

Effect of Chiral Domain Walls on the Specific Heat of $\text{Gd}(\text{hfac})_3\text{NITR}$ ($R = \text{Ethyl, Isopropyl, Methyl, Phenyl}$) Molecular Magnetic Chains

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We measured the thermodynamic properties for a class of quasi-one-dimensional (1D) molecular magnets with alternating spins and competing nearest- and next-nearest-neighbor exchange interactions. For the two compounds with higher frustration ($R = \text{ethyl}$ and $R = \text{isopropyl}$), which present a genuine 1D magnetic behavior down to the lowest measured temperatures (0.08 and 0.5 K), a peak at $T \approx 2$ K was observed in the specific heat, and attributed to the excitation of chiral domain walls. [S0031-9007(96)00593-5]

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One-dimensional (1D) localized magnets have been the subject of intensive activity for the last three decades. This continuously renewed interest lies in the fact that it has always been possible to synthesize real systems where even the most surprising theoretical predictions have been tested and successfully verified: e.g., Haldane's conjecture [1] of a disordered ground state for isotropic Heisenberg antiferromagnetic chains with integer spin values has been confirmed in a variety of real compounds [2]; the spin-Peierls transition towards a dimerized antiferromagnetic chain has been clearly observed in Cu-GeO_3 [3]. Also, conclusive experimental evidence has been obtained that nonlinear topological excitations like solitons give a significant contribution to the properties of easy-plane quasi-1D systems in a symmetry-breaking field [4]. In this comforting outline, there is an exception: Harada's prediction [5] of a significant contribution of chiral domain walls to the thermodynamic properties of a magnetic chain with competing exchange interactions has not yet been experimentally verified. Harada [5] proposed that the competition between nearest-neighbor (nn) and next-nearest-neighbor (nnn) exchange can give rise to a helical phase, whose twofold chiral degeneracy (i.e., clockwise and counterclockwise turns of spins along the chain) leads to the excitation of topologically stable chiral domain walls, separating two domains of opposite chirality. The helical short-range order is possible only if the ratio between nnn and nn exchange couplings exceeds a threshold value; the interchain exchange and the uniaxial anisotropy must be very weak. Furthermore, it has been suggested [6] that, in the integer spin case, frustration should favor the Haldane disordered state [1], while in the $s = 1/2$ Heisenberg antiferromagnetic chain with

strongly competing interactions, a spontaneous dimerization is present with a gap for the excitations [7].

In this Letter, we present a study of the thermodynamic properties for a series of molecular-based quasi-1D magnets [8] recently synthesized: $\text{Gd}(\text{hfac})_3\text{NITR}$ [hfac is hexafluoro-acetylacetonate and NITR is 2- R -4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-oxide], where $R = \text{isopropyl, ethyl, methyl, phenyl}$ (hereafter denoted by iPr, Et, Me, Ph). Their magnetic properties are determined by Gd^{3+} rare-earth ions (with spin $S = 7/2$), and nitronyl nitroxide organic radicals R (with $s = 1/2$), alternating along the chain and interacting via competing nn and nnn exchange.

The four compounds were prepared according to the methods previously reported [9–11]. The structures of all of them, except for the NITPh derivative, have been determined through single crystal x-ray diffractometry, and have been found to be very similar. Linear chains are originated by the alternance of $\text{Gd}(\text{hfac})_3$ moieties and nitronyl nitroxide radicals. The chains are well separated one from the other by the presence of the bulky ligands, the shortest interchain Gd-Gd distance being 10.5 Å, and only weak dipolar interactions are supposed to be active between chains, as also observed in an Mn analog for which a $J_{\text{inter}}/J_{\text{intra}}$ ratio smaller than 10^{-5} has been suggested [9]. The 1D character of these Gd-radical chains is confirmed by the single-crystal EPR spectra previously recorded on $\text{Gd}(\text{hfac})_3\text{NITEt}$, which show the magic angle behavior of the linewidth typical of 1D magnetic systems [10].

In Fig. 1 we report the T dependence of the molar magnetic susceptibility $\chi_M T$ of microcrystalline powders of the various compounds, measured by SQUID magnetome-

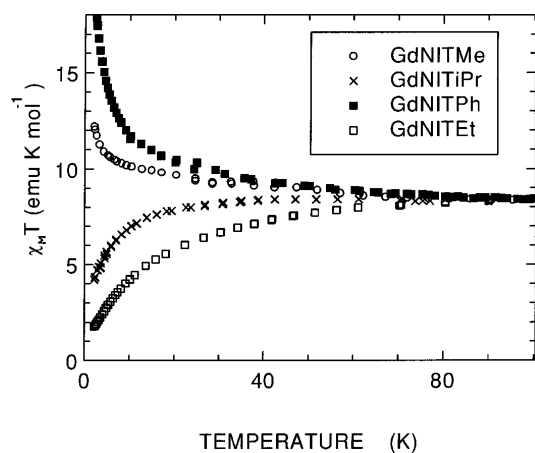


FIG. 1. SQUID data of the molar magnetic susceptibility $\chi_M T$ versus T for $\text{Gd}(\text{hfac})_3\text{NITR}$ for the four title compounds in an applied field $H = 1$ kG.

try in an applied field of 1 kG. For the compounds with $R = \text{Et}$, iPr , $\chi_M T$ was found to decrease with decreasing T , a behavior which resembles that of an antiferromagnet but is impossible to explain in the framework of a model with only nearest-neighbor interactions, because for ferromagnetic nn exchange one would have a ferromagnetic spin arrangement, while for antiferromagnetic nn exchange a ferrimagnetic configuration would be favored: in both cases, one would find $\chi_M T$ to increase with decreasing T . Alternative explanations of strong antiferromagnetic interchain interactions or strong alternation of intrachain nearest-neighbor interactions can be rejected on the basis of structural and magnetic resonance evidence [10]. For $\text{Gd}(\text{hfac})_3\text{NITEt}$, we proposed [12] that the anomalous “antiferromagnetic” behavior, observed also in the compound with $R = \text{iPr}$, might be due to dominant nnn antiferromagnetic exchange, in strong competition with the nn one. The other two compounds with $R = \text{Ph}$, Me present

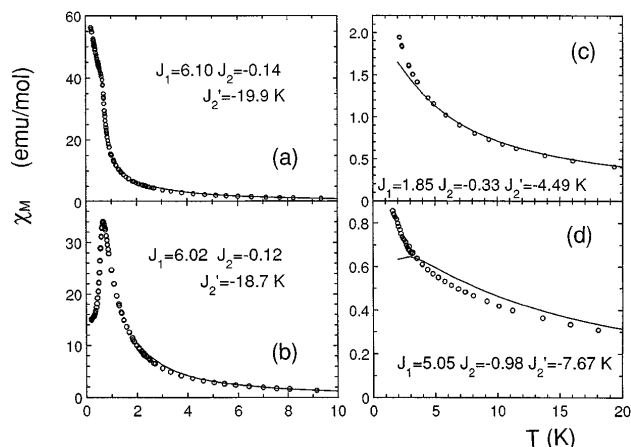


FIG. 2. Low T data (symbols) of the molar magnetic susceptibility of the four compounds, compared with numerical transfer matrix results (full lines) for the classical planar model (1). (a) $R = \text{Me}$, (b) $R = \text{Ph}$, (c) $R = \text{iPr}$, (d) $R = \text{Et}$.

a $\chi_M T$ which increases with decreasing T , indicating a much weaker frustration.

Low T measurements of the molar magnetic susceptibility χ_M are reported in Fig. 2. In the compounds with $R = \text{Ph}$, Me , a phase transition to 3D long-range order at $T_C \approx 0.6$ K was signaled by a change of slope in χ_M . In order to fit the susceptibility data, we performed numerical transfer matrix calculations of the thermodynamic properties for a 1D magnet with spins (S, s) alternating along the chain, subject to competing nn ferromagnetic ($J_1 > 0$) and nnn antiferromagnetic ($J_2 < 0$ and $J_2' < 0$) exchange interactions [12–14], with Hamiltonian

$$\begin{aligned} \mathcal{H} = & -J_1 \sum_{n=1}^{N/2} (\mathbf{S}_{2n-1} \cdot \mathbf{s}_{2n} + \mathbf{s}_{2n} \cdot \mathbf{S}_{2n+1}) \\ & -J_2 \sum_{n=1}^{N/2} \mathbf{S}_{2n-1} \cdot \mathbf{S}_{2n+1} - J_2' \sum_{n=1}^{N/2} \mathbf{s}_{2n} \cdot \mathbf{s}_{2n+2} \\ & -g\mu_B H \sum_{n=1}^{N/2} S_{2n+1}^x - g'\mu_B H \sum_{n=1}^{N/2} s_{2n}^x, \end{aligned} \quad (1)$$

where we take periodic boundary conditions $\mathbf{S}_{N+1} = \mathbf{S}_1$, $\mathbf{s}_{N+2} = \mathbf{s}_2$. To limit the amount of calculations, the spins were approximated by classical planar rotators in the x - y plane (perpendicular to the chain direction), where a magnetic field H is applied. At $T = 0$ and in zero field one easily finds that for $2(\delta + \delta') < 1$ the system undergoes ferromagnetic order, while for $2(\delta + \delta') > 1$ it shows helical order with wave number $\pm Q$, where $\cos Q = 1/2(\delta + \delta')$ and we have defined $\delta = |J_2|S^2/J_1Ss$, $\delta' = |J_2'|s^2/J_1Ss$. A much more complicated scenario is found for nonzero field [13]. A best fitting of the susceptibility data yields an estimate of the Hamiltonian exchange constants for the series of compounds under study: see Fig. 2 [15]. For the two compounds with $R = \text{Et}$, iPr , our data support the hypothesis of a dominating nnn antiferromagnetic exchange, leading to helical long-range order with $Q = \pm 0.397\pi$ and $\pm 0.399\pi$, respectively. These values are to be compared with the limiting value $Q = \pm \pi/2$ which one would have for $\delta, \delta' \rightarrow \infty$. For the other two compounds, with $R = \text{Me}$, Ph , frustration effects are found to be weaker: the fitted exchange constants imply a helical long-range order characterized by $Q = \pm 0.206\pi$ and $\pm 0.175\pi$, respectively [16].

In Fig. 3 we report the temperature dependence of the molar specific heat of the four title compounds, measured between 0.2 and 5 K by a quasiadiabatic heat pulse technique. The measurements on the $R = \text{Et}$ compound were performed down to 80 mK in a calorimeter employing the relaxation method, operating in a ^3He - ^4He refrigerator in the Kamerlingh Onnes Laboratorium in Leiden. In both sets of equipment the absolute error in the heat capacity was not greater than 1%. The specific heat data of the weakly frustrated compounds, $R = \text{Me}$, Ph , are shown together in Fig. 3(a) in a double-log plot. They both show at high temperatures a tendency towards a T^3 dependence (solid line), characteristic of the lattice contribution

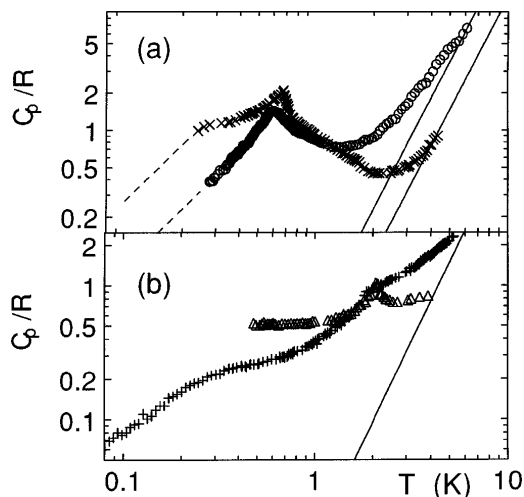


FIG. 3. Molar specific heat of $\text{Gd}(\text{hfac})_3\text{NITR}$. (a) Crosses: $R = \text{Me}$; open circles: $R = \text{Ph}$. (b) Crosses: $R = \text{Et}$; open triangles: $R = \text{iPr}$. Dashed line: $T^{3/2}$ spin-wave contribution. Full line: T^3 lattice contribution.

at low temperatures. Its extrapolation to lower temperatures demonstrates that the lattice contribution is 2 orders of magnitude lower than the magnetic one at 1 K. Both compounds show a neat λ peak at $T_C = 0.68$ and 0.6 K for the $R = \text{Me}$ and Ph compounds, respectively. On the low temperature side of the peak, both compounds show a tendency to a $T^{3/2}$ temperature dependence, i.e., the predicted behavior for a 3D ferromagnetic quantum spin-wave contribution at very low temperatures. The total anomalous entropy content, calculated taking into account the low temperature extrapolation and subtracting the lattice contributions, is $\Delta S/R = 2.76(7)$ and $2.65(8)$ for the $R = \text{Me}$ and Ph compounds, respectively ($R = N_A k_B$), very close to $4 \ln 2$, as expected for two sublattices, one with $S = 7/2$ and the second with $s = 1/2$ spins. The entropy content above T_C is 1.04 and 1.84, respectively. Such a high value for the high temperature tail, much higher than for a 3D peak, is characteristic of the presence of strong short-range order due to the 1D character of the magnetic system. This is especially so in the case of $R = \text{Ph}$. The λ peak is interpreted, thus, as the establishment of 3D long-range order due to interchain interaction. In Fig. 3(b) we show the data for the strongly frustrated compounds with $R = \text{Et}$ and iPr . In both compounds the experimental curves are drastically different from the previous cases. The high temperature heat capacity tail did not tend to the T^3 lattice contribution for the measured temperatures. However, if one considers the similarity of structure with the $R = \text{Me}$, Ph compounds, it is reasonable to use the highest lattice contribution as an estimation for $R = \text{Et}$, iPr . In the low temperature region only the $R = \text{Et}$ compound could be measured down to 80 mK, while the $R = \text{iPr}$ one was measured down to 500 mK. The heat capacity below the anomaly shows a tendency to a plateau in the region near $T = 500$ mK for both compounds. In the $R = \text{Et}$ com-

pound, at lower temperature $C_p(T)$ starts decreasing almost linearly: $C_p(T) = 0.80(5)T$. (For $R = \text{iPr}$ a similar behavior may be expected, even though new data for $T \leq 500$ mK are required.) This is a very important result since (a) it allowed us to extrapolate to $T = 0$ and evaluate the total entropy $\Delta S/R = 2.74(4)$, just a bit lower (4%) than $4 \ln 2$, so we are sure of having observed all the magnetic contribution, and (b) the linear T dependence allowed us to conclude that the system remains one-dimensional and antiferromagnetically coupled down to the lowest temperatures. In fact, this is the predicted behavior for a 1D antiferromagnetic quantum spin-wave contribution at low temperatures. In contrast, for a 1D system with a 3D transition, the slope of the low temperature tail of the specific heat anomaly would be $T^{3/2}$ or T^3 for a 3D ferromagnet or antiferromagnet, respectively [17]. Moreover, for the $R = \text{Et}$ and iPr compounds, the measured susceptibilities do not show any change of slope in correspondence to $T \approx 2$ K, the location of the specific heat anomaly.

All these facts allow us to assure one that the magnetic behavior of the $R = \text{Et}$, iPr compounds is 1D even at the lowest temperatures measured. Then, the peaks observed are not due to 3D ordering but to a different mechanism. In both cases the peak appears at $T_{\text{peak}} \approx 2$ K; its height amounts to $\Delta C_{\text{peak}}/R = 0.4$ and 0.2 for the $R = \text{iPr}$ and Et cases, respectively. These anomalies are shown in Fig. 4. Also the hypothesis of a Schottky anomaly can be readily ruled out, since the observed peak position would imply unrealistically high values for the anisotropy of $\text{Gd}(\text{III})$ [12]. Thus, taking into account also the previous analysis of the susceptibility data, we are led to hypothesize that the peaks at $T_{\text{peak}} \approx 2$ K could be due to the excitation of topologically stable chiral domain walls, separating two domains of opposite chirality, firstly predicted by Harada [5]. To confirm this interpretation, we performed numerical transfer matrix calculations of the magnetic specific heat C_M/R versus T for the classical planar model: see Fig. 5, where the interaction parameters obtained from the magnetic susceptibility (Fig. 2) were used. Even though for $T \rightarrow 0$, the calculated classical specific

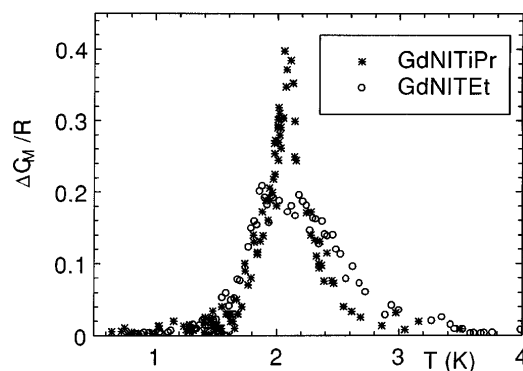


FIG. 4. Experimentally determined excess specific heat $\Delta C_M/R$ versus T for the compounds with $R = \text{iPr}$ (stars) and $R = \text{Et}$ (open circles).

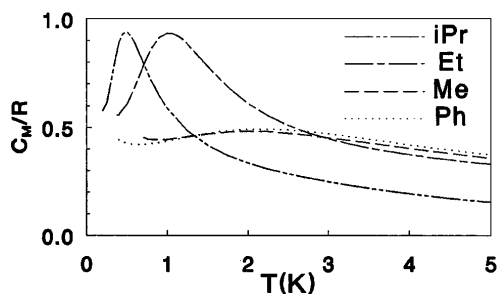


FIG. 5. Numerical transfer matrix calculations of the magnetic specific heat C_M/R versus T using the interaction parameters quoted in Fig. 2.

heat tends to 0.5 owing to the energy equipartition theorem, thus preventing a comparison with the measured low T tail of the specific heat anomaly, our approximate transfer matrix calculations allow us to justify, in a qualitative way, the different behavior shown by the two classes of compounds. Indeed, for the compounds with lower frustration ($R = \text{Ph, Me}$) we find a broad peak, with no indication for the excitation of chiral domain walls. For the compounds with a higher degree of frustration ($R = \text{Et, iPr}$), a sharp peak—which is the signature of the excitation of chiral domain walls [5]—develops. These findings are comforting, even though the calculated peak positions ($T_{\text{peak}} \lesssim 1$ K) are in poor agreement with the experimental ones: again, this can be ascribed to the inadequacy of a classical planar model in order to reproduce such a model-sensitive property as the specific heat. Clearly, for a detailed comparison, a correct quantum treatment of the $s = 1/2$ radical, alternating along the chain with the classical $S = 7/2$ Gd^{+3} ion, would be required [18]. Moreover, a Heisenberg model would be more appropriate for the Gd(III) ion, which has a $^8S_{7/2}$ state.

In conclusion, our specific heat data for the quasi-1D compounds $\text{Gd}(\text{hfac})_3\text{NITEt}$ and $\text{Gd}(\text{hfac})_3\text{NITiPr}$ provide the first experimental evidence for the contribution of chiral domain walls to the thermodynamic properties of a 1D magnetic system with competing nn and nnn exchange interactions, as predicted by Harada [5].

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