

CdEr₂Se₄: A New Erbium Spin Ice System in a Spinel Structure

J. Lago,^{1,*} I. Živković,^{2,3} B. Z. Malkin,⁴ J. Rodriguez Fernandez,⁵ P. Ghigna,⁶ P. Dalmas de Réotier,⁷
A. Yaouanc,⁷ and T. Rojo^{1,†}

¹*Department of Inorganic Chemistry, Univ. del Pas Vasco, 48080 Bilbao, Spain*

²*Institute of Physics, Post Office Box 304, HR-10 000 Zagreb, Croatia*

³*Laboratory for Quantum Magnetism, Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland*

⁴*Kazan State University, 420008 Kazan, Russia*

⁵*Departamento CITIMAC, Fac. Ciencias, Univ. de Cantabria, 39005 Santander, Spain*

⁶*Dipartimento di Chimica Fisica M. Rolla, Universit di Pavia, V.le Taramelli 16, I-27100 Pavia, Italy*

⁷*Institut Nanosciences et Cryognie, Commissariat à l'énergie atomique/Direction des sciences de la matière, 38054 Grenoble, France*
(Received 4 September 2009; revised manuscript received 19 May 2010; published 15 June 2010)

Here we present a detailed study of the spinel CdEr₂Se₄ and show it to be a new instance of spin ice, the first one in an erbium material and the first one in a spinel. Definitive experimental evidence comes from the temperature dependence of the magnetic entropy, which shows an excellent agreement with the predicted behavior for a spin ice state. Crystal field calculations demonstrate that the change in the local environment from that of the titanates completely alters the rare-earth anisotropy giving rise, in the case of Er³⁺, to the required Ising anisotropy, when Er₂Ti₂O₇ behaves as an XY antiferromagnet. This finding opens up the possibility of new exotic ground states within the CdR₂Se₄ and CdR₂Se₄ families.

DOI: 10.1103/PhysRevLett.104.247203

PACS numbers: 75.50.Kj, 75.10.Dg, 75.40.Gb, 76.75.+i

The rare-earth (*R*) pyrochlores (*R*₂*M*₂O₇) have been found to display a rich variety of exotic magnetic behavior, a direct consequence of the impossibility, imposed by the geometry of the lattice, of finding a classical ground state by minimizing all pairwise exchange interactions. Theoretically, a system of antiferromagnetically coupled Heisenberg spins in a pyrochlore lattice should remain in a collective paramagnetic state as $T \rightarrow 0$ [1]. In practice, the macroscopic degeneracy can be lifted by lesser contributions to the spin Hamiltonian. In particular, the crystalline electric field (CEF) anisotropy term can dramatically alter the nature of the ground state, making it quasi specific to each rare-earth species. Thus, in the titanate series R₂Ti₂O₇, the observed ground states in a zero applied field include nonconventional AFM states for the dipole-Heisenberg (*R* = Gd [2]) and the XY (*R* = Er [3,4]) systems, a spin liquid state (*R* = Tb [5], half-way between Heisenberg and Ising), spin ice for the Ising Ho and Dy systems [6,7], and a dynamic disordered state (for Yb, with planar anisotropy [8–10]). The CEF anisotropy thus appears as the main cause for the rich phenomenology observed in the frustrated pyrochlores. But, at the same time, it constitutes a major limiting factor regarding the number of systems displaying a particular behavior as it effectively makes each *R* ion the only one of its kind.

Normal spinels AR₂X₄ constitute an alternative realm in which to look for exotic magnetism as the *R* ions occupying the octahedral sites in the structure form an identical pyrochlore sublattice to that in the titanates. In fact, work by Lau and co-workers on the series CdR₂X₄ (*X* = S, Se) [11] has shown clear indications of geometrical frustration in these materials. Interestingly, the local environment of the rare-earth in the spinels is different to that in the

pyrochlores. This alters the CEF level scheme of the *R* ion and can potentially lead to completely different behavior for the same magnetic species in the two series despite the analogy in the overall geometry of the magnetic sublattice.

In this Letter we show this to be the case. We present a detailed study of the cubic spinel CdEr₂Se₄ (*Fd* $\bar{3}m$) and show that the change in the coordination environment of the Er³⁺ ions from that of the pyrochlores Er₂*M*₂O₇ (*M* = Ti, Sn) causes a change of the CEF anisotropy from planar to Ising, leading to spin ice behavior at low temperatures. To our knowledge, this is the first report of a spin ice system in an erbium compound.

Polycrystalline samples of CdEr₂Se₄ [12] were synthesized by solid state reaction in evacuated sealed quartz tubes at 800 °C. dc-susceptibility measurements were performed with a Quantum Design SQUID. ac-susceptibility data were collected in a dilution refrigerator with an ac field of 33 mOe in the frequency range from 4 to 10 kHz. Specific heat measurements were made with a PPMS from Quantum Design. Finally, muon spin relaxation (μ SR) measurements were carried out at the $S\mu$ S facility at PSI, Switzerland.

In the spin ice compounds known to date—the Ho and Dy pyrochlores—spin ice behavior results from the combination of two factors: effective ferromagnetic coupling and strong uniaxial anisotropy arising from the *D*_{3d} local field that effectively locks the spins along the trigonal $\langle 111 \rangle$ axes and yields the so-called “2 in 2 out” spin state [13,14]. Experimentally, in the absence of a detailed neutron scattering study of magnetic correlations, the definitive proof of its existence is only provided by specific heat measurements of the zero-point entropy, which comes to

be equal to $(R/2) \ln(3/2) = 1.68 \text{ J mol}^{-1} \text{ K}^{-1}$, the residual entropy associated with proton disorder in water ice [15] and, in spin ice, with the extensive degeneracy of the frozen state associated with the ice-rules [14].

Figure 1 shows the magnetic contribution (C_{MAG}/T) to the specific heat for CdEr_2Se_4 , obtained after subtracting the phonon and CEF contributions from the experimental data [the best fit is obtained with a Debye temperature $\theta_D = 167.84(39) \text{ K}$ and the first excited CEF level at $46.96(29) \text{ K}$ above the ground state; see inset of Fig. 1]. C_{MAG} shows no sign of long-range order but a broad peak centered at $\sim 0.95 \text{ K}$ with a rapid fall to zero in the low-temperature side, associated in the titanates with the freezing of the R^{3+} moments in the spin ice state [7]. Most importantly, the entropy recovered by integration of C_{MAG}/T between 0.3 and 20 K is about $4.2 \text{ J mol}^{-1} \text{ K}^{-1}$, which differs from $S = R \ln 2$ expected for the noninteracting Ising spins by $1.56 \text{ J mol}^{-1} \text{ K}^{-1}$, a value close to the

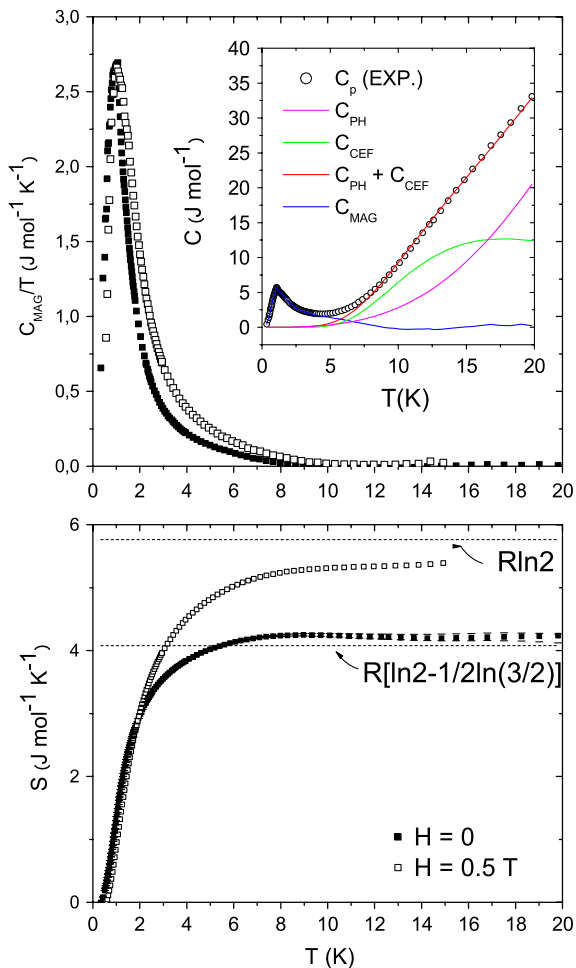


FIG. 1 (color online). Magnetic specific heat and corresponding integrated entropy (per mole of Er) for CdEr_2Se_4 , showing a reasonable agreement with the predicted S value for the degenerate 2 in 2 out spin ice state, $R \ln 2 - (R/2) \ln(3/2)$. The error in $S(T)$ has been estimated from the error bars of the parameters fitted in the calculation of C_{MAG} . Inset: phonon, CEF, and magnetic contributions to $C(T)$.

zero-point entropy of a spin ice ground state. The recovery of the zero-point entropy on application of a magnetic field [the integrated entropy S up to 13 K in a field of 0.5 T amounts to more than 90% of the total spin entropy, compared to 76% in zero field (Fig. 3 bottom)], is also consistent with spin ice behavior, as has been shown for $\text{Dy}_2\text{Ti}_2\text{O}_7$ [7]. Note that although the integration of C_{MAG}/T has been made for $T \geq 0.3 \text{ K}$, the absence of any ordering feature in the $\text{ac-}\chi$ below the freezing temperature, T_p , (see below) completely rules out a large discrepancy in S from our calculated value. Note also that extrapolating the experimental curve below 0.3 K using a Schottky function adds only $0.025 \text{ J mol}^{-1} \text{ K}^{-1}$ to the total entropy, 2 orders of magnitude smaller than the quoted value of $4.2 \text{ J mol}^{-1} \text{ K}^{-1}$.

Figure 1 therefore constitutes irrefutable experimental evidence of the spin ice behavior in CdEr_2Se_4 . The task is now to establish that the system satisfies the anisotropy and exchange requirements for its existence. In CdEr_2Se_4 , the first indication of strong anisotropy of the Er^{3+} ions comes from the field dependence of the dc magnetization (Fig. 2). On cooling, the magnetization approaches saturation at a value close to half of the free ion maximum $\mu = 9\mu_B$, indicative of strong anisotropy and, *a priori*, reminiscent of the behavior in spin ice [16]. However, a half-magnetization plateau does not uniquely support $\langle 111 \rangle$ uniaxial anisotropy as it is also found in $\text{Er}_2\text{Ti}_2\text{O}_7$ [16] with planar anisotropy. Further evidence is thus needed to prove this point and it comes from a calculation of the effect the change in the local coordination environment of the Er^{3+} ions has on the single-ion CEF levels. In fact, a close look at the spinel and pyrochlore structures of CdEr_2Se_4 and $\text{Er}_2\text{Ti}_2\text{O}_7$, respectively, shows that, in the titanate, each R^{3+} ion is surrounded by eight oxygens forming a distorted cube with two shortened R-O distances lying along the $\langle 111 \rangle$ axes. In the spinel structure, on the other hand, each R^{3+} has six nearest-neighbor Se^{2-} ions in an almost perfect octahedral environment. None of the Er-Se bonds points along the threefold axes. We have calcu-

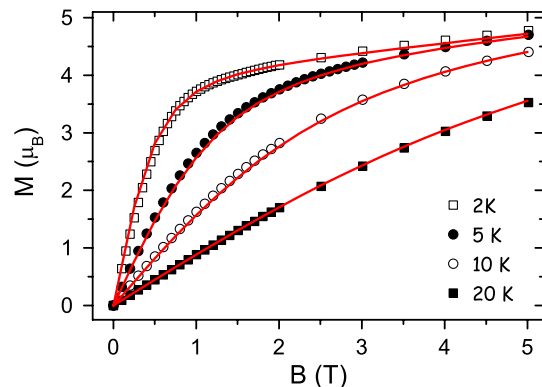


FIG. 2 (color online). Experimental (symbols) and calculated (solid lines) field dependence of the magnetization of a polycrystalline sample of CdEr_2Se_4 .

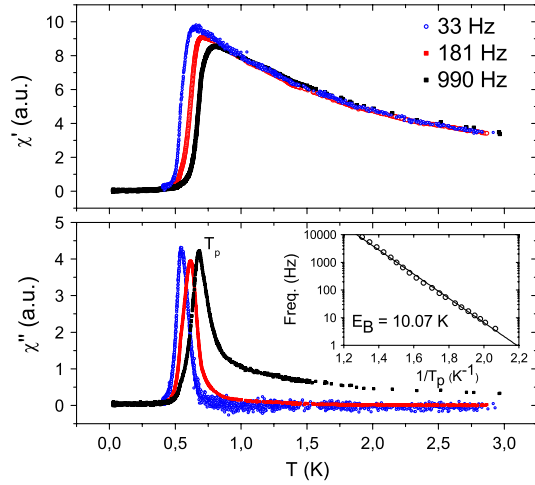


FIG. 3 (color online). Temperature dependence of the real and imaginary parts of the ac susceptibility at different frequencies. Inset: frequency dependence of the freezing temperature T_p . The line is a fit to a thermally activated behavior yielding an energy barrier of approximately 10 K.

lated the energy levels and corresponding wave functions of the Er^{3+} ions in the crystal field generated at the R sites in the spinel structure and the results show that it gives rise to completely different behavior to that of the pyrochlore, with the R^{3+} magnetic moments lying along the trigonal axes as in the Dy and Ho pyrochlores (in contrast, to the XY behavior in the Er titanate [4]). The effective parametric CEF Hamiltonian used in the calculation has the form

$$H = B_0^2 C_0^2 + B_0^4 C_0^4 + B_3^4 (C_3^4 - C_{-3}^4) + B_0^6 C_0^6 + B_3^6 (C_3^6 - C_{-3}^6) + B_6^6 (C_6^6 + C_{-6}^6), \quad (1)$$

where B_n^m are the CEF parameters and C_n^m the spherical tensor operators of rank m . Initial values of the CEF parameters were calculated within the framework of the exchange-charge model (ECM) [17] and then varied to fit the experimental field dependence of the magnetization at low temperature ($T = 5$ K). The best fit was obtained with $B_0^2 = -164.8$, $B_0^4 = -560.8$, $B_3^4 = -667.3$, $B_0^6 = 92.8$, $B_3^6 = -142$ and $B_6^6 = 79$ (cm^{-1}). Note that despite the almost perfect octahedral geometry of the first coordination shell of the Er^{3+} ions (six Se^{2-} ions at the distance 0.2866 nm), the CEF contains a strong axial quadrupolar component due to the Coulomb field of distant ions. The change of signs of the B_0^2 and B_0^4 parameters as compared to the corresponding CEF parameters in titanates [18] is the main reason for different magnetic properties of spinels and pyrochlores containing the same rare-earth ions. The energies of the ground multiplet sublevels of Er^{3+} in CdEr_2Se_4 resulting from the diagonalization of the Hamiltonian (1) equal 0, 29.4, 58.2, 61.7, 70.2, 175, 188, 192 cm^{-1} . The calculated gap to the first excited level (42.6 K) is thus not far from the value derived from the analysis of the specific heat data, 47 K. The wave functions of the ground state Kramers doublet are $|\pm\rangle =$

$0.8792|\pm 15/2\rangle \mp 0.4418|\pm 9/2\rangle + 0.1571|\pm 3/2\rangle \pm 0.0843|\mp 3/2\rangle$, where $|J_z\rangle = |^4I_{15/2}, J_z\rangle$ are the eigenfunctions of the z component of the angular momentum with z being the easy magnetization axis $\langle 111 \rangle$. The values of the g tensor in the ground state are $g_{xx} = g_{yy} = 0$ and $g_{zz} = 16.05$, clearly demonstrating the strong uniaxial anisotropy required for spin ice behavior.

The measured magnetic properties of CdEr_2Se_4 can be correctly modeled using the CEF parameters above. Thus, for instance, the field dependence of the magnetic moment at different temperatures is well matched by the theoretical values (solid lines in Fig. 2), calculated as the average of the magnetic moments of noninteracting Er^{3+} ions induced by the fields along the symmetry axes of the cubic crystal. A similar quality fit is obtained for the temperature dependence of the susceptibility (not shown). Note that the calculation neglects both the weak exchange interactions between the Er^{3+} ions and the dipolar fields at the Er^{3+} . Also, the moments were calculated for a 100% direct spinel, i.e., no inversion between Er and Cd positions. Original work on this compound reported 7.5% inversion [12] but we were not able to detect any in our samples by x-ray diffraction.

The Weiss temperature $\theta_W = -1.25(63)$ K derived from the Curie-Weiss fit of the dc susceptibility (corrected for demagnetization assuming spherical geometry) of a polycrystalline sample at high temperatures ($T > 180$ K, not shown) indicates predominant antiferromagnetic exchange correlations. However, as for the spin ice pyrochlores [13], a detailed theoretical analysis of the dc susceptibility reveals a dominant role of dipole-dipole interactions, which are capable of inducing the effective ferromagnetic coupling between the nearest-neighbor Er^{3+} ions. From the measured Weiss temperature we obtained the nearest-neighbor exchange energy $J_{nn} = -0.15$ K, a value about an order of magnitude lower than the corresponding exchange energies in Ho and Dy titanates with remarkably shorter nearest-neighbor R-R distance ($r_{nn} \sim 0.357$ nm against 0.41 in CdEr_2Se_4). The nearest-neighbor dipolar interaction is $D_{nn} = (5/3)(g_{zz}\mu_B/2)^2/r_{nn}^3 = 0.97$ K, thus yielding a ratio $J_{nn}/D_{nn} = -0.155$. This value places CdEr_2Se_4 well inside the spin ice regime in the phase diagram of Ref. [13], where it corresponds to a point that matches well the temperature of the observed C_{MAG} maximum.

Spin dynamics have been studied by means of ac susceptibility and muon spin relaxation (μSR) and, although preliminary, the picture that emerges is consistent with the spin ice nature of the system. In the spin ice titanates, the dynamic response is characterized by the existence of three regimes: an activated high temperature regime dominated by a single-ion Orbach-like [19] process involving the first excited CEF level at ~ 200 K, followed on cooling by a T -independent plateau ascribed to quantum tunnelling between the two Ising states in the ground-state doublet. Below 2–3 K there is a reentrance of a thermally

activated process which quenches at around 1 K. At this point the system freezes into a particular microstate of the ice-rules manifold. Yet, despite the freezing, spin dynamics can still be detected as $T \rightarrow 0$ in the μ SR time window for both Ho and Dy titanates [20,21]. Recently, the low-temperature dynamics in spin ice have been explained in terms of the creation and diffusion of topological defects that resemble magnetic monopoles (a pair of oppositely charged monopoles is created by the flip of a single spin leaving two adjacent tetrahedra with “3 in 1 out” and “3 out 1 in” configurations. The two monopoles can diffuse apart) [22–24]. In CdEr_2Se_4 the onset of the frozen spin ice regime is signaled by the peak in $\text{ac-}\chi''$ centered at around 0.6 K. Within the monopole context, this freezing should be interpreted as the quenching of the thermal energy required for the creation and diffusion of monopoles below T_p . Its frequency dependence (inset of Fig. 3) reflects the consequent thermally activated behavior of the spin correlation time τ and is analogous to the behavior in the titanates [25–29]. However, in contrast to these [30], it can be fit to an Arrhenius expression $f = f_0 \exp(-E_B/T_p)$ over the entire T -frequency range accessed by our measurements. The derived energy barrier ($E_B = 10$ K) is nonetheless much larger than predicted for the formation of a free defect ($2J_{\text{eff}}$ with $J_{\text{eff}} = D_{nn} + J_{nn} \simeq 0.80$ K), which can be explained as a result of the effect of the Coulomb interaction between the two oppositely charged defects on the creation and diffusion of the monopoles [23]. The observed behavior below T_p is also characteristic of spin ice, with the spin system appearing frozen in the susceptibility window whereas μ SR measurements (not shown) still reveal the persistence of spin dynamics down to mK temperatures. A tentative explanation to this conundrum has been proposed by Bramwell and co-workers for $\text{Dy}_2\text{Ti}_2\text{O}_7$ in terms again of the movement of magnetic monopoles [24] although these authors do not provide any explanation to the existence of monopole excitations in a temperature range in which $k_B T \ll 2J_{\text{eff}}$. In any case, other than confirming an analogous experimental behavior in the current system, our data do not allow us any further conclusion at the moment.

Summarizing, we have shown experimentally that CdEr_2Se_4 is a new spin ice system, the first one containing Er, which we corroborate with our CEF calculations. These show that the local environment is crucial in determining the ground state of the different members of the CdR_2Se_4 family. Thus, for Er it gives rise to Ising anisotropy and the observed spin ice behavior. Finally, our measurements indicate that spin dynamics in CdEr_2Se_4 are also consistent with the expected behavior for a spin ice.

The authors would like to acknowledge L. Jaubert for useful discussions as well as H. Luetkens and C. Baines for technical assistance during the μ SR measurements at PSI. Part of this work was financially supported by the Spanish Ministerio de Educación (projects MAT2007-66737-C02-01 and MAT2008-06542-C04).

*jorge.lago@ehu.es

†teo.rojo@ehu.es

- [1] J. Villain, *Z. Phys. B* **33**, 31 (1979).
- [2] J. R. Stewart, G. Ehlers, A. S. Wills, S. T. Bramwell, and J. S. Gardner, *J. Phys. Condens. Matter* **16**, L321 (2004).
- [3] H. W. J. Blöte, R. F. Wielinga, and W. J. Huiskamp, *Physica (Amsterdam)* **43**, 549 (1969).
- [4] J. D. M. Champion *et al.*, *Phys. Rev. B* **68**, 020401(R) (2003).
- [5] J. S. Gardner *et al.*, *Phys. Rev. Lett.* **82**, 1012 (1999).
- [6] M. J. Harris, S. T. Bramwell, D. F. McMorrow, T. Zeiske, and K. W. Godfrey, *Phys. Rev. Lett.* **79**, 2554 (1997).
- [7] A. P. Ramirez, A. Hayashi, R. J. Cava, R. Siddharthan, and B. S. Shastry, *Nature (London)* **399**, 333 (1999).
- [8] J. A. Hodges *et al.*, *Phys. Rev. Lett.* **88**, 077204 (2002).
- [9] J. S. Gardner, G. Ehlers, N. Rosov, R. W. Erwin, and C. Petrovic, *Phys. Rev. B* **70**, 180404(R) (2004).
- [10] H. B. Cao, A. Gukasov, I. Mirebeau, and P. Bonville, *J. Phys. Condens. Matter* **21**, 492202 (2009).
- [11] G. C. Lau, R. S. Freitas, B. G. Ueland, P. Schiffer, and R. J. Cava, *Phys. Rev. B* **72**, 054411 (2005).
- [12] H. Fujii, T. Okamoto, and T. Kamigaichi, *J. Phys. Soc. Jpn.* **32**, 1432 (1972).
- [13] B. C. den Hertog and M. J. P. Gingras, *Phys. Rev. Lett.* **84**, 3430 (2000).
- [14] S. T. Bramwell and M. J. P. Gingras, *Science* **294**, 1495 (2001).
- [15] L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).
- [16] S. T. Bramwell, M. N. Field, M. J. Harris, and I. P. Parkin, *J. Phys. Condens. Matter* **12**, 483 (2000).
- [17] B. Z. Malkin, in *Spectroscopy of Solids Containing Rare Earth Ions*, edited by A. A. Kaplyanskii and R. M. Macfarlane (North Holland, New York, 1987), Chap. 2, p. 13.
- [18] B. Z. Malkin, A. R. Zakirov, M. N. Popova, S. A. Klimin, E. P. Chukalina, E. Antic-Fidancev, P. Goldner, P. Aschehoug, and G. Dhalle, *Phys. Rev. B* **70**, 075112 (2004).
- [19] R. Orbach, *Proc. Phys. Soc. London* **77**, 821 (1961).
- [20] M. J. Harris, S. T. Bramwell, T. Zeiske, D. F. McMorrow, and P. J. C. King, *J. Magn. Magn. Mater.* **177–181**, 757 (1998).
- [21] J. Lago, S. J. Blundell, and C. Baines, *J. Phys. Condens. Matter* **19**, 326210 (2007).
- [22] C. Castelnuovo, R. Moessner, and S. L. Sondhi, *Nature (London)* **451**, 42 (2008).
- [23] L. D. C. Jaubert and P. C. W. Holdsworth, *Nature Phys.* **5**, 258 (2009).
- [24] S. T. Bramwell, S. R. Giblin, S. Calder, R. Aldus, D. Prabhakaran, and T. Fennell, *Nature (London)* **461**, 956 (2009).
- [25] A. Ryzkhin, *J. Exp. Theor. Phys.* **101**, 481 (2005).
- [26] K. Matsuhira, Y. Hinatsu, K. Tenya, and T. Sakakibara, *J. Phys. Condens. Matter* **12**, L649 (2000).
- [27] J. Snyder, J. S. Slusky, R. J. Cava, and P. Schiffer, *Nature (London)* **413**, 48 (2001).
- [28] K. Matsuhira, Y. Hinatsu, and T. Sakakibara, *J. Phys. Condens. Matter* **13**, L737 (2001).
- [29] K. Matsuhira, Y. Hinatsu, Y. Tenya, A. Hiroshi, and T. Sakakibara, *J. Phys. Soc. Jpn.* **71**, 1576 (2002).
- [30] J. Snyder, B. G. Ueland, J. S. Slusky, H. Karunadasa, R. J. Cava, and P. Schiffer, *Phys. Rev. B* **69**, 064414 (2004).