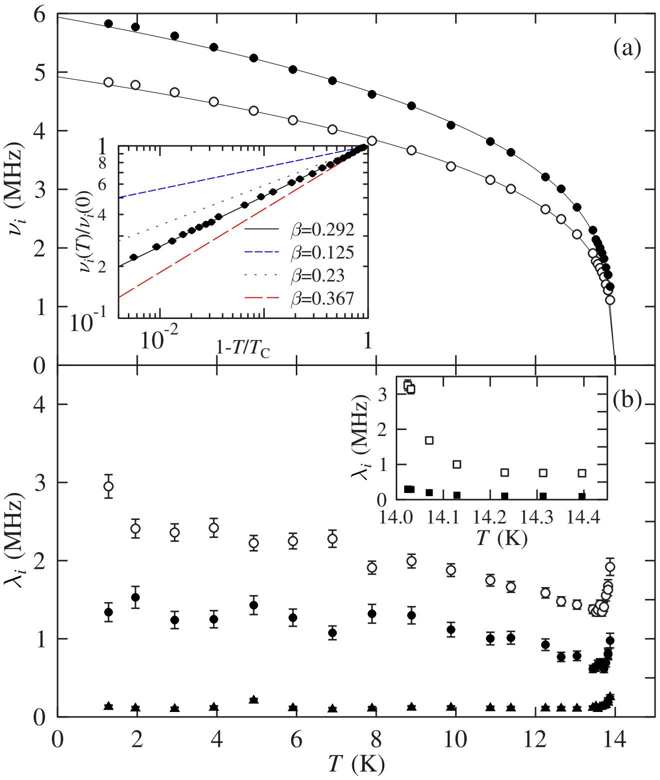

FIG. 3. (Color online) Results of fitting data measured below T_C to Eq. (1). (a) Evolution of the muon-spin precession frequencies ν_1 (closed circles) and ν_2 (open circles) with temperature. Solid lines are fits to the function $\nu_i(T)=\nu_i(0)(1-T/T_C)^{\beta}$ as described in the text. *Inset*: Scaling plot of the precession frequencies with parameters $T_C=13.95(3)$ K and $\beta=0.292$. Dotted lines show the results expected for the 2D Ising model ($\beta=0.125$), 2D *XY* model ($\beta=0.23$), and 3D Heisenberg model ($\beta=0.367$). (b) Relaxation rates λ_1 (closed circles), λ_2 (open circles), and λ_3 (closed triangles), as a function of temperature showing a rapid increase as T_C is approached from below. *Inset*: Relaxation rates λ_4 (closed squares) and λ_5 (open squares) for $T>T_C$, which also increase close to T_C.

probe the behavior of Cs_2AgF_4 for $t_r \geq 5.5\times10^{-3}$, for which we do not observe any crossover.

A knowledge of T_C and the intraplane coupling J, allows us to estimate the interplane coupling J'. Recent studies of layered $S=1/2$ Heisenberg ferromagnets using the spin-rotation invariant Green's function method,[20] show that the interlayer coupling may be described by an empirical formula

$$\left|\frac{J'}{J}\right| = \exp\left(b - a\frac{|J|}{k_B T_C}\right), \qquad (2)$$

with $a=2.414$ and $b=2.506$. Substituting our value of $T_C=13.95$ K and using[7] $|J|/k_B=44.0$ K, we obtain $|J'|/k_B=0.266$ K and $|J'/J|=1.9\times10^{-2}$. The application of this procedure to K_2CuF_4 (for which[8] $T_C=6.25$ K and $|J|/k_B=20.0$ K) results in $|J'|/k_B=0.078$ K and $|J'/J|=3.9\times10^{-3}$. This suggests that, although highly anisotropic, the interlayer coupling is stronger in Cs_2AgF_4 than in K_2CuF_4. This may account for the lack of dimensional crossover in Cs_2AgF_4 down to $t_r=5.5\times10^{-3}$.

Both transverse depolarization rates λ_1 and λ_2 are seen to decrease with increasing temperature [Fig. 3(b)] except close to T_C where they rapidly increase. The large values of $\lambda_{1,2}$ at low temperatures may reflect the reduced frequency response of the signal due to the muon pulse width described above. The component in the spectra with the larger precession frequency ν_1 has the smaller depolarization rate λ_1 at all temperatures. These features provide further evidence for a magnetic phase transition at $T_C=13.95$ K. The large upturn in the depolarization rates close to T_C, which is also seen in the longitudinal relaxation rate λ_3 (which is small and nearly constant except on approach to T_C), may be attributed to the onset of critical fluctuations close to T_C. We note that a nonzero value of the longitudinal relaxation rate λ_3 implies that the relaxation of the muon spins in the ordered regime has a dynamic character.[14]

Above T_C the character of the measured spectra changes considerably [Figs. 2(a) and 2(b)] and we observe lower-frequency oscillations characteristic of the dipole-dipole interaction of the muon and the ^{19}F nucleus.[21] The Ag^{2+} electronic moments, which dominate the spectra for $T<T_C$, are no longer ordered in the paramagnetic regime, and fluctuate very rapidly on the muon time scale. They are therefore motionally narrowed from the spectra, leaving the muon sensitive to the quasistatic nuclear magnetic moments. This interpretation is supported by μ^+SR measurements of K_2CuF_4, where similar behavior was observed.[22] In many materials containing fluorine, the muon and two fluorine ions form a strong "hydrogen bond" usually separated by slightly less than twice the F^- ionic radius ($\approx$2.6 Å). The linear F-μ^+-F spin system consists of four distinct energy levels with three allowed transitions between them [inset, Fig. 2(b)] giving rise to the distinctive three-frequency oscillations observed. The signal is described by a polarization function[21] $D(\omega_d t)=\frac{1}{6}[3+\Sigma_{j=1}^{3}u_j\cos(\omega_j t)]$, where $u_1=1$, $u_2=(1+1/\sqrt{3})$, and $u_3=(1-1/\sqrt{3})$. The transition frequencies [shown in Fig. 2(b)] are given by $\omega_j=3u_j\omega_d/2$, where $\omega_d=\mu_0\gamma_\mu\gamma_F/4\pi r^3$, γ_F is the ^{19}F nuclear gyromagnetic ratio, and r is the μ^+-^{19}F separation. This function accounts for the observed frequencies very well, leading us to conclude that the F-μ^+-F bonds are highly linear.

A successful fit of our data was obtained by multiplying $D(\omega_d t)$ by an exponential function with a small relaxation rate λ_4, crudely modeling fluctuations close to T_C. The addition of a further exponential component $A_5\exp(-\lambda_5 t)$ was also required in order to account for those muon sites not strongly dipole coupled to fluorine nuclei. Hence, the data were fitted to $A(t)$ given by

$$A(t) = A_4 D(\omega_d t)\exp(-\lambda_4 t) + A_5\exp(-\lambda_5 t) + A_{bg}. \qquad (3)$$

We found ω_d to be constant at all measured temperatures, taking the value $\omega_d=2\pi\times0.211(1)$ MHz, corresponding to a F-μ^+ separation of 1.19(1) Å [giving a F-F separation 2.38(2) Å], typical of linear bonds.[21] The relaxation rates only vary appreciably within 0.2 K of the magnetic transition [inset, Fig. 3(b)], increasing as T_C is approached from above, probably due to the onset of critical fluctuations. This provides further evidence for our assignment of $T_C=13.95$ K.

Our determination of $\nu_i(0)$ and observation of the linear F-μ^+-F signal allow us to identify candidate muon sites in Cs_2AgF_4. Although the magnetic structure of the system is not known, magnetic measurements[7] suggest the existence of loosely coupled FM Ag^{2+} layers arranged antiferromagnetically along the *c* direction. Dipole fields were calculated for such a candidate magnetic structure with Ag^{2+} moments in the *ab* planes oriented parallel (antiparallel) to the *a* direction for $z=0$ ($z=1/2$). The calculation was limited to a sphere containing $\approx 10^5$Ag ions with localized moments of $0.8\mu_B$.[7] The above considerations suggest that the muon sites will be situated midway between two F^- ions. Two sets of candidate muon sites may be identified in the planes containing the fluorine ions. Magnetic fields corresponding to $\nu_2(0)$ are found in the [CsF] planes (i.e., those with $z=0.145$ and $z=0.355$) at the positions (1/4, 1/4, z), (1/4, 3/4, z), (3/4, 1/4, z), and (3/4, 3/4, z). Sites corresponding to the frequency $\nu_1(0)$ are more difficult to assign, but good candidates are found in the $[AgF_2]$ planes (at $z=0,1/2$) at positions (1/4,1/2,z), (3/4,1/2,z), (1/4,0,z) and (3/4,0,z). The candidate sites are shown in Fig. 1. We note that there are twice as many [CsF] planes in a unit cell than there are $[AgF_2]$ planes in agreement with our observation that components with frequency ν_2 occur with twice the amplitude of those with ν_1. Such an assignment then implies that the presence of the muon distorts the surrounding F^- ions such that their separation is ~2.38 Å (see above). This contrasts with the in-plane F-F separation in the unperturbed material of 4.55 Å ([CsF] planes) and ~3.2 Å ($[AgF_2]$ planes).[7] Thus the two adjacent F^- ions in the [CsF] planes each shift by ~1.1 Å from their equilibrium positions towards the μ^+, while those in the magnetic $[AgF_2]$ planes shift by ~0.4 Å. This demonstrates that the muon introduces a non-negligible local distortion. If, however, by analogy with the V_k defect center in alkali halides,[23] the F-μ^+-F complex acts like an independent molecule in the crystal the distortion in the Ag^{2+} ion positions will be much less significant than the distortion of the F^- ions.

Part of this work was carried out at the ISIS facility, Rutherford Appleton Laboratory, UK. This work is supported by the EPSRC (UK). T.L. acknowledges support from the Royal Commission for the Exhibition of 1851. J.F.C.T and S.E.M acknowledge the U.S. National Science Foundation. We thank A.M. Stoneham for useful discussions.

---

*t.lancaster1@physics.ox.ac.uk

†Present address: Spallation Neutron Source and Center for Molecular Biophysics, Oak Ridge National Laboratory, Bethel Valley Road, Oak Ridge, Tennessee, USA.

[1] P. A. Lee, N. Nagaosa, and X.-G. Wen, Rev. Mod. Phys. **78**, 17 (2006).

[2] M. A. Kastner, R. J. Birgeneau, G. Shirane, and Y. Endoh, Rev. Mod. Phys. **70**, 897 (1998).

[3] E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).

[4] R. J. Cava, B. Batlogg, T. T. Palstra, J. J. Krajweski, W. F. Peck, A. P. Ramirez, and L. W. Rupp, Phys. Rev. B **43**, 1229 (1991).

[5] W. Grochala and R. Hoffmann, Angew. Chem., Int. Ed. **40**, 2742 (2001).

[6] R.-H. Odenthal, D. Paus, and R. Hoppe, Z. Anorg. Allg. Chem. **407**, 144 (1974).

[7] S. E. McLain, M. R. Dolgos, D. A. Tennant, J. F. C. Turner, T. Barnes, T. Proffen, B. C. Sales, and R. I. Bewley, Nat. Mater. **5**, 561 (2006).

[8] I. Yamada, J. Phys. Soc. Jpn. **33**, 979 (1972).

[9] Y. Ito and J. Akimitsu, J. Phys. Soc. Jpn. **40**, 1333 (1976).

[10] D. I. Khomskii and K. I. Kugel, Solid State Commun. **13** 763 (1973).

[11] D. Dai, M.-H. Whangbo, J. Köhler, C. Hoch, and A. Villesuzanne, Chem. Mater. **18**, 3281 (2006).

[12] The asymmetry $A(t)$ is related to the polarization of the muon-spin ensemble $P(t)$ by $A(t)=aP(t)$, where a is a constant ($\lesssim 1/3$) determined by the asymmetric nature of the muon decay and by the experimental geometry.

[13] S. J. Blundell, Contemp. Phys. **40**, 175 (1999).

[14] R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, and R. Kubo, Phys. Rev. B **20**, 850 (1979).

[15] S. J. Blundell, *Magnetism in Condensed Matter* (Oxford University Press, Oxford, 2001).

[16] S. T. Bramwell and P. C. W. Holdsworth, J. Phys.: Condens. Matter **5**, L53 (1993).

[17] K. Hirakawa and H. Ikeda, J. Phys. Soc. Jpn. **35**, 1328 (1973).

[18] T. Hashimoto, Y. Kojima, and T. Ikegami, J. Magn. Magn. Mater. **15-18**, 1025 (1980).

[19] M. Suzuki and H. Ikeda, J. Phys. Soc. Jpn. **50**, 1133 (1981).

[20] D. Schmalfuß, J. Richter, and D. Ihle, Phys. Rev. B **72** 224405 (2005).

[21] J. H. Brewer, S. R. Kreitzman, D. R. Noakes, E. J. Ansaldo, D. R. Harshman, and R. Keitel, Phys. Rev. B **33**, 7813 (1986).

[22] C. Mazzoli, G. Allodi, G. Guidi, R. De Renzi, P. Ghigna, and C. Baines, Physica B **326**, 427 (2003).

[23] W. Hayes and A. M. Stoneham, *Defects and Defect Processes in Nonmetallic Solids* (Wiley, New York, 1985; Dover, New York, 2004).