Thermodynamics of alternating spin chains with competing nearest- and next-nearest-neighbor interactions: Ising model

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The thermodynamical properties of an alternating spin (S,s) one-dimensional (1D) Ising model with competing nearest- and next-nearest-neighbor interactions are exactly calculated using a transfer-matrix technique. In contrast to the case $S=s=\frac{1}{2}$, previously investigated by Harada, the alternation of different spins $(S\neq s)$ along the chain is found to give rise to two-peaked static structure factors, signaling the coexistence of different short-range-order configurations. The relevance of our calculations with regard to recent experimental data by Gatteschi *et al.* in quasi-1D molecular magnetic materials, R (hfac)$_3$ NITEt (R=Gd, Tb, Dy, Ho, Er, ...), is discussed; hfac is hexafluoro-acetylacetonate and NITEt is 2-Ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl-3-oxide.

I. INTRODUCTION

One-dimensional (1D) magnetic models have attracted much interest in recent years, both because they are much easier to treat theoretically than the three-dimensional (3D) ones, and because of the discovery of several quasi-1D magnetic materials.[1] Most of them are formed by transition-metal ions of the $3d$ series, and their properties can generally be interpreted in terms of a nearest-neighbor (NN) exchange interaction, whose sign determines the type of short-range order: e.g., ferrimagnetic in $CsNiF_3$, antiferromagnetic in $(CH_3)_4NMnCl_3$ (TMMC), ferrimagnetic in $CuMn(S_2C_2O_2)_2$ 7.5 H_2O.[1,2]

At the present time, more complicated 1D magnetic systems are being synthetized in organic as well as inorganic solid-state chemistry.[3] Recently, Gatteschi and coworkers obtained and investigated a class of quasi-1D molecular-based magnetic materials,[4] R(hfac)$_3$NITEt (R =Gd, Tb, Dy, Ho, Er, ...),[5] whose magnetic properties are determined by rare-earth ions with spin S and nitronyl nitroxide organic radicals with spin $s=\frac{1}{2}$, and which turn out to be the first example of alternating-spin magnetic chains with dominant next-nearest-neighbor (NNN) interactions.[6] [hfac is hexafluoro-acetylacetonate and NITEt is 2-Ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl-3-oxide.]

All these materials appear to be good quasi-1D magnetic systems, owing to the long distance (~ 10 Å) between magnetic ions belonging to different chains.[7] Also, measurements of the angular dependence of the electron paramagnetic resonance (EPR) linewidth[6,8] in a single crystal of the prototype system Gd(hfac)$_3$NITEt gave a clear indication that the ratio of the inter-to-intrachain exchange constants is smaller than 10^{-3}.

Low-temperature susceptibility measurements in the analogous chain compounds Y(hfac)$_3$NITEt (Ref. 9) and Eu(hfac)$_3$NITEt (Ref. 7) (where the Gd^{3+} is replaced, respectively, by diamagnetic Y^{3+} and by Eu^{3+}, which has a nonmagnetic ground state) suggested that the $s=\frac{1}{2}$ organic radicals interact via an antiferromagnetic Heisenberg exchange.

In general, the R(hfac)$_3$NITEt (R =Gd, Tb, Dy, Ho, Er, ...) magnetic chains present an overall antiferromagnetic behavior in the paramagnetic phase, i.e., the isothermal susceptibility χ has a maximum at a finite temperature.[4-8] Preliminary attempts to interpret such experimental data in terms of models with intrachain interaction limited to nearest neighbors and possibly interchain coupling led to unrealistic (too high) values of the intra- and interchain exchange fitting parameters.[7] Instead, a rough model of two interpenetrating 1D lattices, one formed by the organic radicals and one by the rare-earth ions, with antiferromagnetic isotropic coupling within each lattice but not between different lattices, gave much more reasonable results in the case of Gd(hfac)$_3$NITEt,[7] thus providing strong support for the model of an alternating-spin magnetic chain with NNN antiferromagnetic interactions dominating over the NN ferromagnetic one. Owing to such spin frustration effects, more complex spin structures are allowed in addition to the simple ferromagnetic and antiferromagnetic ones: e.g., a "two-spin-up-two-spin-down," a helical, or even a degenerate and disordered ground state, depending on the spin symmetry and the ratio between the competing exchange interactions.[6]

The Gd^{3+} ion has a $^8S_{7/2}$ ground state: therefore, any exchange interaction should be essentially isotropic and a Heisenberg model is expected to describe the system. When Gd is substituted by other rare-earth atoms (Tb, Dy, Ho, Er, etc.), anisotropy effects associated with the unquenched orbital angular momenta can give rise to planar or Ising-like behavior.[5]

Such an experimental situation led us to study a magnetic model of spins (S,s) alternating along a linear lattice with competing nearest- and next-nearest-neighbor exchange couplings.

In the case of spins equal on all sites, the 1D Ising (with $S=s=\frac{1}{2}$),[10–13], planar,[14–16] and Heisenberg[17] models with competing NN and NNN exchange couplings were thoroughly investigated by several authors. In particular, the partition function and the two-spin correlation functions were exactly calculated in the framework of the transfer-matrix technique[13–17] and different types of temperature dependence and of short-range order were found, depending on the ratio between the NN and NNN couplings.

It is the purpose of the present paper to perform a similar transfer-matrix study in the case of an *alternating spin* (S,s) 1D Ising model, as a starting point in the task of interpreting the experimental data for the thermodynamic properties of the new class of $R(\text{hfac})_3\text{NITEt}$ molecular magnetic chains.

Owing to the presence of the NNN interaction, one is led to diagonalize an $M\times M$ *nonsymmetric* real matrix, with $M=(2s+1)(2S+1)$. The results are obtained in a numerical form; analytical expressions are given in the limiting cases $T\to 0$ and $T\to\infty$. When the spins along the chain have the same magnitude, $S=s=\frac{1}{2}$, the results by Harada[13] are correctly recovered.

The most peculiar effect of the alternation of different spins $(S\neq s)$ along the chain is displayed by the static structure factor $\mathcal{S}(q)$, a property which can be measured by a diffuse neutron-scattering experiment: at low temperatures, it presents *two* peaks (with different heights), signaling the coexistence of different short-range-order configurations in the system.

The layout of the paper is as follows: Section II is devoted to the transfer-matrix method applied to the alternating-spin (S,s) Ising chain with competing NN and NNN exchange interactions. The results for the various thermodynamic properties (magnetic susceptibility, specific heat, static structure factor, correlation length, etc.) are presented and discussed in Sec. III. In Sec. IV we comment on our results in connection with the experimental data in the $R(\text{hfac})_3\text{NITEt}$ quasi-1D magnetic materials. Finally, we draw the conclusions in Sec. V.

II. TRANSFER-MATRIX METHOD

Let us start with the Hamiltonian of an Ising chain with N spins (N is taken to be an even number, without lack of generality when the thermodynamic limit $N\to\infty$ is taken), $N/2$ of which have spin S and occupy the odd sites of a linear lattice, while the other $N/2$ spins have $s=\frac{1}{2}$ and occupy the even sites:

$$\begin{aligned}\mathcal{H}=&-J_{Rr}\sum_{n=1}^{N/2}(S_{2n-1}^{z}s_{2n}^{z}+s_{2n}^{z}S_{2n+1}^{z})\\&-J_{RR}\sum_{n=1}^{N/2}S_{2n-1}^{z}S_{2n+1}^{z}-g_R\mu_B H\sum_{n=1}^{N/2}S_{2n-1}^{z}\\&-J_{rr}\sum_{n=1}^{N/2}s_{2n}^{z}s_{2n+2}^{z}-g_r\mu_B H\sum_{n=1}^{N/2}s_{2n}^{z}\ .\end{aligned}\tag{1}$$

We assume the NN exchange to be ferromagnetic $(J_{Rr}>0)$ and the NNN ones to be antiferromagnetic $(J_{RR}<0, J_{rr}<0)$. An external magnetic field is applied along the z direction; g_r, g_R denote the gyromagnetic factors of the s and S spins, respectively. As usual, we take the lattice spacing $a=1$ and assume periodic boundary conditions: $S_{N+1}^{z}=S_1^z, s_{N+2}^{z}=s_2^z$.

In the case $S=s=\frac{1}{2}$, the ground state of an Ising chain with both NN and NNN exchange couplings in an external field was thoroughly studied by Morita and Horiguchi.[11] For $J_1\equiv J_{Rr}>0$ and $J_2\equiv J_{RR}=J_{rr}<0$ they proved that in zero field two different long-range spin orderings are possible at $T=0$, depending on the ratio $\delta_0=|J_2|/J_1$: for $\delta_0<\frac{1}{2}$ one has ferromagnetism; for $\delta_0=\frac{1}{2}$ the ground state is degenerate and disordered; for $\delta_0>\frac{1}{2}$ a periodic configuration with two "up" spins followed by two "down" spins is energetically favored. For reasons of brevity, hereafter we shall call this state the "antiferromagnetic" one.

In the case $S\neq s$ and $J_{RR}\neq J_{rr}$, we shall not give a rigorous proof for the ground state in the general case. Limiting ourselves to $J_{Rr}>0$, $J_{RR}<0$, $J_{rr}<0$, and $H=0$, we compare the energies of the ferromagnetic spin configuration and of the "antiferromagnetic" one:

$$\begin{aligned}E_0^{(f)}&=-J_{Rr}SsN\left[1-\frac{\delta_R+\delta_r}{2}\right],\\E_0^{(\text{"}a\text{"})}&=-J_{Rr}SsN\left[\frac{\delta_R+\delta_r}{2}\right],\end{aligned}\tag{2}$$

where we have defined

$$\delta_R=\frac{|J_{RR}|S^2}{J_{Rr}Ss},\quad \delta_r=\frac{|J_{rr}|s^2}{J_{Rr}Ss}\ .\tag{3}$$

Thus, the ferromagnetic long-range order is energetically favored for $\delta_R+\delta_r<1$, while the "antiferromagnetic" one is preferred for $\delta_R+\delta_r>1$.

At finite temperatures, the 1D Ising model cannot support long-range order.[18] However, a strong short-range order is present even in the paramagnetic phase and its nature is revealed by the position of the peak in the static structure factor $\mathcal{S}(q)$ which is experimentally accessible via a diffuse neutron-scattering experiment. This quantity, along with other thermodynamic properties, can be exactly calculated using the transfer-matrix method.

In the case $S=s=\frac{1}{2}$ and $J_{RR}=J_{rr}$, it is possible, via a dual transformation, to map the 1D Ising model with NN and NNN interactions into an equivalent (i.e., with the same partition function Z) 1D model with only NN coupling: for $H=0$, analytic results were obtained for both Z and the pair-correlation functions.[10,12,13]

In the case of an alternating-spin (S,s) chain with different NNN couplings between even and odd sites $(J_{RR}\neq J_{rr})$, this mapping is no more possible, but, owing to the finite range of the interactions, one can still give an exact transfer-matrix formulation of the thermodynamics of such a 1D model, even though the results can generally be given only in a numerical form.

The canonical partition function Z can be written as $(\beta=1/k_BT)$:

$$Z_N=\mathrm{Tr}\{e^{-\beta\mathcal{H}}\}=\sum_{S_1^z}\sum_{s_2^z}\cdots\sum_{S_{N-1}^z}\sum_{s_N^z}T(S_1^z,s_2^z;S_3^z,s_4^z)\cdots T(S_{N-1}^z,s_N^z;S_1^z,s_2^z)\ , \tag{4}$$

where $S^z=-S,-S+1,\ldots,S-1,S$ and we assume $s=\frac{1}{2}$, so that $s^z=\pm\frac{1}{2}$. The kernel T is defined by:

$$T(S_1^z,s_2^z;S_3^z,s_4^z)=\exp[\tfrac{1}{2}\beta J_{Rr}(S_1^z s_2^z+2s_2^z S_3^z+S_3^z s_4^z)]\exp[\beta J_{RR}S_1^z S_3^z]\exp\left[\frac{\beta}{2}g_R\mu_B H(S_1^z+S_3^z)\right]$$
$$\times\exp[\beta J_{rr}s_2^z s_4^z]\exp\left[\frac{\beta}{2}g_r\mu_B H(s_2^z+s_4^z)\right]\ . \tag{5}$$

A similar four-point, real, nonsymmetric kernel was obtained previously by Carazza, Rastelli, and Tassi[15,16] in their study of the classical 1D planar model with competing interactions. The fact that the kernel is nonsymmetric, i.e., $T(S_1^z,s_2^z;S_3^z,s_4^z)\neq T(S_3^z,s_4^z;S_1^z,s_2^z)$, leads one to solve *two* integral equations, in order to find the left (φ) and right (ψ) eigenfunctions:[19]

$$\sum_{S_1^z}\sum_{s_2^z}\varphi_m(S_1^z,s_2^z)T(S_1^z,s_2^z;S_3^z,s_4^z)=\lambda_m\varphi_m(S_3^z,s_4^z)\ ,$$
$$\sum_{S_3^z}\sum_{s_4^z}T(S_1^z,s_2^z;S_3^z,s_4^z)\psi_m(S_3^z,s_4^z)=\lambda_m\psi_m(S_1^z,s_2^z)\ , \tag{6}$$

while the left and right eigenvalues λ_m are identical. The remarkable point is that, owing to the nonsymmetry of the real kernel (5), the spectrum of its eigenvalues may include pairs of complex conjugate values and also the eigenfunctions can be complex. However, even in the nonsymmetric case, if all the eigenvalues are nondegenerate, the following orthonormality and completeness relations can be shown to hold:[20]

$$\sum_{S_1^z}\sum_{s_2^z}\varphi_l(S_1^z,s_2^z)\psi_m(S_1^z,s_2^z)=\delta_{l,m}\ ,$$
$$\sum_m\varphi_m(S_1^z,s_2^z)\psi_m(S_{1'}^z,s_{2'}^z)=\delta_{1,1'}\delta_{2,2'}\ . \tag{7}$$

From Eqs. (7) one deduces the following expansion for the kernel in terms of eigenvalues and eigenfunctions:

$$T(S_1^z,s_2^z;S_3^z,s_4^z)=\sum_m\lambda_m\psi_m(S_1^z,s_2^z)\varphi_m(S_3^z,s_4^z)\ . \tag{8}$$

Inserting Eq. (8) in the expression (4) for the partition function and making use of the orthonormality and completeness relations (7), one obtains

$$Z_N=\sum_m(\lambda_m)^{N/2}\ , \tag{9}$$

where the sum is over the $(2s+1)(2S+1)$ eigenvalues of the transfer integral equations (6). The fact that possible complex eigenvalues must always occur in complex conjugate pairs guarantees that the partition function is real. If all the eigenvalues are nondegenerate and the largest (in modulus) one, λ_0, is real, in the thermodynamic limit the partition function is simply given by

$$\lim_{N\to\infty}Z_N=\lambda_0^{N/2}\ . \tag{10}$$

The free energy is

$$F_N=-k_BT\ln Z_N=-\frac{N}{2}k_BT\ln\lambda_0\ . \tag{11}$$

Hence, by numerical derivation one can obtain χ, the isothermal susceptibility in zero field:

$$\chi=\lim_{H\to0}\frac{\partial^2F}{\partial H^2}=\frac{N}{2}k_BT\left[\frac{1}{\lambda_0}\frac{\partial^2\lambda_0}{\partial H^2}-\frac{1}{\lambda_0^2}\left[\frac{\partial\lambda_0}{\partial H}\right]^2\right]_{H=0}\ , \tag{12}$$

and the heat capacity C

$$C=-T\frac{\partial^2F}{\partial T^2}=\frac{N}{2}k_B\left[\frac{2T}{\lambda_0}\frac{\partial\lambda_0}{\partial T}-\frac{T^2}{\lambda_0^2}\left[\frac{\partial\lambda_0}{\partial T}\right]^2+\frac{T^2}{\lambda_0}\frac{\partial^2\lambda_0}{\partial T^2}\right]\ . \tag{13}$$

The spin-correlation functions require the knowledge of both eigenvalues and eigenfunctions. For the magnetization on the odd and even sites, respectively, one has

$$\langle S_1^z\rangle=\sum_{S_1^z}\sum_{s_2^z}\varphi_0(S_1^z,s_2^z)\psi_0(S_1^z,s_2^z)S_1^z\ ,$$
$$\langle s_2^z\rangle=\sum_{S_1^z}\sum_{s_2^z}\varphi_0(S_1^z,s_2^z)\psi_0(S_1^z,s_2^z)s_2^z\ . \tag{14}$$

Of course in zero field these quantities vanish owing to the absence of long-range order in 1D.[18]

As for the two-spin-correlation functions, owing to the alternation of the (S,s) spins along the chain, one has to distinguish between odd-odd (RR), even-even (rr), and odd-even (Rr) pair correlations:

$$\langle S_1^z S_{1+2n}^z\rangle=\sum_m\left[\frac{\lambda_m}{\lambda_0}\right]^n d_{0m}^{(R)}d_{m0}^{(R)}\ ,$$
$$\langle s_1^z s_{2+2n}^z\rangle=\sum_m\left[\frac{\lambda_m}{\lambda_0}\right]^n d_{0m}^{(r)}d_{m0}^{(r)}\ , \tag{15}$$
$$\langle S_1^z s_{2+2n}^z\rangle=\sum_m\left[\frac{\lambda_m}{\lambda_0}\right]^n d_{0m}^{(R)}d_{m0}^{(r)}=\langle s_2^z S_{3+2n}^z\rangle\ ,$$

where

$$d_{lm}^{(R)}=\sum_{S_1^z}\sum_{s_2^z}\varphi_l(S_1^z,s_2^z)\psi_m(S_1^z,s_2^z)S_1^z\ ,$$
$$d_{lm}^{(r)}=\sum_{S_1^z}\sum_{s_2^z}\varphi_l(S_1^z,s_2^z)\psi_m(S_1^z,s_2^z)s_2^z\ . \tag{16}$$

The spatial Fourier transform of the two-spin-correlation function is

$$\chi(q)=\lim_{N\to\infty}\frac{\mu_B^2}{k_BT}\sum_{i=1}^{N}\sum_{j=1}^{N}g_ig_j[\langle\sigma_i^z\sigma_j^z\rangle-\langle\sigma_i^z\rangle\langle\sigma_j^z\rangle]\exp[iq(R_j-R_i)]\ , \tag{17}$$

where $\sigma_i^z=S_i^z, g_i=g_R$ for odd i and $\sigma_i^z=s_i^z, g_i=g_r$ for even i. Making use of the translational invariance and of the periodic boundary conditions, in the thermodynamic limit one has

$$\begin{aligned}\mathcal{S}(q)\equiv\frac{\chi(q)k_BT}{N\mu_B^2}=&g_R^2\left\{\frac{1}{2}[\langle(S_1^z)^2\rangle-\langle S_1^z\rangle^2]+\sum_{n=1}^{\infty}[\langle S_1^zS_{1+2n}^z\rangle-\langle S_1^z\rangle^2]\cos(2nq)\right\}\\&+g_r^2\left\{\frac{1}{2}[\langle(s_2^z)^2\rangle-\langle s_2^z\rangle^2]+\sum_{n=1}^{\infty}[\langle s_2^zs_{2+2n}^z\rangle-\langle s_2^z\rangle^2]\cos(2nq)\right\}\\&+2g_Rg_r\left\{\sum_{n=0}^{\infty}[\langle S_1^zs_{2+2n}^z\rangle-\langle S_1^z\rangle\langle s_2^z\rangle]\cos[(2n+1)q]\right\}.\end{aligned} \tag{18}$$

The static structure factor $\mathcal{S}(q)$, which can be measured by a diffuse neutron-scattering experiment, provides direct information about (i) the kind of short-range order present in the system at finite temperatures, through the position of its maximum $q_{\max}$; (ii) the extension of the region of correlated spins, through the half width at half maximum. Expanding $\mathcal{S}(q)$ for small $\Delta q=q_{\max}-q$, one can define the correlation length ξ as

$$\frac{1}{\xi^2}=-2\frac{\mathcal{S}(q_{\max})}{\partial^2\mathcal{S}(q)/\partial q^2|_{q=q_{\max}}}\ . \tag{19}$$

It is worthwhile to note that this definition of ξ is the same as the one by Harada,[13] but differs from those given in Refs. 10 and 12.

III. RESULTS AND DISCUSSION

In this section we present in graphical form the results of our transfer-matrix calculations of the thermodynamics of the alternating-spin (S,s) 1D Ising model with competing NN and NNN interactions.

A. Isothermal susceptibility

In Fig. 1 we show the numerical results for the isothermal susceptibility in zero field of an Ising chain with $S=\frac{7}{2}$, $s=\frac{1}{2}$, calculated from Eq. (12). In this figure and in all the other ones we put $g_R=g_r=2$. The quantity $(\chi T)^*\equiv\chi k_BT/N\mu_B^2$ is reported versus reduced temperature $T^*\equiv k_BT/J_{Rr}Ss$ for different values of the ratios between NNN and NN exchange couplings, δ_R and δ_r [see Eq. (3)]. As expected on the basis of the ground-state configurations, in the limit $T\to0$ the product χT presents a ferromagnetic behavior, i.e., it diverges for $\delta_R+\delta_r<1$, while for $\delta_R+\delta_r>1$ it tends exponentially to 0, similar to an antiferromagnet. In the opposite limit of $T\to\infty$, the isothermal susceptibility in zero field reaches the asymptotic value

$$\frac{\chi k_BT}{N\mu_B^2}\sim\frac{1}{2}[g_r^2F(s)+g_R^2F(S)]\ , \tag{20}$$

where

$$\begin{aligned}F(S)=&\frac{1}{2S+1}\sum_{S^z}(S^z)^2\ ,\\=&\tfrac{1}{3}S(S+1),\quad\text{integer } S\ ,\\=&\tfrac{1}{12}[(2S+1)^2-1],\quad\text{half-integer } S\ .\end{aligned} \tag{21}$$

As for the quantity χ, it is clear that for $\delta_R+\delta_r<1$ it decreases monotonically from $+\infty$ to 0 with increasing temperature, while for $\delta_R+\delta_r>1$ it passes through a maximum, since χ vanishes both for $T\to0$ and $T\to\infty$.

B. Specific heat

We now present the results for the temperature dependence of the specific heat in zero field, obtained by numerical differentiation of the largest (in modulus) eigenvalue λ_0 with respect to temperature [Eq. (13)]. In the case of spins equal on the odd and even sites $(S=s=\frac{1}{2})$ and equal NNN couplings $(J_2\equiv J_{RR}=J_{rr})$, λ_0 is known[13] in analytic form to be $(J_1\equiv J_{Rr})$

$$\lambda_0=\exp(2\beta J_2s^2)[\cosh(\beta J_1s^2)+\sqrt{\sinh^2(\beta J_1s^2)+\exp(-4\beta J_2s^2)}]^2\ , \tag{22}$$

and the corresponding specific heat C/Nk_B is plotted in Fig. 2 versus T^* for selected values of $\delta_0=|J_2|/J_1$.[21]

Figure 3 reports the same quantity for an alternating-spin chain with $S=\frac{7}{2}$, $s=\frac{1}{2}$. For the sake of comparison with the previous case, the values of the NNN couplings were chosen such that $\delta\equiv\delta_R=\delta_r$.

Very similar results are obtained in the two cases. For $T\to0$, an exponential dependence, typical of the Ising model, is found. With increasing temperature, a peak develops in the heat capacity owing to the excitation of

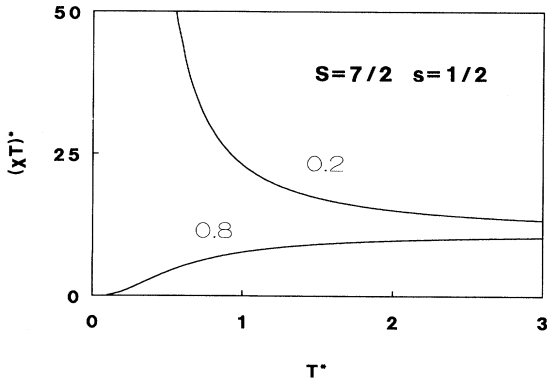

FIG. 1. Isothermal susceptibility $(\chi T)^* \equiv \chi k_B T/N\mu_B^2$ vs reduced temperature $T^* \equiv k_B T/J_{Rr}Ss$ for an alternating-spin ($S=\frac{7}{2}$, $s=\frac{1}{2}$) Ising chain with competing NN and NNN exchange couplings, calculated from Eq. (12) for selected values of $\delta \equiv \delta_R = \delta_r$ [see Eq. (3)], as indicated by the labels.

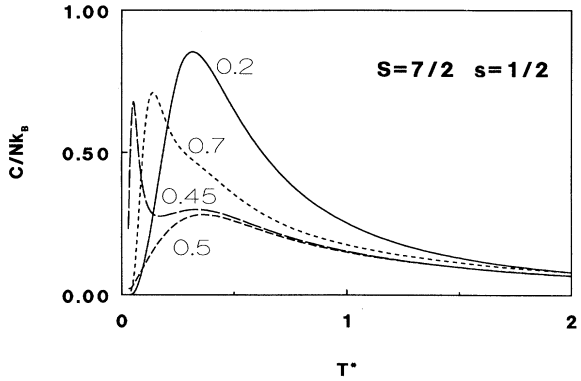

FIG. 3. Specific heat C/Nk_B vs reduced temperature T^* for an alternating-spin ($S=\frac{7}{2}$, $s=\frac{1}{2}$) Ising chain with competing interactions, calculated from Eq. (13). The different curves refer to selected values of $\delta \equiv \delta_R = \delta_r$, as indicated by the labels.

domain walls in the chain, both in the ferromagnetic ($\delta_R+\delta_r<1$) and "antiferromagnetic" ($\delta_R+\delta_r>1$) regimes. One can roughly estimate the excitation energies of such domain walls to be

$$\Delta E_w^{(f)} = J_{Rr}Ss(1-\delta_R-\delta_r), \quad \text{for } \delta_R+\delta_r<1\ ,$$
$$\Delta E_w^{("a")} = -J_{Rr}Ss(1-\delta_R-\delta_r), \quad \text{for } \delta_R+\delta_r>1\ . \tag{23}$$

Notice that in the "antiferromagnetic" case, the energy $\Delta E_w^{("a")}$ refers to a domain wall which breaks the coupling between two spins, S and s, which are antiparallel (i.e., belong to different—"up-up" or "down-down"—pairs). A domain wall breaking the coupling between two spins, S and s, which are parallel (i.e., belong to the same pair) would have a much higher excitation energy:

$$\overline{\Delta E_2^{("a")}} = J_{Rr}Ss(1+\delta_R+\delta_r), \quad \text{for } \delta_R+\delta_r>1\ . \tag{24}$$

From Eq. (23) it is clear that for $\delta_R+\delta_r$ in the proximity of 1, the excitation energies of both the ferromagnetic and antiferromagnetic domain walls are very small, so that a peculiar two-peaked structure is observed: a sharp peak develops at low temperature, owing to the domain walls excitation, well separated from a broad peak at higher temperature. Only the latter is present in the limiting case $\delta_R+\delta_r=1$, corresponding to a degenerate and disordered ground state. For $\delta_R+\delta_r$ very different from 1, the two peaks merge.

C. Static structure factor and correlation length

Figure 4 shows the static structure factor $\mathcal{S}(q)$ of an Ising chain with competing interactions and spin $S=s=\frac{1}{2}$. Figure 5 displays the same quantity in the case of an alternating-spin chain with $S=\frac{7}{2}$, $s=\frac{1}{2}$. $\mathcal{S}(q)$ was calculated from Eq. (18) for selected values of $\delta \equiv \delta_R = \delta_r$ at a fixed reduced temperature ($T^*=0.25$). At such a finite, but sufficiently low temperature, the peaks in $\mathcal{S}(q)$ reflect the kind of short-range order present in the system. The

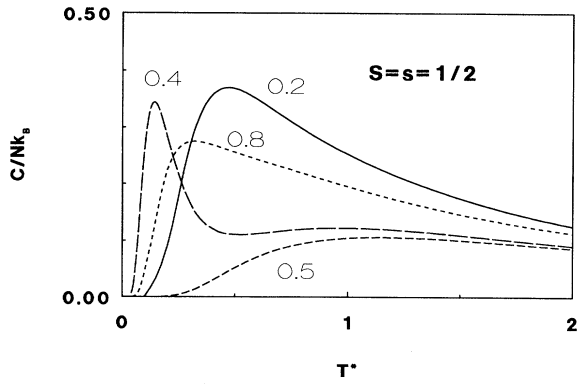

FIG. 2. Specific heat C/Nk_B vs reduced temperature T^* for an Ising chain with $S=s=\frac{1}{2}$ and competing NN ($J_1=J_{Rr}$) and NNN ($J_2=J_{RR}=J_{rr}$) exchange couplings, calculated from Eq. (13). The different curves refer to selected values of $\delta_0=|J_2|/J_1$, as indicated by the labels.

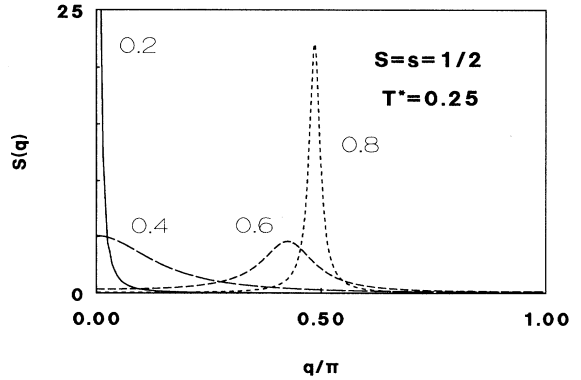

FIG. 4. Static structure factor $\mathcal{S}(q)$ of an Ising chain with $S=s=\frac{1}{2}$ and $J_{RR}=J_{rr}$ calculated from Eq. (18) at a fixed reduced temperature ($T^*=0.25$). The different curves refer to selected values of δ_0, as indicated by the labels.

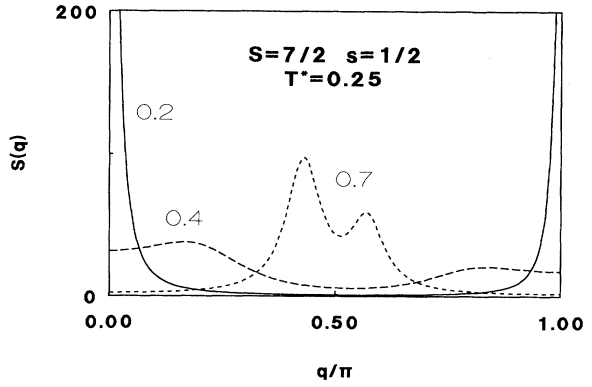

FIG. 5. Static structure factor $\mathcal{S}(q)$ of an alternating-spin ($S=\frac{7}{2}$, $s=\frac{1}{2}$) Ising chain, calculated from Eq. (18) at fixed $T^*=0.25$ for selected values of $\delta\equiv\delta_R=\delta_r$, as indicated by the labels.

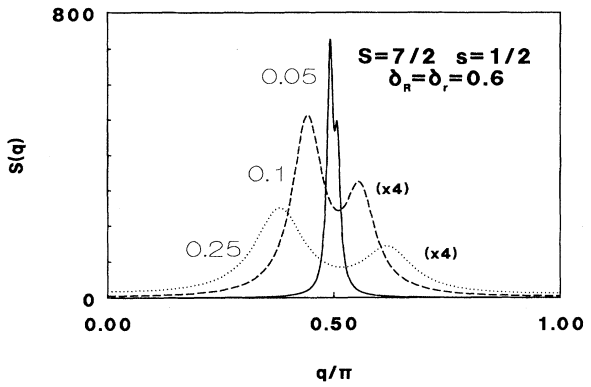

FIG. 6. Static structure factor $\mathcal{S}(q)$ of an alternating-spin ($S=\frac{7}{2}$, $s=\frac{1}{2}$) Ising chain, calculated from Eq. (18) for fixed $\delta_R=\delta_r=0.6$ at selected values of T^*. Full line: $T^*=0.05$; dashed line: $T^*=0.1$; dotted line: $T^*=0.25$. *Nota bene:* the latter two curves have been enhanced by a factor of 4.

most interesting feature is that, while in the case $S=s=\frac{1}{2}$, the static structure factor presents only one peak, for $S\neq s$ *two* peaks with different heights are clearly visible, signaling the coexistence between different short-range order configurations.

It is worthwhile to note that two-peaked structure factors were found at low temperatures also by Carazza, Rastelli, and Tassi[15] in their study of the planar spin chain with competing interactions up to third neighbors. In that case, coexistence of different kinds of short-range order (ferro, antiferro, and helimagnetic) was found in the neighborhood of the $T=0$ first-order transition lines.

In our case, the origin of the two-peaked structure factors is different, since they are observed also far from the ferromagnetic-antiferromagnetic phase boundary $\delta_R+\delta_r=1$. Indeed, the two-peaked feature is a direct consequence of the alternation of different ($S\neq s$) spins along the chain, as one can easily infer from Eq. (18) making the $T\to 0^+$ limit. In fact, in the case of ferromagnetic short-range order ($\delta_R+\delta_r<1$) one has for the static structure factor ($g\equiv g_R=g_r$),

$$\frac{\mathcal{S}(q)}{g^2}\approx(S^2+s^2)\left\{\sum_{n=1}^{\infty}\cos(2nq)\right\}+2Ss\left\{\sum_{n=0}^{\infty}\cos[(2n+1)q]\right\}. \tag{25}$$

It turns out that, while $q=0$ is an absolute maximum both for $S=s$ and $S\neq s$, $q=\pi$ is an absolute *minimum* for $S=s$ and a relative *maximum* for $S\neq s$. A similar crude approximation in the "antiferromagnetic" case ($\delta_R+\delta_r>1$) leads to find only one maximum at $q=\pi/2$ for both $S=s$ and $S\neq s$. In order to account for a two-peaked structure factor it would be necessary to take into consideration the different temperature dependences of the NNN two-spin-correlation functions, $\langle S_1^z S_{1+2n}^z\rangle$ and $\langle s_2^z s_{2+2n}^z\rangle$, for $S\neq s$.

The evolution with temperature of the static structure factor $\mathcal{S}(q)$ for an Ising chain with competing interactions and $S=\frac{7}{2}$, $s=\frac{1}{2}$ is reported in Fig. 6 for a fixed value of $\delta\equiv\delta_R=\delta_r=0.6$. At $T=0$ one would have a δ peak centered at $q=\pi/2$ since $\delta_R+\delta_r>1$; with increasing temperature a two-peaked structure develops, even though the absolute maximum $q_{\max}$ is unique.

The temperature dependence of the quantity $q_{\max}$ is shown in Fig. 7 for the alternating-spin ($S=\frac{7}{2}$, $s=\frac{1}{2}$) Ising chain for selected values of $\delta\equiv\delta_R=\delta_r$. For $\delta_R+\delta_r<1$, a ferromagnetic ground state is favored ($q_{\max}=0$); with increasing temperature, a transition to a phase with $q_{\max}\neq 0$ can occur at a temperature T_L which decreases with $\delta_R+\delta_r$ approaching 1 [see also discussion after Eq. (27)]. For $\delta_R+\delta_r>1$, at $T=0$ one has a "two-spin-up-two-spin-down" ground state with $q_{\max}=\pi/2$; for finite T, $q_{\max}$ decreases.

In the limit $T\to\infty$, it is possible to obtain an analytic expression for $q_{\max}$. In fact, expanding the partition function and the two-spin-correlation functions to lowest order in $\beta|J_{RR}|$, $\beta|J_{rr}|$, βJ_{Rr}, one obtains for the static structure factor,

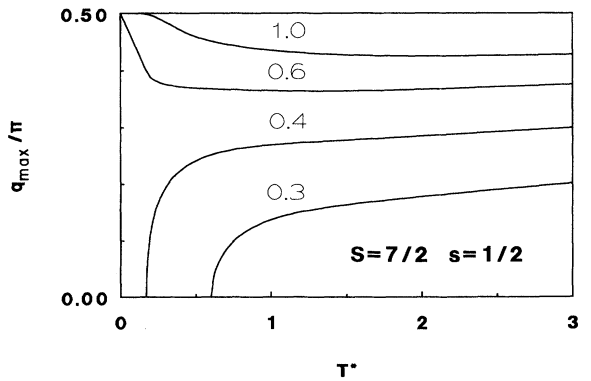

FIG. 7. Temperature dependence of the absolute maximum $q_{\max}$ of the static structure factor $\mathcal{S}(q)$ for an alternating-spin chain with $S=\frac{7}{2}$, $s=\frac{1}{2}$ at selected values of $\delta\equiv\delta_R=\delta_r$, as indicated by the labels.

$$\mathcal{S}(q)\sim+\frac{g_R^2}{2}F(S)[1+2F(S)\beta|J_{RR}|\cos 2q]$$
$$+\frac{g_r^2}{2}F\left[s=\frac{1}{2}\right]\left[1+2F\left[s=\frac{1}{2}\right]\beta|J_{rr}|\cos 2q\right]+2g_Rg_rF(S)F\left[s=\frac{1}{2}\right]\beta J_{Rr}\cos q\ , \tag{26}$$

so that a maximum can be obtained either for $\sin q_{\max}=0$ or for

$$\cos q_{\max}=\frac{1}{2}\left[\frac{g_R}{g_r}\frac{|J_{RR}|}{J_{Rr}}\frac{F(S)}{F(s=\frac{1}{2})}+\frac{g_r}{g_R}\frac{|J_{rr}|}{J_{Rr}}\frac{F(s=\frac{1}{2})}{F(S)}\right]^{-1}. \tag{27}$$

In the general case $S\neq s$, from Eq. (27) one can derive a criterion to predict whether there exists a definite temperature T_L above which the static structure factor has an absolute maximum at $q_{\max}\neq 0$ whereas below which $q_{\max}=0$. In fact, it is sufficient to verify if the Hamiltonian parameters satisfy both the conditions (a) and (b): (a) $|\cos q_{\max}|<1$ (so that $q_{\max}\neq 0$), for $T\to\infty$; (b) $\delta_R+\delta_r<1$ (so that $q_{\max}=0$), for $T\to 0$.

In the limit $S=s=\frac{1}{2}$ and $J_{RR}=J_{rr}$, the result by Harada[13] is recovered, i.e., either $\sin q_{\max}=0$ or $\cos q_{\max}=1/(4\delta_0)$. Thus, for $0<\delta_0<\frac{1}{4}$ and for $\delta_0>\frac{1}{2}$ one has, respectively, $q_{\max}=0$ and $q_{\max}\neq 0$ at any temperature, and only for $\frac{1}{4}<\delta_0<\frac{1}{2}$ a pseudo-Lifshitz point T_L is found.[12] (In 1D, a true Lifshitz point cannot exist for the Ising model with competing interactions, since for $\delta_0=\frac{1}{2}$ the system shows no long-range order as $T\to 0$.)

In Fig. 8 the temperature dependence of $q_{\max}$ is reported for a fixed value of $\delta\equiv\delta_R=\delta_r=0.3$ and selected values of the spin S, while $s=\frac{1}{2}$. In the limiting case $S=s=\frac{1}{2}$ the results by Harada[13] are reproduced.

In Fig. 9 we report the temperature dependence of the inverse correlation length $1/\xi$ for the alternating-spin ($S=\frac{7}{2}$, $s=\frac{1}{2}$) Ising chain, as calculated from Eq. (19). For $T\to 0$ one has the usual exponential dependence, typical of the Ising model. It is clearly seen that in correspondence to the temperature T_L, the correlation length decreases to 0, a feature already observed by Harada[13] in the case $S=s=\frac{1}{2}$, which corresponds to the cancellation between the competing (ferromagnetic NN and antiferromagnetic NNN) interactions.

IV. EXPERIMENTAL RESULTS IN R(Hfac)$_3$NITEt

In the preceding sections we have presented a systematic transfer-matrix study of the alternating-spin (S,s) Ising model with competing NN and NNN exchange interactions. Now we want to discuss the relevance of our calculation with respect to the new class of quasi-1D molecular magnetic materials, R(hfac)$_3$NITEt, whose magnetic properties are determined by rare-earth ions (R=Gd, Tb, Dy, Ho, Er, ...) with spin S and organic radicals with spin $s=\frac{1}{2}$.[4–8]

The feature of an overall antiferromagnetic behavior of the isothermal susceptibility in the paramagnetic phase, experimentally observed in these systems,[4–8] is qualitatively explained in the framework of the alternating-spin Ising model which we have investigated. In fact we have shown that if the antiferromagnetic NNN exchange dominates over the NN ferromagnetic one ($\delta_R+\delta_r>1$), a "two-spin-up-two-spin-down" ground state is energetically favored and the isothermal susceptibility presents an antiferromagneticlike behavior, i.e., vanishes exponentially for $T\to 0$ (see Fig. 1) and tends to a constant value for $T\to\infty$ [see Eq. (20)], so that χ has a maximum at finite temperature.

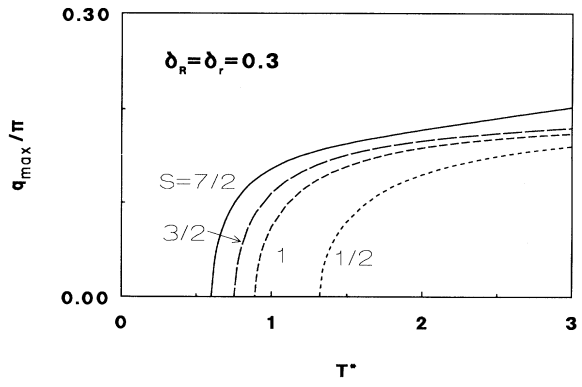

FIG. 8. Temperature dependence of the absolute maximum $q_{\max}$ of the static structure factor $\mathcal{S}(q)$, for fixed $\delta_R=\delta_r=0.3$ and $s=\frac{1}{2}$, at selected values of S, as indicated by the labels.

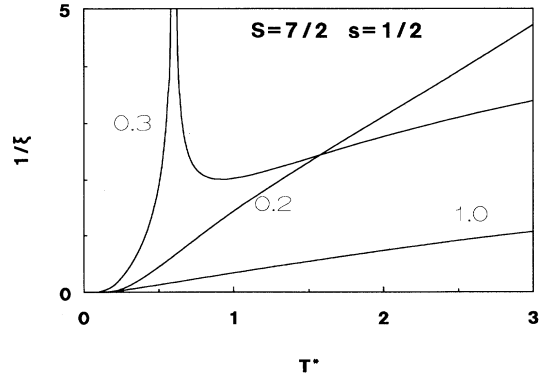

FIG. 9. Temperature dependence of the inverse of the correlation length, as calculated from Eq. (19) for an alternating-spin ($S=\frac{7}{2}$, $s=\frac{1}{2}$) Ising chain, at selected values of $\delta\equiv\delta_R=\delta_r$, as indicated by the labels.

In the framework of spin models with a continuous symmetry, like the planar and the Heisenberg ones, the competition between NNN and NN exchange couplings would lead to a helical ground state;[14–17] in this case, the isothermal susceptibility χ is expected to be constant at $T=0$, so that χT would vanish *linearly* for $T\rightarrow 0$. Indeed, such a feature has been experimentally observed in the $Gd(hfac)_3NITEt$ chain in zero field,[22] which does not show any 3D transition temperature down to about 1 K.[5] However, for a quantitative comparison, it would be necessary to develop a transfer-matrix study for the Heisenberg model with alternating spins (S,s) and competing NN and NNN interactions.

In the other magnetic chains with anisotropic rare-earth ions, which are expected to be better described by a planar or Ising model, the low-temperature dependence of the 1D isothermal susceptibility cannot be ascertained, owing to the onset of the 3D phase transition at temperatures ranging from 1.2 to 3.2 K.[5,22] Single-crystal measurements of the susceptibility[5,22] in some of the anisotropic chain systems show that the Ising model we have investigated is never completely appropriate. However, at not too low temperatures our transfer-matrix calculation of χT, Eq. (12), can be used to give a preliminary fit of the exchange parameters. For example, in the case of $Ho(hfac)_3NITEt$, with effective $S=1$ and $g_R=8.6$ for the metal ion, one is able to reproduce the maximum at 7 K observed for χ in a field of 200 Oe, using reasonable values of the parameters (R = Ho, r = organic radical): $J_{RR}=-5.04$ K, $J_{R-r}=3.74$ K, $J_{rr}=-11.08$ K.[5,22]

Additional experimental work on single-crystal samples of rare-earth–organic-radical molecular magnets is in progress in order to better characterize them, e.g., measurements of the magnetic specific heat at low temperatures.[22]

Also, it would be very interesting to perform quasielastic neutron-scattering experiments, in order to ascertain in a direct way the nature of the short-range order via the position of the maximum $q_{\max}$ in the static structure factor $\mathcal{S}(q)$.

V. CONCLUSIONS

We have presented a numerical transfer-matrix study of the thermodynamical properties of an alternating-spin (S,s) 1D Ising model with competing NN and NNN exchange couplings.

The partition function and the two-spin-correlation functions have been expressed in terms of the eigenvalues and (left and right) eigenvectors of an $M\times M$ *nonsymmetric* real matrix, with $M=(2s+1)(2S+1)$. Some analytical results have been obtained for $T\rightarrow 0$ and $T\rightarrow\infty$. In the limiting case $S=s=\frac{1}{2}$, the results by Harada[13] have been correctly recovered.

For $S\neq s$, some thermodynamical properties show features very similar to the $S=s=\frac{1}{2}$ case. Among them we mention:

(1) a crossover from diverging (ferromagneticlike) to vanishing (antiferromagneticlike) isothermal susceptibility in the limit $T\rightarrow 0$, upon variation of the ratio between the competing NNN and NN exchange couplings;

(2) a sharp peak in the temperature dependence of the specific heat, as a consequence of the excitation of domain walls in the chain, for suitable values of the exchange parameters;

(3) a nonmonotonic temperature dependence of the correlation length, for opportune values of the competing NN and NNN exchange: indeed, one finds a vanishing correlation length at a finite temperature T_L, the pseudo-Lifshitz point.[12,13]

We have found that the most striking effect of the alternation of different spins ($S\neq s$) along the chain is shown by the static structure factor, which at low temperatures can present *two* peaks (with different heights), signaling the coexistence of different short-range-order configurations in the system.

Finally, we have shown that our simple Ising model is able to qualitatively explain the experimental feature of an overall antiferromagnetic behavior of the isothermal susceptibility observed[4–8] in $R(hfac)_3NITEt$ (R = Gd, Tb, Dy, Ho, Er, . . .). In order to obtain a quantitative fit of the competing NN and NNN exchange parameters, a similar transfer-matrix study for the planar and Heisenberg models should be performed. Also, additional low-temperature experimental results are necessary for a better characterization of such quasi-1D molecular materials.

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[1] M. Steiner, J. Villain, and C. G. Windsor, Adv. Phys. **25**, 88 (1976).

[2] M. Verdaguer, A. Gleizes, J. P. Renard, and J. Seiden, Phys. Rev. B **29**, 5144 (1984).

[3] *Organic and Inorganic Low-Dimensional Crystalline Materials*, NATO Advanced Study Institute Series B: Physics Vol. 168 edited by P. Delhaes and M. Drillon (Plenum, New York, 1987).

[4] D. Gatteschi and R. Sessoli, J. Magn. Magn. Mater. **104-107**, 2092 (1992).

[5] D. Gatteschi, C. Benelli, A. Caneschi, and R. Sessoli, in *Proceedings of the 37th MMM Conference, Houston, Texas, 1992* [J. Appl. Phys. (to be published)].

[6] C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, and P. Rey, Inorg. Chem. **29**, 4223 (1990).

[7] C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, and P. Rey,

Inorg. Chem. **28**, 275 (1989).
[8]C. Benelli, A. Caneschi, D. Gatteschi, and L. Pardi, in *Electron Spin Resonance of Disordered Systems,* edited by N. D. Yordanov (World Scientific, Singapore, 1989), p. 291.
[9]C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, and P. Rey, Inorg. Chem. **28**, 3230 (1989).
[10]J. Stephenson, Can. J. Phys. **48**, 1724 (1970).
[11]T. Morita and T. Horiguchi, Phys. Lett. A **38**, 223 (1972).
[12]W. Selke and M. E. Fisher, Phys. Rev. B **20**, 257 (1979); R. M. Hornreich, R. Liebmann, H. G. Schuster, and W. Selke, Z. Phys. B **35**, 91 (1979).
[13]I. Harada, J. Phys. Soc. Jpn. **52**, 4099 (1983).
[14]I. Harada, J. Phys. Soc. Jpn. **53**, 1643 (1984).
[15]B. Carazza, E. Rastelli, and A. Tassi, Z. Phys. B **80**, 293 (1990).
[16]B. Carazza, E. Rastelli, and A. Tassi, Z. Phys. B **83**, 301 (1991).
[17]I. Harada and H. J. Mikeska, Z. Phys. B **72**, 391 (1988).
[18]R. Peierls, Proc. Cambridge Philos. Soc. **32**, 477 (1936).
[19]W. H. Press, B. P. Flannery, S. A. Tenkolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, England, 1986), p. 337.
[20]J. Stoer and R. Burlish, *Introduction to Numerical Analysis* (Springer-Verlag, New York, 1980), p. 356.
[21]In Ref. 13, Harada did not report the temperature dependence for the heat capacity. In his notations, $\beta J_1 s^2 = K_1$, $\beta J_2 s^2 = K_2$, and $\lambda_0 = \lambda_+^2$.
[22]D. Gatteschi *et al.* (private communication).