Mixing of magnetic states in a Cr_8 molecular ring

M. Affronte,[1] T. Guidi,[2] R. Caciuffo,[2] S. Carretta,[3] G. Amoretti,[3] J. Hinderer,[4] I. Sheikin,[4] A. G. M. Jansen,[4] A. A. Smith,[5] R. E. P. Winpenny,[5] J. van Slageren,[6] and D. Gatteschi[6]

[1]*INFM - S³ National Research Center on nanoStructures and bioSystems at Surfaces and Dipartimento di Fisica, Università di Modena e Reggio Emilia, via G. Campi 213/A, I-41100 Modena, Italy*

[2]*INFM and Dipartimento di Fisica ed Ingegneria dei Materiali, Università Politecnica delle Marche, via Brecce Bianche, I-60131 Ancona, Italy*

[3]*INFM and Dipartimento di Fisica, Università di Parma, v. Parco Area delle Scienze 7/A, I-43100 Parma, Italy*

[4]*GHMFL MPI-FKF and CNRS, BP 166, 25, Avenue des Martyrs, F-38042 Grenoble, France*

[5]*Department of Chemistry, University of Manchester, Oxford Road, Manchester M139PL, United Kingdom*

[6]*INSTM and Dipartimento di Chimica, Università di Firenze, Via della Lastruccia 3, I-50019 Sesto Fiorentino, Italy*

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Effects of mixing of magnetic states in a molecular Cr_8 ring were investigated by torque magnetometry and heat capacity measurements. Results are interpreted within the framework of the spin Hamiltonian approach allowing us to fit the pattern of energy levels derived by neutron spectroscopy. The torque signal gives evidence of mixing of states with the same parity while the Schottky anomaly vanishes at $B_{c1}=6.9$ T and $B_{c2}=14.0$ T, the fields at which the $S=|0,0\rangle$ state crosses $S=|1,-1\rangle$ and $S=|1,-1\rangle$ crosses $S=|2,-2\rangle$, respectively, showing no repulsion between states with different parity, in contrast to what was observed on ferric wheels.

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I. INTRODUCTION

Molecular rings are a subclass of molecular magnets. More specifically, they are collections of single-molecule antiferromagnets embedded—and perfectly oriented—within a crystalline structure. A family of ferric wheels, shortly named as Fe_6, Fe_{10}, Fe_{12}, and Fe_{18}, have been intensively studied in the last few years.[1–4] These molecular rings comprise an even number of Fe^{3+} spin ($s=5/2$) centers in a cyclic structure with a dominant antiferromagnetic coupling between the nearest neighbors and weaker axial anisotropic interactions. In zero field the ground state of the ring is a singlet while the series of characteristic excitations[5,6] are expected to merge to those of an infinite chain as the number of spin centers increases. Molecular rings have been also proposed as candidates for the observation of the quantum tunneling of the Néel vector through the anisotropy barrier,[7] although the conditions to be met in real samples are still matter of debate. Recently a new class of molecular Cr^{3+} ($s=3/2$) rings have been synthesized and characterized by magnetic and HF-EPR measurements[8] and inelastic neutron scattering (INS)[9] and they look suitable for observation of quantum phenomena. Specific investigations on possible perturbations with decoherence effects are, however, necessary and this was one motivation for the present work.

The essential spin Hamiltonian describing a magnetic ring is[9]

$$H=J\sum_i \mathbf{s}_i\cdot\mathbf{s}_{i+1}+\sum_i \mathbf{s}_i\cdot\mathbf{D}_i\cdot\mathbf{s}_i+\sum_{i>j}\mathbf{s}_i\cdot\mathbf{D}_{ij}\cdot\mathbf{s}_j+\mu_B\sum_i g_i\mathbf{B}\cdot\mathbf{s}_i, \quad (1)$$

where the first term is the dominant isotropic exchange interaction, whereas the second and third terms describe the anisotropic local crystal-field and the intracluster dipole-dipole interaction.[10] The intracluster dipole-dipole interaction $\mathbf{D}_{ij}$ can be evaluated within the point-dipole approximation.[11] The last one is the Zeeman term in which, according to the HF-EPR results,[8] isotropic g factors can be assumed. Concerning the local crystal field, it can be simply described as

$$\sum_i \mathbf{s}_i\cdot\mathbf{D}_i\cdot\mathbf{s}_i=D\sum_i\left[s_z^2(i)-\frac{1}{3}s_i(s_i+1)\right]+E\sum_i[s_x^2(i)-s_y^2(i)], \quad (2)$$

For an octanuclear Cr^{3+} ring the total dimension of the Hilbert space is 65536. We already showed how the S-mixing effects can be included in the calculation by using the two-step procedure described in Ref. 9 which exploits a technique developed in Ref. 12. Therefore, by applying the abovementioned procedure, the complete Hamiltonian (1) can be diagonalized in the reduced subspace spanned by the lowest eleven multiplets and by the lowest manifold with total spin $S=4$.[13] This method provided a very accurate description of the INS data by taking $J=1.46$ meV with $D=-0.029$ meV and $E=-0.004$ meV.[9] In the present work, the crystal-field parameter E has been assumed equal to zero, since its effect on the calculated quantities is negligible. The energy levels of Cr_8 are depicted in Fig. 1 as a function of an external magnetic field. In zero field the ground state is $S=0$ and when an external magnetic field is applied it progressively switches to $S=1$, $S=2$, etc., at corresponding critical values B_{cn}. The analysis of INS data proved that mixing of states belonging to different spin multiplets is

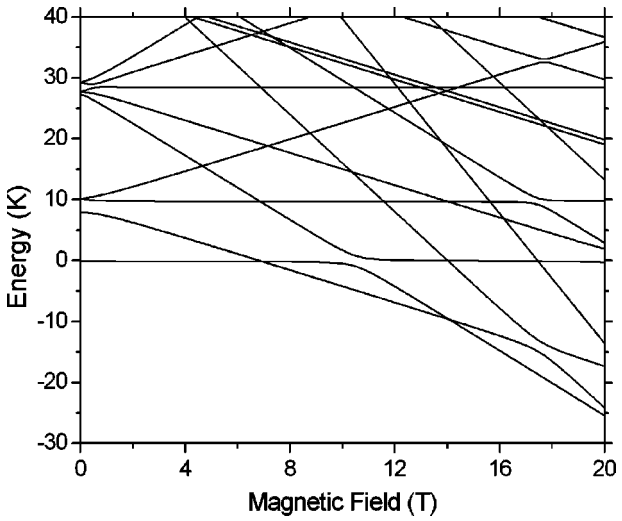

FIG. 1. Energy levels of Cr_8 calculated by the spin Hamiltonian (1) with parameters obtained by results of inelastic neutron scattering (Ref. 9). The angle between the magnetic field and the unique axis of the Cr_8 ring is $\theta = 65°$.

nonnegligible[9] and in this work we search further effects of the S mixing on the thermodynamic properties of Cr_8. Interestingly, the effects of mixing of states are enhanced at the level anticrossings. According to results of the diagonalization of Eq. (1), for instance, true level crossings are expected at B_{c1} and B_{c2}, when $S=|0,0\rangle$ crosses $S=|1,-1\rangle$ and when $S=|1,-1\rangle$ crosses $S=|2,-2\rangle$, respectively (see Fig. 1). However, calculations also show that the introduction of a Dzyaloshinsky-Moriya (DM) interaction term may lead to a significant mixing between the lowest states of different parity in Cr_8. In this eventuality, by applying a suitable magnetic field we would induce anticrossings between the two lowest lying levels instead of the crossings shown in Fig. 1. These anticrossings will cause significant modifications in the thermodynamic properties of the system. These effects are also expected for the ferric wheels.[14] In Ref. 15 we showed that combined techniques like torque magnetometry, NMR and heat capacity measurements, provide a powerful tool to study the level crossing mechanism in molecular clusters. Surprisingly we found a strong level repulsion at B_{c1} and B_{c2} in Fe_6:Li ferric wheel and different scenarios were proposed to explain those results.[15] One purpose of this work is to check this issue in a different cyclic system. Here we present results of high field torque magnetometry and heat capacity measurements on Cr_8 single crystals and we directly compare them with those obtained by the diagonalization of the spin Hamiltonian (1).

II. EXPERIMENTAL RESULTS

The synthesis and the characterization of $[Cr_8F_8Piv_{16}]$ (Piv=pivalic acid, trimethyl acetic acid) single crystals, Cr_8 in short, are reported in detail in Ref. 8. The heat capacity of small single crystals (1–2 mg) was first measured as a function of temperature (down to 1.9 K) by means of a Quantum Design PPMS-7T system. Combined torque and heat capacity measurements were then performed down to 0.7 K at the *Grenoble High Magnetic Field Laboratory* as described in Ref. 15.

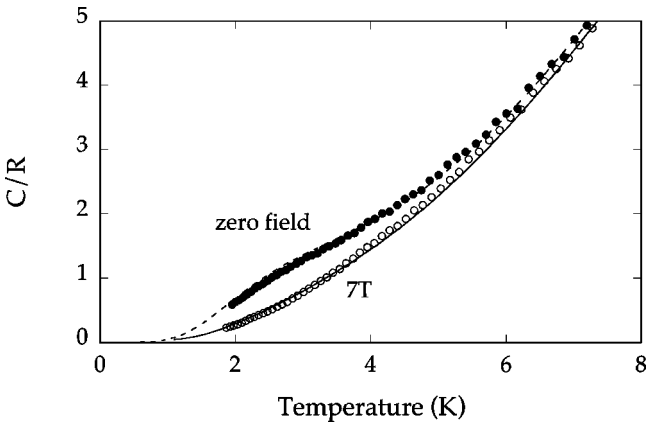

FIG. 2. Specific heat, normalized to the gas constant R, of a Cr_8 single crystal measured in zero field and with a 7 T magnetic field lying close to the ring plane. Lines are calculated as explained in the text.

In Fig. 2 the specific heat C of a Cr_8 single crystal is reported as a function of temperature. In zero field a Schottky anomaly with a maximum at ~ 2.9 K is easily visible and the $C(T)$ curve reproduces quite well data obtained on powders.[9] The $C(T)$ curve becomes flat as a 7 T magnetic field, lying close to the ring plane, is applied. This is a consequence of the fact that the energy separation between the $S=0$ and the $S=1$ state gets small and consequently the Schottky anomaly moves to very low temperatures with small contribution at 2 K. In Fig. 2 the theoretical curves $C=C_m+C_{latt}$ are also reported, where the magnetic contribution $C_m/R\beta^2$ ($\beta^{-1}=k_BT$) was calculated as

$$\frac{\Sigma_i \epsilon_i^2 \exp(-\beta\epsilon_i)\Sigma_i \exp(-\beta\epsilon_i) - [\Sigma_i \epsilon_i \exp(-\beta\epsilon_i)]^2}{[\Sigma_i \exp(-\beta\epsilon_i)]^2} \quad (3)$$

with energy levels ϵ_i obtained by the spin Hamiltonian (1) containing the microscopic parameters evaluated by inelastic neutron scattering.[9] The lattice contribution is well accounted by

$$C_{\text{latt}}/R = \frac{234 r T^3}{(\Theta_D + \delta T^2)^3}, \quad (4)$$

where r is the number of atoms per molecule (215 in our case), $\Theta_D = (154 \pm 10)$ K, and $\delta = 0.367$ K^{-1} are determined by least-squares best fitting procedure. It is worth stressing that the $C(T,H)$ data are well fitted by the theoretical curves with no need to change the spin Hamiltonian parameters. Since the $C(T,H)$ is rather smooth, the effects of S mixing are not relevant here.

Figure 3 shows the torque signal measured on a Cr_8 single crystal at $T=0.9$ K as a function of an external magnetic field. The two steps of the torque signal evidence the magnetic fields $B_{c1}=6.9$ T and $B_{c2}=14.0$ T at which the system switches from $S=|0,0\rangle$ to $S=|1,-1\rangle$ and from $S=|1,-1\rangle$ to $S=|2,-2\rangle$ state, respectively. The crossing fields B_{c1} and

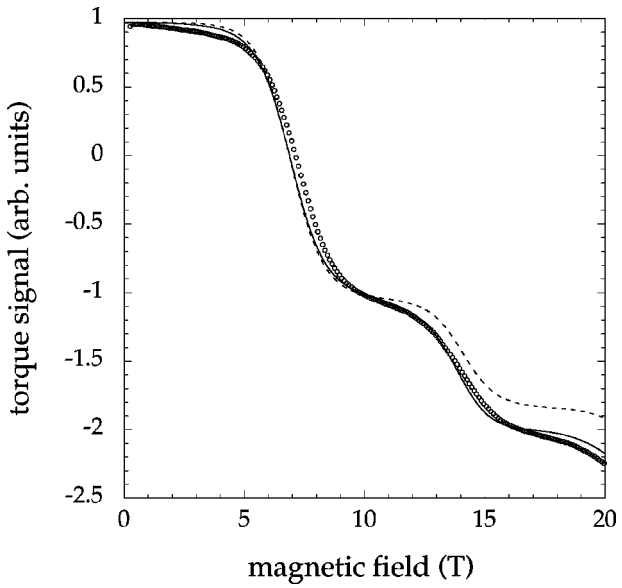

FIG. 3. Torque signal measured as a function of magnetic field at 0.9 K (circles). The magnetic field direction forms an angle $\theta \sim 65°$ with respect to the unique axis of the Cr_8 ring. Simulations are calculated as described in the text and one (solid line) includes S mixing, for the other one (broken line) S mixing is neglected.

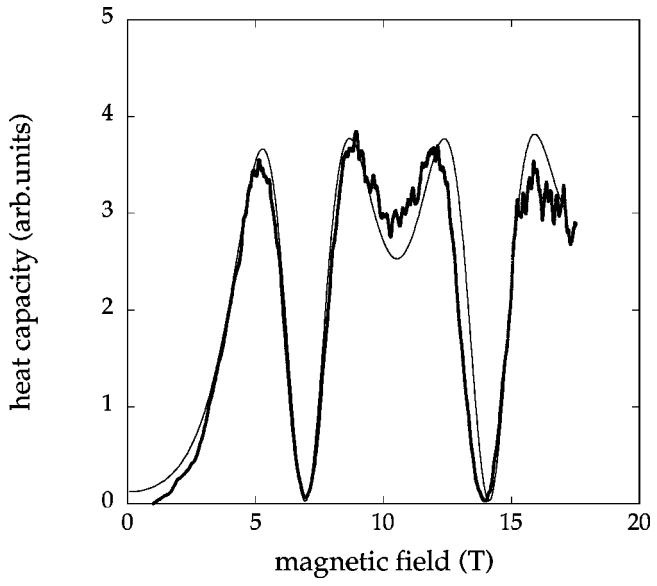

FIG. 4. Heat capacity, in arbitrary units, as a function of magnetic field at 0.9 K. The magnetic field direction forms an angle of $\theta \sim 65°$ with respect to the unique axis of the Cr_8 ring. The solid line represents a two level Schottky anomaly with the energy gap $\Delta(B)$ calculated by the Hamiltonian (1) (see Fig. 1).

B_{c2} correspond to an angle $\theta \sim 65°$ between the unique axis and the magnetic field direction whereas the sign of the torque signal indicates that the unique z axis of the ring is a hard magnetic axis.[8] It is worth noting that between two crossing fields the torque signal is not flat. This feature was also observed on ferric wheels.[14] This is an interesting characteristic that will be discussed below.

The heat capacity, measured simultaneously to the torque signal on the same single crystal, is plotted in Fig. 4. At $T = 0.9$ K, the lattice contribution is very small (see Fig. 2), and the magnetic contribution C_m is essentially determined by the two lowest levels. Hence, for system with two levels separated by an energy gap $\Delta(B)$, C_m is simply $(\Delta/k_BT)^2 \exp(\Delta/k_BT)[1+\exp(\Delta/k_BT)]^{-2}$ that is expected to reach a maximum when $\Delta(B) \simeq 2.5 k_B T$ while it must vanish at B_{cn} if the two levels are degenerate, i.e., $\Delta = 0$. Figure 4 shows that deep minima occur at B_{c1} and B_{c2}. These main features of the $C(B)$ curve are well reproducible by slightly changing temperature (from 0.7 to 1.2 K), excitation frequency (from 0.4 to 1.0 Hz) and orientation ($\theta = 30°$). The solid line is calculated by considering the energy separation between the ground and the first excited state, for an angle of $\sim 65°$ at $T = 0.9$ K. The experimental data nicely fit theoretical predictions and clearly show that the repulsion between the $S = |0,0\rangle$ and $S = |1,-1\rangle$ states and that between the $S = |1,-1\rangle$ and $S = |2,-2\rangle$ ones is vanishingly small in Cr_8, thus confirming the theoretical prediction for the true crossing of these levels.

III. DISCUSSION

Hereafter, we compare experimental with theoretical results in detail. First, it should be stressed that the Hamiltonian parameters were previously obtained by inelastic neutron scattering results and only few free parameters were introduced to fit thermodynamic data. The agreement between the experimental results and calculations is excellent and this confirms that the parameters of the spin Hamiltonian (1) were determined with high precision.

The newest results of this work come from the torque and the $C(B)$ curves shown in Figs. 3 and 4, respectively. The torque **T** acting on a ring can be computed once the Hamiltonian (1) has been diagonalized. Setting the magnetic field in the xz plane (the ring lies in the xy plane), we have only the T_y component, hence differentiating the Zeeman term in Eq. (1) with respect to θ (Ref. 14):

$$T_y = -g\mu_B B(\langle S_x \rangle \cos\theta - \langle S_z \rangle \sin\theta). \tag{5}$$

In Fig. 3 we report two simulations of the torque signal: one obtained by the diagonalization of the full Hamiltonian in the reduced Hilbert space (solid line) and the other one calculated by neglecting S mixing (broken line). The anisotropic interactions, such as the crystal field and the dipole-dipole coupling, being described by nonzero-rank tensor operators, mix states belonging to different spin multiplets. In particular, the mixing between the $S = 0$ state and the lowest $S = 2$ manifolds, and between the lowest $S = 1$ and $S = 3$ multiplets cannot be neglected. Moreover, to correctly account for the high-field region (above ~ 15 T) of the torque measurements, the lowest $S = 4$ manifold, that was neglected in our previous work,[9] has to be included in the calculation. The inclusion of the $S = 4$ multiplet enhances the absolute value of the torque signal by about 3–4 % for fields higher than ~ 15 T and it accounts for the slope of the plateau above 15 T. On the other hand, states which belong to different irreducible representation of the symmetry group of

the Hamiltonian do not mix and can cross by applying a magnetic field. This is the case, for example, for the level crossings between the $S=0$ and $S=1$ states and between the $S=1$ and $S=2$ states at B_{c1} and B_{c2}, respectively. The S mixing effects are clearly visible in Fig. 1, where several anticrossings between states of the same parity are present. Simulations indicate that the torque signal between two crossing field B_{cn} is flat if no mixing is considered but it gets a slope as soon as a mixing between states is taken into account. Experimental data clearly show that torque is not flat between two crossing fields and we may conclude that this is a clear signature of the mixing of states with the same parity.

The study of the heat capacity allows us to monitor the evolution of the energy gap $\Delta(B)$ between the lowest-lying states and in particular possible level repulsion at B_{cn}. The presence of the two deep minima of $C(B)$ at the crossing fields $B_{c1}=6.9$ T and $B_{c2}=14.0$ T clearly shows that the level repulsion is vanishing small, thus confirming a true level crossing. We just mention that NMR experiments performed on Cr_8 single crystals show a very sharp peak of the proton relaxation rate at B_{cn} (Ref. 16) consistently with what we report here. These results contrasts what we found in Fe_6:Li single crystals.[15] As we discussed in our previous work,[15] the origin of a finite nonvanishing minimum at B_{cn} can be intrinsic (i.e., due to a level repulsion) or extrinsic, due to sample quality. Crystal mosaicity or a dispersion of the coupling constants among different rings may actually give rise to broadening of the spin flip transition. The high quality of the Cr_8 crystals certainly limits these extrinsic factors. In a previous work[14] we discussed a possible intrinsic origin of level repulsion and in particular we showed how Dzyaloshinsky-Moriya interactions,[17,18] not included in the Hamiltonian (1), can actually mix states with different parity. Yet, the heat capacity data reported in this work prove that antisymmetric interactions do not give rise to repulsion between the two lowest-lying states in Cr_8 and therefore we conclude that the spin Hamiltonian (1) contains all the essential terms to describe the Cr_8 molecular ring. This is probably not true for Fe_6:Li.

In conclusion, we have studied in detail the effects of mixing of magnetic states on the thermodynamic properties of a molecular Cr_8 ring. The anisotropic terms contained in the spin Hamiltonian (1) mix states with the same parity, such as $S=0$ and $S=2$ and so on, but not states with a different parity, such as $S=0$ and $S=1$ and so on. The mixing of states with the same parity have effects in the torque signal, but very little in the heat capacity. For Cr_8 a clear signature of the absence of repulsion between states with different parity is given by the heat capacity that vanishes at the crossing fields.

ACKNOWLEDGMENTS

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[1] A. Caneschi, A. Cornia, A.C. Fabretti, S. Foner, D. Gatteschi, R. Grandi, and L. Schenetti, Chem.-Eur. J. **2**, 1379 (1996); G.L. Abbati, A. Caneschi, A. Cornia, A.C. Fabretti, D. Gatteschi, W. Malavasi, and L. Schenetti, Inorg. Chem. **36**, 6443 (1997).

[2] K.L. Taft, C.D. Delfs, G.C. Papefthymiou, S. Foner, D. Gatteschi, and S.J. Lippard, J. Am. Chem. Soc. **116**, 823 (1994); A. Caneschi, A. Cornia, A.C. Fabretti, and D. Gatteschi, Angew. Chem., Int. Ed. **39**, 1295 (1999);

[3] G.L. Abbati, A. Caneschi, A. Cornia, A.C. Fabretti, and D. Gatteschi, Inorg. Chim. Acta **297**, 291 (2000).

[4] S.P. Watton, P. Fuhrmann, L.E. Pence, A. Caneschi, A. Cornia, G.L. Abbati, and S.J. Lippard, Angew. Chem., Int. Ed. **36**, 2774 (1997).

[5] J. Schnack and M. Luban, Phys. Rev. B **63**, 014418 (2000).

[6] O. Waldmann, Europhys. Lett. **60**, 302308 (2002).

[7] A. Chiolero and D. Loss, Phys. Rev. Lett. **80**, 169 (1998); F. Meier and D. Loss, *ibid.* **86**, 5373 (2001); B. Normand, X. Wang, X. Zotos, and D. Loss, Phys. Rev. B **63**, 184409 (2001).

[8] J. van Slageren, R. Sessoli, D. Gatteschi, A.A. Smith, M. Helliwell, R.E.P. Winpenny, A. Cornia, A.-L. Barra, A.G.M. Jansen, E. Rentschler, and G.A. Timco, Chem.-Eur. J. **8**, 277 (2002).

[9] S. Carretta, J. van Slageren, T. Guidi, E. Liviotti, C. Mondelli, D. Rovai, A. Cornia, A.L. Dearden, F. Carsughi, M. Affronte, C.D. Frost, R.E.P. Winpenny, D. Gatteschi, G. Amoretti, and R. Caciuffo, Phys. Rev. B **67**, 094405 (2003).

[10] More in general, $\mathbf{D}_{ij}$ may also include anisotropic exchange, see also Refs. 14,17.

[11] A. Bencini and D. Gatteschi, *EPR of Exchange Coupled Systems* (Springer Verlag, Berlin, 1990).

[12] E. Liviotti, S. Carretta, and G. Amoretti, J. Chem. Phys. **117**, 3361 (2002).

[13] Since the complete Hamiltonian does not commute with the square of the total spin operator S^2, different multiplets can mix and the complete 65536×65536 matrix should be diagonalized. In Ref. 12, a unitary transformation has been employed in order to include the S-mixing effects in the effective single-spin Hamiltonian describing the anisotropic splitting of the ground multiplet. The same technique can be used to evaluate the mixing between each of the lowest lying multiplets and the others due to the anisotropic part of the Hamiltonian. In fact, the A^2/Δ and B^2/Δ coefficients defined in Ref. 12 represent a quantitative measure of the mixing between two multiplets. By this approach, we can restrict our calculation to the subspace containing only the states whose mixing with the lowest manifolds is maximum.

[14] F. Cinti, M. Affronte, and A.G.M. Jansen, Eur. Phys. J. B **30**, 461 (2002).
[15] M. Affronte, A. Cornia, A. Lascialfari, F. Borsa, D. Gatteschi, J. Hinderer, M. Horvatić, A.G.M. Jansen, and M.H. Julien, Phys. Rev. Lett. **88**, 167201 (2002).
[16] A. Lascialfari, F. Borsa, and M.H. Julien (private communication).
[17] H. Nakano and S. Miyashita, J. Phys. Soc. Jpn. **70**, 2151 (2001).
[18] Y. Shapira and V. Bindilatti, J. Appl. Phys. **92**, 4155 (2002).