PHYSICAL REVIEW B **82**, 100402(R) (2010)

Evidence from thermodynamic measurements for a singlet crystal-field ground state in pyrochlore $Tb_2Sn_2O_7$ and $Tb_2Ti_2O_7$

Y. Chapuis,[1] A. Yaouanc,[1] P. Dalmas de Réotier,[1] C. Marin,[1] S. Vanishri,[1] S. H. Curnoe,[2] C. Vâju,[1,3] and A. Forget[4]
[1]*CEA/DSM/Institut Nanosciences et Cryogénie, F-38054 Grenoble, France*
[2]*Physics and Physical Oceanography, Memorial University, St. John's, Newfoundland, Canada A1B 3X7*
[3]*Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*
[4]*CEA/DSM/Institut Rayonnement Matière de Saclay, F-91191 Gif sur Yvette, France*

(Received 12 May 2010; revised manuscript received 30 July 2010; published 2 September 2010)

The magnetic entropy variation for the ordered spin-ice $Tb_2Sn_2O_7$ and the spin-liquid $Tb_2Ti_2O_7$ measured up to ~ 20 K shows that the crystal-field ground state for both systems is a singlet split from the first excited level by a thermal energy of ~ 2 K. It is the superexchange interactions between the Tb^{3+} spins which induce the terbium magnetic moments. Our results are analyzed in terms of a tetragonal perturbation for $Tb_2Ti_2O_7$ and this perturbation plus a molecular field for $Tb_2Sn_2O_7$.

DOI: 10.1103/PhysRevB.82.100402 PACS number(s): 75.10.Dg, 75.30.Kz, 75.40.−s

Geometrically frustrated magnetic materials are now intensively studied, both theoretically and experimentally. In particular, the pyrochlore crystal structure $R_2M_2O_7$ (R stands for a rare-earth ion and M for a nonmagnetic p or d metal) built of corner sharing tetrahedra usually inhibits the formation of a collinear long-range magnetic order, leading to a variety of magnetic behaviors, such as spin ices, spin liquids, and complex noncollinear magnetic orders.[1,2]

Among the pyrochlore compounds, the insulators $Tb_2Ti_2O_7$ and $Tb_2Sn_2O_7$ are probably the less understood systems. They crystallize at room temperature with the cubic space group $Fd\bar{3}m$. The local symmetry at a Tb^{3+} ion is D_{3d}. It is important to note that structural distortions below ~ 20 K have been reported from x-ray measurements for $Tb_2Ti_2O_7$.[3] These distortions are a signature of a transition from cubic to tetragonal structures. However, the phase transition was not observed. Anyhow, the x-ray data show that the rare-earth local symmetry is reduced at low temperature. Neutron diffraction for $Tb_2Sn_2O_7$ shows that the crystal structure is tetragonal in the magnetically ordered state.[4,5]

$Tb_2Sn_2O_7$ is a so-called ordered spin-ice system below $T_c = 0.88(1)$ K.[4,5] For a given tetrahedron the four spins are close to the $\langle 111 \rangle$ anisotropy axes in a two-in two-out magnetic configuration. In contrast to the classical spin-ice compounds ($Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$), the magnetic unit cell, which is the crystallographic unit cell, repeats itself. The ordered spin-ice structure is explained within the phenomenological model of Champion *et al.*[6] which assumes a ferromagnetic first neighbor exchange interaction combined with a finite anisotropy. In fact, a μSR experiment has shown that the magnetic ground state is homogeneous (no phase separation) and dynamical in nature.[5,7] While this has been hotly debated,[8,9] it seems now to be accepted.[10,11]

On the other hand, the sibling compound $Tb_2Ti_2O_7$ is classified as a spin-liquid system because it does not display any magnetic order, at least down to 0.05 K, despite the onset of short-range antiferromagnetic correlations developing at ~ 50 K.[12,13] The absence of a long-range magnetic order is a long-standing mystery.[14–16]

Based on inelastic neutron-scattering measurements, a crystal-field level scheme for the Tb^{3+} ions in the two compounds of interest here has been proposed assuming the D_{3d} point symmetry to be valid.[17] The local threefold axis is the crystallographic axis $\langle 111 \rangle$. It is also the quantization axis which we denote as z. A scheme was previously given for $Tb_2Ti_2O_7$.[13] For both compounds, the ground state is predicted to be a crystal-field non-Kramers doublet and the first excited doublet lies at a thermal energy of ~ 20 K. Using the Steven's operator formalism for the crystal-field Hamiltonian, it has been shown that properly scaled crystal-field parameters deduced in Ref. 17 allow the description of all the published crystal-field data for the stannate and titanate series.[18] In this Rapid Communication matrix elements will be computed using these latter results.

An extremely low-energy excitation has been detected by inelastic neutron scattering for the two systems.[17] The detected excitation may indicate a splitting of the ground-state doublet. However, it was only observed at relatively large wave vectors. It was also argued that the excitation may not be related to the crystal distortion: nearest-neighbor short-range magnetic correlations among spins could split the ground-state doublet, in particular, for $Tb_2Sn_2O_7$.[17,19] In addition, inelastic neutron data recorded under high field for $Tb_2Ti_2O_7$ were analyzed assuming a splitting of the ground-state doublet in zero field due to a tetragonal distortion.[20] However, it is known that the ground state of the compound is field dependent.[21,22]

As shown by the work on the spin-ice $Dy_2Ti_2O_7$,[23] a careful measurement of the magnetic entropy of a system in zero field is the experimental technique of choice for establishing beyond any doubt its number of magnetic degrees of freedom at low temperature. Here we report measurements of the magnetic entropy variation for $Tb_2Sn_2O_7$ and $Tb_2Ti_2O_7$ which show nicely that the Tb^{3+} ion crystal-field ground state is a singlet in both cases. The previously introduced tetragonal distortion provides a simple interpretation of the entropy data for the titanate. On the other hand, for the stannate a molecular field has also to be taken onto account.

In fact, the low-temperature magnetic entropy variation per mole of Tb for $Tb_2Ti_2O_7$ has already been measured and found to be larger than $R\ln(2)$, where R is the ideal-gas constant.[13,24,25] This has been taken as a support of the

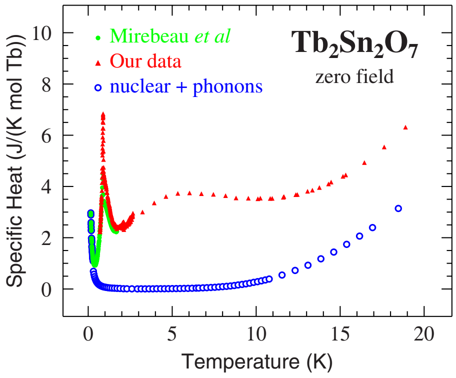

FIG. 1. (Color online) Total specific heat C_{tot} versus temperature measured for a powder sample of $Tb_2Sn_2O_7$. The contribution C_{lat} from the phonons, i.e., the lattice, is deduced from measurements on the isostructural diamagnetic compound $Lu_2Sn_2O_7$ using a scaling law as explained in the main text. The nuclear contribution C_{nuc} is directly taken from the estimation of Mirebeau *et al.* (Ref. 4).

doublet-doublet picture. At close look, this seems surprising. Let us assume two doublets separated by an energy $k_B\Delta$. If the temperature is such that $T \gg \Delta$, the entropy is R ln(4) per mole. In the other extreme case, that is when $T \ll \Delta$, it is equal to R ln(2). Since a thermodynamic measurement gives only access to the entropy variation, we compute R ln(2) for the variation between the low- and high-temperature limits. Hence, the inference of a crystal-field ground-state doublet drawn from the thermodynamic data of Refs. 13, 24, and 25 is incorrect. Note that it is more convenient to analyze the temperature dependence of the entropy than the one of the specific heat itself because the latter method would request to describe in detail the signal associated to a phase transition, for instance.

A powder sample of $Tb_2Sn_2O_7$ was synthesized using a conventional powder technique, as explained in Ref. 5. No single crystal is available. For $Tb_2Ti_2O_7$ polycrystalline rods were prepared. In order to test the robustness of the results, three single crystals were then grown by the traveling solvent floating zone technique. The same technique was used previously for $Gd_2Ti_2O_7$.[26] Zero-field specific heat were recorded above 0.4 K using a Quantum Design physical property measurement system. At lower temperatures, the measurements were performed in a ^{3}He-^{4}He dilution refrigerator using a dynamic adiabatic technique. In the experimental plots to be shown below, the entropy variation will be normalized to get consistency with the crystal-field level scheme.

We present the thermal dependence of the total specific heat $C_{\text{tot}}(T)$ of $Tb_2Sn_2O_7$ in Fig. 1, as well as the sum of the nuclear $C_{\text{nuc}}(T)$ and lattice $C_{\text{lat}}(T)$ contributions. The latter is deduced from the measured specific heat of the diamagnetic compound $Lu_2Sn_2O_7$, i.e., $C_{\text{Lu}}(T)$, using the scaling law $C_{\text{lat}}(T)=C_{\text{Lu}}(T/r)$, where r is the ratio of the Debye temperatures for $Tb_2Sn_2O_7$ and $Lu_2Sn_2O_7$.[27]

In Fig. 2 we display the magnetic specific heat of $Tb_2Sn_2O_7$ versus temperature: $C_{\text{mag}}(T)=C_{\text{tot}}(T)-[C_{\text{lat}}(T)+C_{\text{nuc}}(T)]$. We also present the associated magnetic entropy variation.

We consider a crystal-field level scheme consisting of a nondegenerate ground state, followed by an excited single level at energy $k_B\delta$ above the ground state and a doublet at a thermal energy of $\Delta=17$ K. This latter value corresponds to the $Tb_2Sn_2O_7$ case.[17,18] The predictions of this model are shown in Fig. 3 for selected values of δ. As expected, as soon as the ground-state doublet is split the total entropy variation exceeds R ln(2). The dotted line in Fig. 2 models S_{mag} with a splitting δ=2.5(2) K. Note, in addition, that our data are consistent with the absence of residual entropy at low temperature. Inelastic neutron scattering detects at 1.6 K a splitting of 1.5–1.9 K,[17] somewhat smaller than the one found here. However at 0.04 K, i.e., below T_c, the splitting measured by neutron is about 3 K.[11] Our result lies between these two values and we shall further discuss it below.

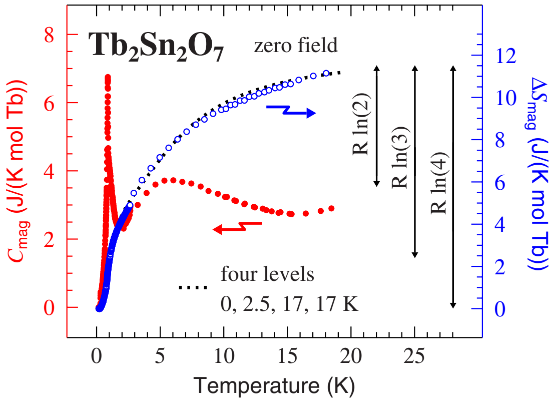

FIG. 2. (Color online) Magnetic specific heat (left scale) and magnetic entropy variation (right scale) versus temperature measured in zero field for $Tb_2Sn_2O_7$. The dotted line is the result from a fit with the crystal-field level scheme indicated in the figure.

Using the same methodology, we have estimated ΔS_{mag} for $Tb_2Ti_2O_7$; see Fig. 4. A detailed report is in preparation. Slight differences are visible in $\Delta S_{\text{mag}}(T)$ for the three crystals we have investigated. Nonetheless, while additional measurements are required below 0.4 K to determine

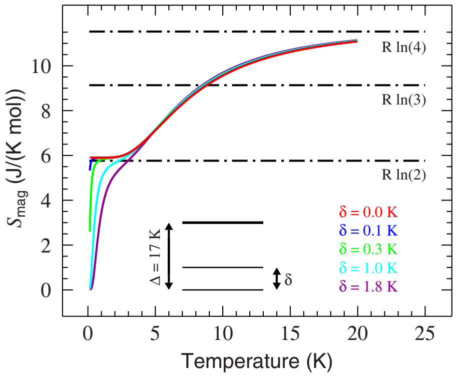

FIG. 3. (Color online) Temperature dependence of the absolute entropy S_{mag} associated with four crystal-field levels: a nondegenerate ground state, an excited single level located at δ, and a doublet at 17 K. The curves are drawn for five values of δ (0.0, 0.1, 0.3, 1.0, and 1.8 K). The crystal-field energies are given in temperature scale. S_{mag} is plotted for temperatures ranging from 0.13 to 20 K. This covers the whole temperature range probed by our measurements.

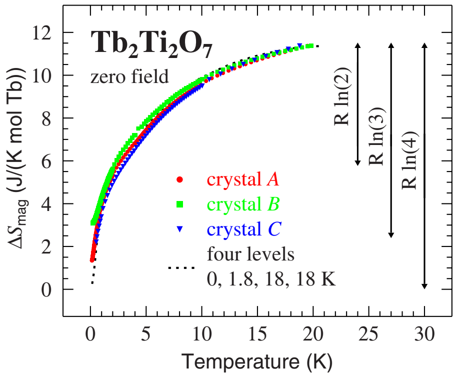

FIG. 4. (Color online) Magnetic entropy variation versus temperature measured in zero field for three differently prepared crystals of $Tb_2Ti_2O_7$ (Ref. 18). The dotted line is the result of a fit with the crystal-field level scheme indicated in the figure.

whether there is a residual entropy (in particular, for sample C), it is obvious that the measured entropy variation is far larger than $R\ln(2)$, indicating that the ground state is also nondegenerate. The dotted line in Fig. 4 arises from the fit of the ΔS_{mag} data with $\delta = 1.8(2)$ K, consistent with the results of neutron measurements at 1.9 K.[17]

We have checked for both systems that the crystal-field energy levels located at a thermal energy larger than 20 K (first level is a singlet slightly above 123 K) do not contribute significantly to ΔS_{mag} up to 20 K. A possible small splitting of the first excited doublet does not have as well a noticeable effect on the value of δ extracted from the fit to the ΔS_{mag} data.

Our deduction that the crystal-field ground state is a singlet for the two compounds is independent of the model used to analyze the entropy data. This is the key result of this Rapid Communication. The values of the splitting could be slightly influenced by the dispersion of the first excited state. This has been neglected.

Let us focus now on the interpretation of the splitting δ deduced from the entropy variation data. For this purpose, we shall use perturbation theory for two degenerate levels, see, for example, Ref. 28, which relates the perturbation Hamiltonian $\mathcal{H}_{per}$ to the splitting induced by the perturbation,

$$k_B\delta = [(\langle + |\mathcal{H}_{per}| + \rangle - \langle - |\mathcal{H}_{per}| - \rangle)^2 + 4|\langle - |\mathcal{H}_{per}| + \rangle|^2]^{1/2}. \tag{1}$$

The doublet wave functions which characterize the unperturbed Hamiltonian are denoted as $|\pm\rangle$. As shown elsewhere for the trigonal symmetry (D_{3d} symmetry),[17] the ground-state wave functions for the stannate are written as $|\pm\rangle = 0.922|\pm 5\rangle \mp 0.243|\pm 2\rangle + 0.016|\mp 1\rangle \mp 0.301|\mp 4\rangle$. For the titanate we have $|\pm\rangle = -0.958|\pm 4\rangle \pm 0.129|\pm 1\rangle - 0.121|\mp 2\rangle \mp 0.226|\mp 5\rangle$.

We first consider $Tb_2Ti_2O_7$ since it is the simplest case. To account for the reduction in the local symmetry at the rare earth, we write $\mathcal{H}_{per} = \mathcal{H}_t$, where $\mathcal{H}_t = -\mathcal{D}_t J_Z^2$ with $\mathcal{D}_t > 0$. This parameter measures the scale of the crystal-field distortion from cubic symmetry and J_Z is the projection of the Tb^{3+} ion total angular momentum along the Z axis which is taken to be parallel to the [001] crystal axis. Projecting out $\mathcal{H}_t$ in the reference frame in which the trigonal symmetry crystal-field Hamiltonian was written, i.e., in the $\{x, y, z\}$ frame for which the y and z axes are parallel to the $[1\bar{1}0]$ and [111] cubic axes, respectively, and consequently Z is contained in the xOz plane,

$$\mathcal{H}_t = -\mathcal{D}_t\left[\frac{2}{3}J_x^2 + \frac{1}{3}J_z^2 + \frac{\sqrt{2}}{3}(J_xJ_z + J_zJ_x)\right]. \tag{2}$$

Since $\langle + |\mathcal{H}_t| + \rangle = \langle - |\mathcal{H}_t| - \rangle$, from Eq. (1) we compute $k_B\delta = 2|\langle - |\mathcal{H}_t| + \rangle| = 6.59\mathcal{D}_t$. Using the measured δ value, we estimate $\mathcal{D}_t/k_B = 0.27(3)$ K. Interestingly, using inelastic neutron scattering under high field, $\mathcal{D}_t/k_B = 0.19$ K has been inferred.[20] However, as already noted, the ground state is field dependent. Our result is derived from zero-field measurements. The crystal-field ground-state wave function is simply $|\phi_g\rangle = (|+\rangle - |-\rangle)/\sqrt{2}$, and therefore the state is not magnetic. It is the superexchange interactions between the Tb^{3+} ions which induce a finite magnetic moment.

Let us now focus our attention to $Tb_2Sn_2O_7$. In addition to the tetragonal distortion, we need to account for magnetic order below T_c. This will be done in the molecular-field approximation. This means that we write $\mathcal{H}_{per} = \mathcal{H}_t + \mathcal{H}_m$. For simplicity, we shall assume the molecular field to be parallel to the local Tb^{3+} magnetic moment, i.e., at an angle θ_m out of the [111] direction. We write $\mathcal{H}_m = g_J\mu_B B_m(\cos\theta_m J_z - \sin\theta_m J_x)$, where $\theta_m \simeq 13.7°$, a mean value of the values given in Refs. 4 and 5, and B_m is the molecular field. We compute

$$\langle + |\mathcal{H}_{per}| + \rangle - \langle - |\mathcal{H}_{per}| - \rangle = \langle + |\mathcal{H}_m| + \rangle - \langle - |\mathcal{H}_m| - \rangle$$

$$= 7.78 g_J\mu_B B_m \tag{3}$$

and

$$|\langle - |\mathcal{H}_{per}| + \rangle| = |\langle - |\mathcal{H}_t| + \rangle| = 4.69\mathcal{D}_t. \tag{4}$$

We can now rewrite Eq. (1), inserting the numerical values just obtained and noting that $\delta^2 = 6.25(1.00)$ K^2,

$$\delta^2 = (7.78)^2\left(\frac{g_J\mu_B B_m}{k_B}\right)^2 + 4(4.69)^2\left(\frac{\mathcal{D}_t}{k_B}\right)^2. \tag{5}$$

It is interesting to evaluate the first term on the right-hand side of this equation. We use the simple result $g_J\mu_B B_m = 3k_B T_c/(J+1)$ (Ref. 29) and since $J = 6$ and $T_c = 0.88(1)$ K, we compute $g_J\mu_B B_m/k_B = 0.38$ K. The first term on the right-hand side of Eq. (5) is then equal to 8.7 K^2. Therefore Eq. (5) cannot be fulfilled unless B_m is somewhat reduced compared to our estimate. It is further reduced because the trigonal doublet is known to be split at 1.6 K,[17] i.e., $\mathcal{D}_t > 0$.

To proceed further, we write the ground-state wave function as $|\phi_g\rangle = -\sin(\beta/2)|+\rangle + \cos(\beta/2)|-\rangle$ with[28]

$$\tan\beta = \frac{2|\langle - |\mathcal{H}_{per}| + \rangle|}{\langle + |\mathcal{H}_{per}| + \rangle - \langle - |\mathcal{H}_{per}| - \rangle} = 1.21\frac{\mathcal{D}_t}{g_J\mu_B B_m}. \tag{6}$$

The ground-state moment is equal to $g_J\mu_B\langle + |J_z| + \rangle\cos\beta = 6.0 \times \mu_B\cos\beta$. Using its measured value of

5.65(25) μ_B,[4,5] we deduce $\beta=20(7)°$. Hence, with the help of Eq. (6), we compute

$$\frac{\mathcal{D}_t}{g_J \mu_B B_m} = 0.3(1). \tag{7}$$

In addition, we find $|\phi_g\rangle \simeq |-5\rangle$ for any of these values of β.

Combining Eqs. (5) and (7), we compute $\mathcal{D}_t/k_B = 0.09(5)$ K and $g_J\mu_B B_m/k_B = 0.30(4)$ K. B_m is indeed reduced compared to the earlier estimate. However, further discussion requires first a better theoretical estimate of the exchange field.

In summary, the analysis of the variation in the magnetic entropy shows that the crystal-field ground state is a singlet for $Tb_2Sn_2O_7$ and $Tb_2Ti_2O_7$. Our discussion of the crystal-field splitting supports the view that $Tb_2Ti_2O_7$ has a tetragonal crystal structure at low temperature. Further interpretation of $Tb_2Sn_2O_7$ requires more theoretical and experimental inputs.

We thank V. Glazkov and S. S. Sosin for their help during the specific-heat measurements and their comments on the manuscript and P. Bonville for drawing our attention to the proper axes which must be used for the expression of the crystal electric field Hamiltonian.

---

[1] A. P. Ramirez, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, New York, 2001), Vol. 13.

[2] J. S. Gardner *et al.*, Rev. Mod. Phys. **82**, 53 (2010).

[3] J. P. C. Ruff, B. D. Gaulin, J. P. Castellan, K. C. Rule, J. P. Clancy, J. Rodriguez, and H. A. Dabkowska, Phys. Rev. Lett. **99**, 237202 (2007).

[4] I. Mirebeau, A. Apetrei, J. Rodriguez-Carvajal, P. Bonville, A. Forget, D. Colson, V. Glazkov, J. P. Sanchez, O. Isnard, and E. Suard, Phys. Rev. Lett. **94**, 246402 (2005).

[5] P. Dalmas de Réotier *et al.*, Phys. Rev. Lett. **96**, 127202 (2006).

[6] J. Champion *et al.*, Europhys. Lett. **57**, 93 (2002).

[7] Y. Chapuis *et al.*, J. Phys.: Condens. Matter **19**, 446206 (2007).

[8] K. C. Rule *et al.*, Phys. Rev. B **76**, 212405 (2007).

[9] S. R. Giblin, J. D. M. Champion, H. D. Zhou, C. R. Wiebe, J. S. Gardner, I. Terry, S. Calder, T. Fennell, and S. T. Bramwell, Phys. Rev. Lett. **101**, 237201 (2008).

[10] I. Mirebeau, H. Mutka, P. Bonville, A. Apetrei, and A. Forget, Phys. Rev. B **78**, 174416 (2008).

[11] K. C. Rule *et al.*, J. Phys.: Condens. Matter **21**, 486005 (2009).

[12] J. S. Gardner *et al.*, Phys. Rev. Lett. **82**, 1012 (1999).

[13] M. J. P. Gingras, B. C. den Hertog, M. Faucher, J. S. Gardner, S. R. Dunsiger, L. J. Chang, B. D. Gaulin, N. P. Raju, and J. E. Greedan, Phys. Rev. B **62**, 6496 (2000).

[14] B. C. den Hertog and M. J. P. Gingras, Phys. Rev. Lett. **84**, 3430 (2000).

[15] Y.-J. Kao, M. Enjalran, A. Del Maestro, H. R. Molavian, and M. J. P. Gingras, Phys. Rev. B **68**, 172407 (2003).

[16] M. Enjalran and M. J. P. Gingras, Phys. Rev. B **70**, 174426 (2004).

[17] I. Mirebeau, P. Bonville, and M. Hennion, Phys. Rev. B **76**, 184436 (2007).

[18] Y. Chapuis, Ph.D. thesis, Université Joseph Fourier, 2009.

[19] Y. M. Jana, O. Sakai, R. Higashinaka, H. Fukazawa, Y. Maeno, P. Dasgupta, and D. Ghosh, Phys. Rev. B **68**, 174413 (2003).

[20] K. C. Rule and P. Bonville, J. Phys.: Conf. Ser. **145**, 012027 (2009).

[21] K. C. Rule *et al.*, Phys. Rev. Lett. **96**, 177201 (2006).

[22] H. Cao, A. Gukasov, I. Mirebeau, P. Bonville, and G. Dhalenne, Phys. Rev. Lett. **101**, 196402 (2008).

[23] A. P. Ramirez *et al.*, Nature (London) **399**, 333 (1999).

[24] N. Hamaguchi, T. Matsushita, N. Wada, Y. Yasui, and M. Sato, Phys. Rev. B **69**, 132413 (2004).

[25] X. Ke, D. V. West, R. J. Cava, and P. Schiffer, Phys. Rev. B **80**, 144426 (2009).

[26] A. Yaouanc, P. Dalmas de Réotier, V. Glazkov, C. Marin, P. Bonville, J. A. Hodges, P. C. M. Gubbens, S. Sakarya, and C. Baines, Phys. Rev. Lett. **95**, 047203 (2005).

[27] V. Hardy, S. Lambert, M. R. Lees, and D. McK. Paul, Phys. Rev. B **68**, 014424 (2003).

[28] A. S. Davydov, *Quantum Mechanics* (Pergamon Press, Oxford, 1965).

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