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**Magnetic and thermal properties of 4f-3d ladder-type molecular compounds**

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We report on the low-temperature magnetic susceptibilities and specific heats of the isostructural spin-ladder molecular complexes  $L_2[M(\text{opba})]_3 \cdot x\text{DMSO} \cdot y\text{H}_2\text{O}$ , hereafter abbreviated by  $L_2M_3$  (where  $L=\text{La, Gd, Tb, Dy, Ho}$  and  $M=\text{Cu, Zn}$ ). The results show that the Cu containing complexes (with the exception of  $\text{La}_2\text{Cu}_3$ ) undergo long-range magnetic order at temperatures below 2 K, and that for  $\text{Gd}_2\text{Cu}_3$  this ordering is ferromagnetic, whereas for  $\text{Tb}_2\text{Cu}_3$  and  $\text{Dy}_2\text{Cu}_3$  it is probably antiferromagnetic. The susceptibilities and specific heats of  $\text{Tb}_2\text{Cu}_3$  and  $\text{Dy}_2\text{Cu}_3$  above  $T_C$  have been explained by means of a model taking into account nearest- as well as next-nearest-neighbor magnetic interactions. We show that the intraladder L-Cu interaction is the predominant one and that it is ferromagnetic for  $L=\text{Gd, Tb, and Dy}$ . For the cases of Tb, Dy, and Ho containing complexes, strong crystal field effects on the magnetic and thermal properties have to be taken into account. The magnetic coupling between the (ferromagnetic) ladders is found to be very weak and is probably of dipolar origin.

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**I. INTRODUCTION**

In today's search for smaller, faster, more selective and efficient products and processes, the engineering of well-defined spatial microarrangements of pure and composite materials is of vital importance for the creation of new magnetic devices. A possibility to assemble microstructures in a controlled way is to use molecular-based materials. The design of novel ferromagnetic molecular materials is certainly among the stimulating subjects.<sup>1</sup> In such a context, molecular complexes based on transition metal ions are good candidates because the procedures for predicting the ferromagnetic nature of the interaction in this class of materials have become fairly well established.<sup>2,3</sup> However, such an understanding is much less advanced when a lanthanide ion is involved. Magnetic investigations concerning molecular materials containing lanthanide and transition metal ions have been overlooked until recently due to the weak interactions present and the complications added by the orbital contribution of lanthanide ions.<sup>4</sup> The case of Gd with a  $^8S_{7/2}$  single-ion ground state and a quenched orbital contribution is spe-

cial; most of the interest has been focused on the Gd-Cu combination because of the very frequently found ferromagnetic character of the Gd-Cu interaction.<sup>5-14</sup> Coupling those blocks in a 3D lattice would produce molecular magnets and possibly ferromagnets.

In an extended polynuclear complex, namely,  $\text{Gd}_2(\text{ox}) \times [\text{Cu}(\text{pba})]_3[\text{Cu}(\text{H}_2\text{O})_5] \cdot 20\text{H}_2\text{O}$  [hereafter abbreviated with  $\text{Gd}_2\text{Cu}_3(\text{pba})$ ] with pba=1,3-propanediyl(oxamato), not only was the ferromagnetic coupling of the Gd-Cu interaction recently reported, but also the onset of a long-range magnetic order.<sup>15,16</sup> The crystal structure of this compound consists of layers of double-sheet polymers separated by water molecules. A puckered arrangement of  $\text{Gd}[\text{Cu}(\text{pba})]$  units forms a two-dimensional honeycomb pattern connected by oxalato groups. Discrete  $[\text{Cu}(\text{H}_2\text{O})_5]^{2+}$  entities are interspersed in the gap between the layers. From specific heat measurements, the onset of low-dimensional short-range order was found at temperatures around 1.5 K. By further lowering the temperature, the phase transition to three-dimensional ferromagnetic long-range ordering was observed at  $T_C=1.05$  K. This compound represents a

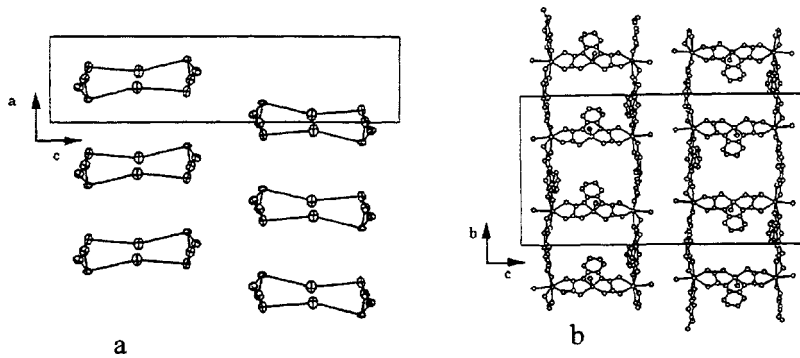


FIG. 1. Relative dispositions of the ladders: (a) schematic view of the ladders projected in the  $ac$  plane; (b) view of two neighboring ladders in the  $bc$  plane. The lanthanide ions are located on the sides of the ladder and occupy each corner, while each transition metal ion is between two lanthanide ions along the sides and in the rungs.

molecular-based ferromagnet involving lanthanide ions.

Although long-range ferromagnetic order has thus been found in  $\text{Gd}_2\text{Cu}_3(\text{pba})$ , this material is isotropic due to the fact that both the Gd ions and the Cu ions are magnetically isotropic. A successful method to increase the intrinsic anisotropy is to synthesize intermetallic lanthanide ( $L$ ) and transition metal ( $M$ ) compounds, where the  $L$  has an orbital contribution, that introduces the anisotropy that the transition metal is lacking. Such a strategy has of course been applied in research on metallic ferromagnets, such as  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . The strong orbit coupling within  $L$ , on one side, and the intense  $L-M$  exchange coupling has the net effect of polarizing the two sublattices in a direction, thus creating a strong uniaxial magnet, albeit, in a restricted temperature region.<sup>17</sup> The same method in trying to increase the uniaxial anisotropy has been applied in a series of molecular compounds based on  $L$  and  $M$  ions, by choosing the  $L$  that induces such anisotropy (first condition), while expecting that the  $L-M$  interaction remains ferromagnetic and of similar intensity to that in the  $\text{Gd}_2\text{Cu}_3(\text{pba})$  compound (second condition). The  $L$  anisotropy of the ground state depends on the crystal field acting on the orbital moment.

In what follows, we shall describe the magnetic and thermal properties of a series of isostructural complexes based on lanthanide and transition metal ions. The general chemical formula of the compounds here studied is  $L_2[M(\text{opba})]_3 \cdot x\text{DMSO} \cdot y\text{H}_2\text{O}$  (hereafter abbreviated by  $L_2M_3$ ) where  $L = \text{La, Gd, Tb, Dy, Ho}$  and  $M = \text{Cu, Zn}$ , and  $\text{opba}$  stands for *ortho*-phenylenebis(oxamato), while DMSO stands for dimethylsulfoxide. In view of previous work (Ref. 18) proving that the  $L$ -Cu exchange for light  $L$  substitutions is antiferromagnetic, thus not fulfilling the second necessary condition above mentioned, we have chosen to explore only the heavy  $L$  substitutions. Out of these, the most promising are the Tb and Dy substitutions, where there are already evidences of ferromagnetic coupling with Cu from susceptibility measurements, while no hint of such was found for Er, Tm, or Yb.<sup>18</sup> Recently, we have also reported, by means of specific heat experiments, the onset of long-range magnetically ordered states in the Tb and Dy substituted compounds.<sup>19</sup> In this article we combine the thermal properties of  $L_2M_3$  together with low-temperature susceptibility measurements, and explain the obtained results by means of theoretical calculations.

Another interesting property of this series of isostructural complexes is that they exhibit a spin ladder structure. Spin

ladders are low-dimensional magnetic quantum systems that consist of two or more strongly magnetically coupled chains of spins and are thus intermediate between one and two dimensional magnetic systems. The magnetic properties of spin-ladder systems have received a renewed experimental and theoretical interest since the discovery that the microscopic mechanisms in such systems may be related to the ones governing high- $T_C$  superconductivity.<sup>20,21</sup> In addition to  $(\text{VO})_2\text{P}_2\text{O}_7$ , that has been recently shown to be an alternating spin chain<sup>22</sup> rather than a spin-ladder as previously thought,<sup>23</sup> a number of cuprate materials have been proposed as examples of spin-ladder systems, such as  $\text{SrCu}_2\text{O}_3$ ,<sup>24</sup>  $\text{LaCuO}_{2.5}$ ,<sup>25</sup>  $(\text{C}_5\text{H}_{12}\text{N})_2\text{CuBr}_4$ ,<sup>26</sup> and  $(\text{5IAP})_2\text{CuBr}_2 \cdot 2\text{H}_2\text{O}$ .<sup>27</sup> The research on novel molecular complexes with ladder geometries is a very important task for a better understanding of the physics behind these complex systems.<sup>28</sup>

## II. STRUCTURAL AND EXPERIMENTAL DETAILS

Information on the structure of the  $L_2M_3$  series of compounds has been provided in detail in Refs. 29, 30. Here, we summarize the most important information in view of the analysis of the magnetic properties given below.

The compounds crystallize very poorly and, consequently, a complete x-ray diffraction analysis could not be performed to determine the structure. Instead, the wide-angle x-ray scattering (WAXS) technique has been used to obtain structural information. Even though the WAXS technique cannot give the exact structure as compared to a full x-ray diffraction study, it has been successfully applied in several cases, for instance to structurally characterize inorganic polymers.<sup>31</sup> Furthermore, a complete structure determination by x-ray diffraction has been carried out on a related and very similar spin-ladder compound, namely,  $\text{Tm}_2[\text{Cu}(\text{opba})]_3 \cdot x\text{DMF} \cdot y\text{H}_2\text{O}$  ( $x \approx 10$ ,  $y \approx 4$ ). This crystal structure has therefore been utilized as a starting point to interpret the WAXS data for the  $L_2M_3$  compounds.

The analyses strongly suggested that the structure of  $L_2M_3$  is likewise based on a discrete, infinite ladderlike motif, as shown in Fig. 1. The sidepieces of the ladder consist of  $L_2[M(\text{opba})]_3$  units developing along the  $b$  direction with an alternation of  $L(\text{III})$  and  $M(\text{II})$  ions. Rungs provided by the precursor  $[M(\text{opba})]^{2-}$ , located between two  $L$  ions, connect the sidepieces. The  $L-M$  distance across an oxamato bridge is  $\approx 5 \text{ \AA}$ , while the distance between two  $L$

ions across a  $M(\text{opba})$  group is  $\approx 11 \text{ \AA}$ . The shortest distance between two  $L$  ions ( $\approx 10 \text{ \AA}$ ) involves nonconnected  $L$  ions belonging to two sidepieces of neighboring ladders.

Each  $L$  ion is surrounded by seven oxygen ions, six of which belong to three opba ligands and one to a water molecule. The  $L$  coordination polyhedrons may be described as capped trigonal antiprisms. All the compounds are highly solvated with DMSO and  $\text{H}_2\text{O}$  molecules, and the exact number of noncoordinated solvent molecules is not known accurately. Some of these molecules are easily removed. Therefore, there is some uncertainty in the molecular weight of the compounds and consequently in the absolute value of the molar susceptibility and specific heat.

The experiments done in the course of this work consisted primarily in measurements of three quantities: magnetic susceptibility, magnetic moment, and specific heat. Magnetic moment and susceptibility data down to 1.7 K were obtained with a commercial SQUID-based magnetometer with an ac option. The ac susceptibility of  $\text{Gd}_2\text{Cu}_3$  in the temperature range  $0.1 \text{ K} < T < 3 \text{ K}$  was measured in Zaragoza with a mutual inductance technique in a dilution refrigerator. The excitation amplitude was 10 mOe and the frequency  $f = 160 \text{ Hz}$ . The signal was measured by means of a low-impedance ac bridge, in which a SQUID was employed as a null detector.<sup>32</sup> The low-temperature susceptibilities down to 5 mK of  $\text{Tb}_2\text{Cu}_3$ ,  $\text{Dy}_2\text{Cu}_3$ , and  $\text{Ho}_2\text{Cu}_3$  were measured in Leiden with an ac susceptometer directly mounted inside the mixing chamber of a dilution refrigerator. The frequency of the experiments was  $f = 520 \text{ Hz}$ . The data in the overlap region between 1.70 and 3 K were used to convert the low-temperature data from arbitrary into absolute units. The specific heat measurements on  $\text{Gd}_2\text{Cu}_3$ ,  $\text{Gd}_2\text{Zn}_3$ , and  $\text{Dy}_2\text{Cu}_3$  in the range  $0.2 \text{ K} < T < 5.7 \text{ K}$  were performed in Zaragoza by using an adiabatic calorimeter cooled by adiabatic demagnetization, using the heat-pulse technique and Ge thermometry. The error on the specific heat has been estimated to be less than 5%.<sup>33</sup> The specific heats of  $\text{Tb}_2\text{Cu}_3$ ,  $\text{Ho}_2\text{Cu}_3$ , and  $\text{Ho}_2\text{Zn}_3$  were measured down to 0.1 K in Leiden using a thermal relaxation technique. The calorimeter was mounted in a dilution refrigerator and connected to a cold sink through a calibrated heat link. All data were collected on powdered samples of the compounds.

### III. MAGNETIC PROPERTIES ABOVE 2 K

Magnetic properties of systems containing lanthanide ions, such as  $L_2M_3$ , are significantly influenced by the interaction between a lanthanide ion and the surrounding ions in its direct environment. As a result, when a free lanthanide ion is placed in a crystal, its  $2J+1$ -fold degeneracy is partially lifted through electrostatic interaction between its  $f$  electrons and the charges of the surrounding ions. The multiplet is split into a number of states, which can appropriately be termed the crystal field (CF) states. Magnetic susceptibility measurements may offer valuable informations on the CF splittings. In this section we shall first present ac-susceptibility data above 2 K of  $\text{La}_2\text{Cu}_3$ ,  $\text{Gd}_2\text{Cu}_3$ , and  $\text{Gd}_2\text{Zn}_3$  for which the CF effects can be neglected. Thereafter we shall briefly review and reanalyze in terms of the CF

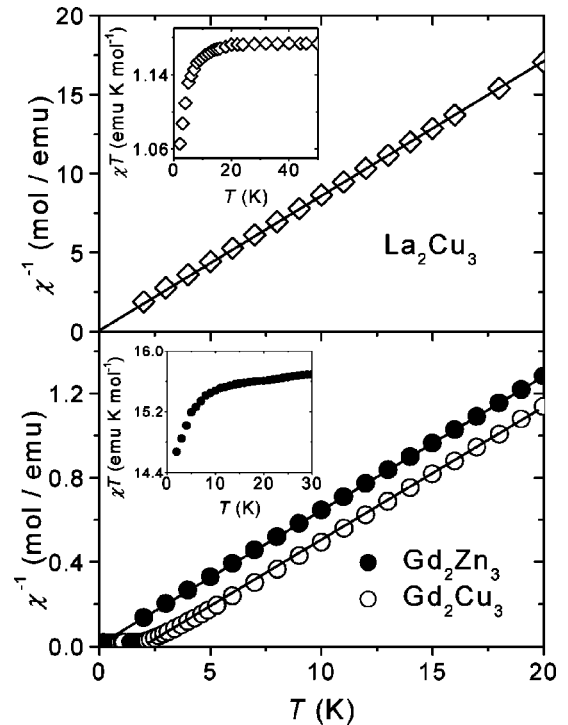


FIG. 2. Top: Experimental molar susceptibility of  $\text{La}_2\text{Cu}_3$ . In the inset: the same data plotted as  $\chi T$  vs  $T$ . Bottom: Inverse of the in-phase susceptibilities of  $\text{Gd}_2\text{Zn}_3$  (●) and  $\text{Gd}_2\text{Cu}_3$  (○). In the inset:  $\chi T$  vs  $T$  for  $\text{Gd}_2\text{Zn}_3$ .

formalism the dc-susceptibility measurements on  $L_2M_3$ , with  $L = \text{Tb, Dy, Ho}$  and  $M = \text{Cu, Zn}$ , which already appeared in Ref. 18.

The ac susceptibility of  $\text{Gd}_2\text{Cu}_3$  was measured with a frequency of 90 Hz and an amplitude of 4 Oe of the exciting field. The dc measurements of Ref. 18 were performed in the temperature range 2–300 K, with a magnetic field of  $10^3 \text{ Oe}$ . Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants as  $-291 \times 10^{-6} \text{ emu/mol}$ . Due to the abovementioned uncertainty in the molecular weights, it was assumed that for each compound the maximum expected value for the Curie constant was reached at 300 K, and the experimental data were rescaled accordingly when necessary.

Hereafter we use the notation  $J$ ,  $J'$ , and  $J''$  for the exchange constants of the  $L$ -Cu, Cu-Cu, and  $L$ - $L$  interactions, respectively (negative values stand for antiferromagnetic interactions).

#### A. $\text{La}_2\text{Cu}_3$ , $\text{Gd}_2\text{Cu}_3$ , and $\text{Gd}_2\text{Zn}_3$

The magnetism of  $\text{La}_2\text{Cu}_3$ , where the lanthanide ion is diamagnetic, allows an estimate of the underlying Cu-Cu interaction. The single-ion magnetic properties of Cu(II) are fairly straightforward. Spin-orbit coupling causes the  $g$  values of the lowest Kramers doublet ( $S = 1/2$ ) to lie in the range 2.0 to 2.3. Figure 2 shows the data of  $\text{La}_2\text{Cu}_3$ , which can be fitted to a Curie-Weiss law with  $\theta = -0.2 \text{ K}$ . This suggests that, even though the distances in the ladder between next-nearest copper ions are as long as  $\approx 10 \text{ \AA}$ , they

still interact with each other with a weak antiferromagnetic superexchange coupling. Taking  $S=1/2$ ,  $\theta=-0.2$  K and  $z=4$  for the number of nearest neighbors for each copper ion, the mean-field expression for the Curie-Weiss temperature<sup>34</sup> provides the value of  $J'/k_B=-0.2$  K for this Cu-Cu interaction.

Gadolinium(III) has a  $^8S_{7/2}$  ground state; the orbital contribution is almost entirely quenched and very isotropic  $g$  values close to the free electron value are found. For temperatures above 2 K, the in-phase ac susceptibility of  $Gd_2Cu_3$  follows a Curie-Weiss law with  $\theta=2.3$  K and  $C=16.4$  emu K mol<sup>-1</sup>, indicating the ferromagnetic nature of the compound (Fig. 2). In the limit  $T \gg \theta$ , the paramagnetic susceptibility can be described by

$$\chi \approx \frac{C}{T} = \frac{2 C_{Gd} + 3 C_{Cu}}{T}, \quad (3.1)$$

where  $C_{Gd}=N\mu_{\text{eff}}^2(\text{Gd})/3k_B$  is the Curie constant of the two gadolinium ions and  $C_{Cu}=N\mu_{\text{eff}}^2(\text{Cu})/3k_B$  is the Curie constant of the three copper ions. Taking  $S_{Gd}=7/2$ ,  $S_{Cu}=1/2$ , and  $g_{Gd}=g_{Cu}=2.00$ , one obtains

$$C=2 C_{Gd} + 3 C_{Cu} = 16.8 \text{ emu K mol}^{-1}$$

which is in satisfactory agreement with the experimental value (16.4 emu K mol<sup>-1</sup>). The same mean-field analysis used above<sup>34</sup> gives the value of  $J/k_B=0.5$  K for the Gd-Cu exchange coupling. The origin of the ferromagnetic nature of the Gd-Cu interaction is further discussed in Sec. V A.

When the copper in  $Gd_2Cu_3$  is substituted by diamagnetic Zn, then the susceptibility of  $Gd_2Zn_3$  could be expected to follow the Curie law for two isolated Gd ions. Nevertheless, Fig. 2 shows that the Curie behavior (with the expected value of  $C=15.7$  emu K mol<sup>-1</sup>) is no longer maintained below 10 K, since a slight decrease of the  $\chi T$  product from 15.7 down to 14.8 emu K mol<sup>-1</sup> at 2 K is observed. The data are better described by a Curie-Weiss law with  $\theta=-0.1$  K. Such a deviation may be due to a weak, antiferromagnetic Gd-Gd interaction of dipolar origin. Since the Gd moment is large, dipole-dipole interactions could show up in the susceptibility at temperatures as high as 10 K, given the nearest-neighbor Gd-Gd distance of 10 Å. Of course it may also be attributed to a weak antiferromagnetic superexchange coupling acting between the Gd ions. The mean-field analysis provides the value of  $J''/k_B=-6 \times 10^{-3}$  K for this interaction, on basis of the obtained  $\theta$  value.

### B. $Tb_2Zn_3$ , $Dy_2Zn_3$ , and $Ho_2Zn_3$

As mentioned, for a lanthanide ion with a nonzero orbital moment, such as Tb, Dy, or Ho, the effect of the crystal field on the magnetic levels has to be taken into account. In order to study the CF splittings for  $L_2M_3$ , we consider the susceptibility measurements for the  $M=\text{Zn}$  compounds to avoid (or reduce) the complication of magnetic exchange interactions. To simplify the analysis we consider the lanthanide ions in a cubic geometry, so that the number of crystal field parameters is minimized. As a further simplification, we consider an octahedral coordination for each lantha-

nide ion instead of the seven coordination found for  $Tm_2[\text{Cu}(\text{opba})]_3 \cdot x\text{DMF} \cdot y\text{H}_2\text{O}$  ( $x \approx 10$ ,  $y \approx 4$ ), which crystallizes in orthorhombic geometry.<sup>29,30</sup> Although these simplifications may seem somewhat unsatisfactory, the lack of a precise knowledge of the actual coordination parameters (distances, angles) for the various  $L$  ions in  $L_2M_3$  does not actually justify more sophisticated treatments. Within this approximation, the prediction of the type and the relative order of the CF split levels is greatly simplified. We use the valuable paper of Lea, Leask, and Wolf<sup>35</sup> (LLW) which predicts both order and type of level in cubic symmetries for each value of the angular momentum and for all ratios of the crystal field parameters.

The crystal field acting on the lanthanide ion in octahedral geometry can be represented by the Hamiltonian

$$\mathcal{H}_{\text{CF}} = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4), \quad (3.2)$$

where the  $O_n^m$  terms are angular momentum operators. The parameter  $B_n$  is related to the strength of the crystal field components

$$B_n = a_n A_n^0 \langle r^n \rangle,$$

where  $a_n$  is the operator equivalent factor,  $\alpha$ ,  $\beta$ ,  $\gamma$  for  $n=2,4,6$ , respectively.  $A_n^0$  are parameters relating the  $n$ th degree potential on the ion from the ionic charges of the lattice, and  $\langle r^n \rangle$  are the expectation values for the distances of the  $4f$  electrons. The product  $A_n^0 \langle r^n \rangle$  is determined to the first order by geometric factors and in principle can be calculated.

LLW have determined the eigenfunction and eigenvalue solutions for the Hamiltonian equation for applicable values of the angular momentum and the full range of  $B_4/B_6$  ratios. They have constructed diagrams for the eigenvalues of the crystal field levels of each angular momentum in terms of a quantity  $x$ , defined as

$$\frac{x}{1-|x|} = \frac{F(4)B_4}{F(6)B_6} = \frac{F(4)\beta A_4^0 \langle r^4 \rangle}{F(6)\gamma A_6^0 \langle r^6 \rangle} = \frac{b_4}{b_6},$$

where  $-1 < x < 1$ , and  $F(4)$  and  $F(6)$  are multiplicative factors. Then, the susceptibility can be easily calculated for a given angular momentum and a gyromagnetic ratio. In the remainder of this section, we discuss the susceptibility data<sup>18</sup> of  $L_2Zn_3$  (with  $L=\text{Tb, Dy, Ho}$ ) compounds and we explain them in terms of the LLW scheme. Only the temperature region below 40 K will be considered, since only the contribution of the lowest lying levels needs to be taken into account. These approximations are allowed in view of the large size of the level splittings compared to the low-temperature region of interest for our experiments (mainly below 10 K). This is confirmed by the specific heat analyses given below, where we shall show that only few CF levels are actually involved in the magnetic ordering processes.

Let us start with  $Tb_2Zn_3$ . Compounds of non-Kramers lanthanide ions, such as Tb(III), often have a singlet electronic ground state separated by an energy  $\Delta$  from an excited singlet state. In a cubic field, the  $^7F_6$  state of Tb is split into two singlets ( $\Gamma_1$  and  $\Gamma_2$ ), one nonmagnetic doublet ( $\Gamma_3$ ) and three triplets [ $\Gamma_4$ ,  $\Gamma_5^{(1)}$ , and  $\Gamma_5^{(2)}$ ].

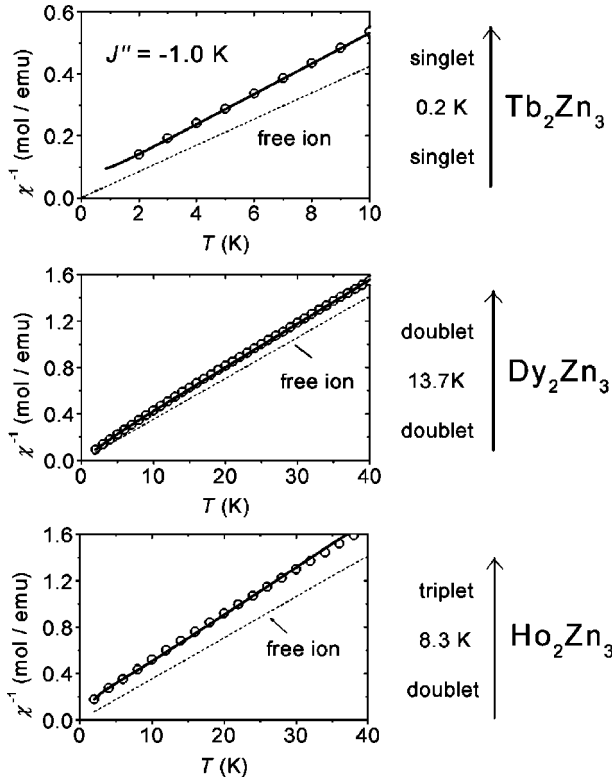


FIG. 3. Top: Experimental inverse susceptibility for  $\text{Tb}_2\text{Zn}_3$ . The solid line is the calculated inverse susceptibility taking into account  $\Delta = 0.2$  K and  $J''/k_B = -1$  K for the Tb-Tb interaction. For explanations, see text. Center: Measured and calculated inverse susceptibility for  $\text{Dy}_2\text{Zn}_3$ . Bottom: Measured and calculated inverse susceptibility for  $\text{Ho}_2\text{Zn}_3$ .

The measured susceptibility of  $\text{Tb}_2\text{Zn}_3$  is shown in Fig. 3. The data at low temperatures are well described by two singlets split by  $\Delta \approx 0.2$  K. In the LLW scheme for octahedral coordination, such a situation corresponds to  $|x| \approx 0.45$  where the ground state can be either  $\Gamma_1$  or  $\Gamma_2$  (see Ref. 35). The assignment will be confirmed by the specific heat analysis presented below. For this simple case of two separated singlets, to improve the quality of the fit, we used ultimately a model in which a weak antiferromagnetic exchange interaction acting between the terbium ions has been taken into account. The model is explained in detail in the Appendix and employed in Sec. V B to explain the very-low-temperature magnetic and thermal properties of  $\text{Tb}_2\text{Cu}_3$ . Based on the Hamiltonian of Eq. (A1), the fit provides the value of  $J''/k_B = -1$  K for the Tb-Tb interaction.

For the case of dysprosium(III), the crystal field splits the  ${}^6H_{15/2}$  ground state into two Kramers doublets ( $\Gamma_6$  and  $\Gamma_7$ ) and three quartets [ $\Gamma_8^{(1)}$ ,  $\Gamma_8^{(2)}$ , and  $\Gamma_8^{(3)}$ ] (see Ref. 35). In octahedral coordination with  $|x| \approx 0.45$ , as estimated for the previous case of Tb, one anticipates a doublet as the ground state ( $\Gamma_6$  or  $\Gamma_7$ ) with the higher state being the other doublet ( $\Gamma_7$  or  $\Gamma_6$ , respectively). The fit to the  $\text{Dy}_2\text{Zn}_3$  data (Fig. 3) is in agreement with a low-lying doublet being either  $\Gamma_6$  or  $\Gamma_7$  separated by  $\Delta = 13.7$  K from  $\Gamma_7$  or  $\Gamma_6$ , respectively. Also this assignment will be confirmed by the analysis of the specific heat (see below).

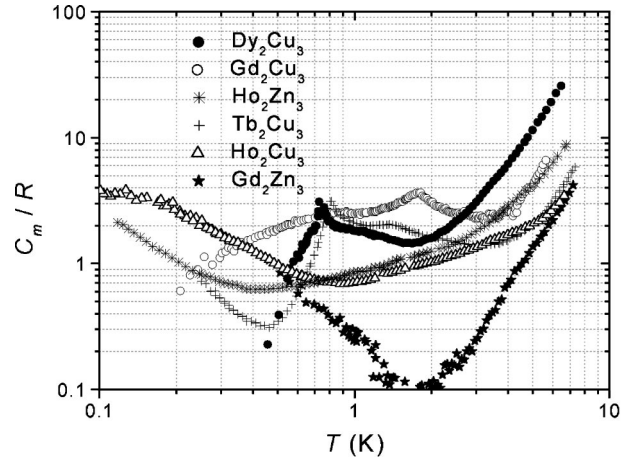


FIG. 4. Experimental specific heats of  $L_2M_3$ .

Holmium(III) is a non-Kramers ion, with a  ${}^5I_8$  ground state. The crystal field splits the ground state into one singlet ( $\Gamma_1$ ), two nonmagnetic doublets [ $\Gamma_3^{(1)}$  and  $\Gamma_3^{(2)}$ ], and four triplets [ $\Gamma_4^{(1)}$ ,  $\Gamma_4^{(2)}$ ,  $\Gamma_5^{(1)}$ , and  $\Gamma_5^{(2)}$ ]. The LLW diagram (see Ref. 35) is complicated, with many level crossings, which make simple choices difficult. For octahedral coordination with  $|x| \approx 0.45$ , as in the Tb and Dy cases, one expects a  $\Gamma_3^{(2)}$  ground state with  $\Gamma_4^{(2)}$  the first excited state within a distance of not more than  $\sim 20$  K. The fit to the  $\text{Ho}_2\text{Zn}_3$  data (Fig. 3) is in agreement with this, yielding the value of  $\Delta = 8.3$  K for the  $\Gamma_3^{(2)}-\Gamma_4^{(2)}$  separation.

To summarize, the susceptibility data presented here for the Tb, Dy, and Ho containing compounds, as well as the specific heat analyses presented below, can be reasonably accounted for by assuming cubic symmetry and octahedral coordination for the lanthanide ions. The consistency of the analyses is derived from the fact that the factor  $x$  could be taken at approximately the same value ( $\approx 0.45$ ) for each compound. This is what one would expect for a series of isostructural compounds in which the lanthanide ions most probably have the same local coordination.

#### IV. VERY LOW-TEMPERATURE PROPERTIES

In the following sections, we present the thermal properties of the  $L_2M_3$  compounds in the temperature range 0.1 to 10 K, and their magnetic properties down to 5 mK. We first analyze the lattice contributions to the measured heat capacities, and then describe the results inferred from susceptibility, magnetization and magnetic specific heat for each compound of the series.

##### A. Phonons contribution

Figure 4 shows the collected zero-field specific heat data of the  $L_2M_3$  compounds as a function of temperature. As a first step, we have estimated the lattice contribution for each compound by fitting the high-temperature data to a sum of a Debye lattice contribution ( $C_l/R = \beta T^3$ ) and a high-temperature limiting tail ( $\propto T^{-2}$ ) of the magnetic anomaly. The results for the  $\beta$  parameter are given in Table I.

TABLE I. Experimental lattice contributions ( $C_l/R = \beta T^3$ ) as estimated from the data in Fig. 4. The values  $\beta$  are expressed in ( $\times 10^{-2} \text{ K}^{-3}$ ).

	Gd <sub>2</sub> Cu <sub>3</sub>	Tb <sub>2</sub> Cu <sub>3</sub>	Dy <sub>2</sub> Cu <sub>3</sub>	Ho <sub>2</sub> Cu <sub>3</sub>	Gd <sub>2</sub> Zn <sub>3</sub>	Ho <sub>2</sub> Zn <sub>3</sub>
$\beta$	3.2	1.5	8.8	1.2	1.1	2.9

The WAXS analysis has shown that the  $L_2M_3$  compounds have similar structures (see Sec. II and references therein). Consequently, one expects also a similar lattice contribution for each of them. Indeed, the estimated  $\beta$  values for five of the compounds studied fall into a fairly narrow range between  $1.1 \times 10^{-2}$  and  $3.2 \times 10^{-2} \text{ K}^{-3}$ . Since the coefficient  $\beta$  depends on the third power of the Debye temperature, such a limited variation appears quite acceptable. The only exception is Dy<sub>2</sub>Cu<sub>3</sub> for which  $\beta = 8.8 \times 10^{-2} \text{ K}^{-3}$ , a value much higher than the others. The reason is presently not known. It is important to note that, however, the magnetic specific heat for Dy<sub>2</sub>Cu<sub>3</sub> obtained after subtracting the phonon specific heat, appears to yield a magnetic entropy that agrees with the value expected for a doublet ground state. The magnetic contributions to the specific heats of all the  $L_2M_3$  compounds discussed in the following sections were obtained by subtracting the abovementioned lattice contributions.

### B. Gd<sub>2</sub>Cu<sub>3</sub> and Gd<sub>2</sub>Zn<sub>3</sub>

We have already seen (Sec. III) that for temperatures above 2 K, the in-phase susceptibility of Gd<sub>2</sub>Cu<sub>3</sub> follows a Curie-Weiss law with  $\theta = 2.3$  K, indicating the ferromagnetic nature of the compound. The low-temperature in-phase susceptibility of Gd<sub>2</sub>Cu<sub>3</sub> is depicted in Fig. 5 as a function of the temperature. A sharp peak is observed at  $T_C = 1.78$  K which is probably due to a transition to long-range magnetic order. A large value of the susceptibility is found at the maximum (65.9 emu/mol). This behavior is typical for a powdered sample of an isotropic ferromagnetic material in which demagnetization effects become important. The theoretical

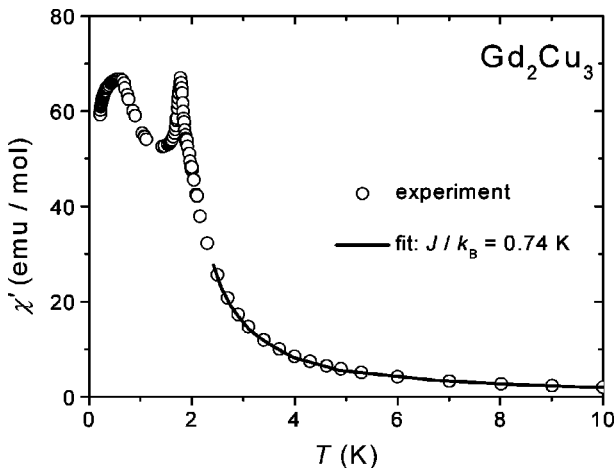


FIG. 5. Experimental molar in-phase susceptibility of Gd<sub>2</sub>Cu<sub>3</sub> versus temperature and theoretical estimation for  $J/k_B = 0.74$  K (see Sec. V A for explanations).

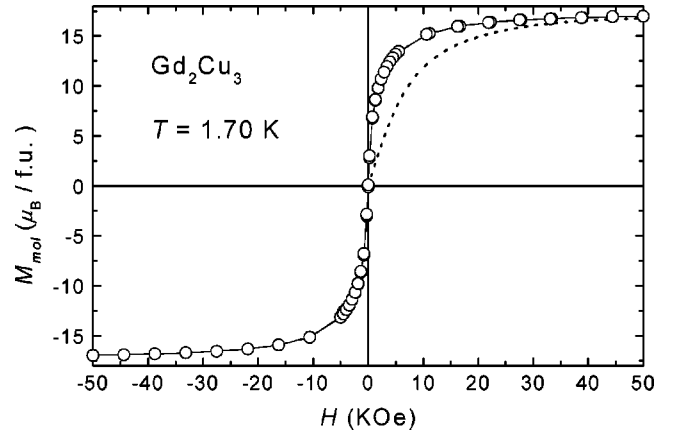


FIG. 6. Field dependence of the magnetization and hysteresis loop at  $T = 1.70$  K for Gd<sub>2</sub>Cu<sub>3</sub>. The dotted line represents the Brillouin functions as calculated from Eq. (4.1).

value estimated for the susceptibility of a ferromagnetic sample of Gd<sub>2</sub>Cu<sub>3</sub> at  $T_C$  is  $\chi'_{\text{ext}}(T_C) = N^{-1} \approx (70 \pm 20)$  emu/mol, where  $N$  is the demagnetizing factor calculated taking into account an ellipsoidal approximation for the geometry of the sample. Within the error this is equal to the experimental result.

An interesting feature, that is discussed later (Section V A), is the in-phase susceptibility variation with the temperature for  $T < T_C$  (Fig. 5). Just below  $T_C$ , the susceptibility goes through a minimum and further lowering the temperature reveals a rounded anomaly for  $0.1 \text{ K} < T < 1 \text{ K}$ .

Figure 6 shows the variation of the experimental magnetization  $M$  versus the field  $H$  for the temperature  $T = 1.70$  K, i.e., just below the critical temperature ( $T_C = 1.78$  K). No hysteresis effect is observed. Additional evidence for the ferromagnetic coupling is gained by comparison of the magnetization measurements to the calculated behavior for the uncoupled case. If the magnetic centers were all uncoupled,  $M$  would vary according to

$$M = 2Ng_{\text{Gd}}\mu_B S_{\text{Gd}} B_{7/2}(\eta_{\text{Gd}}) + 3Ng_{\text{Cu}}\mu_B S_{\text{Cu}} B_{1/2}(\eta_{\text{Cu}}), \quad (4.1)$$

where  $B_{7/2}(\eta_{\text{Gd}})$  and  $B_{1/2}(\eta_{\text{Cu}})$  are the Brillouin functions for Gd and Cu ions, respectively. The saturation magnetization would be given by

$$M = (2g_{\text{Gd}}S_{\text{Gd}} + 3g_{\text{Cu}}S_{\text{Cu}})N\mu_B = 17N\mu_B.$$

The calculated magnetization for  $T = 1.70$  K as derived from Eq. (4.1) is displayed in Fig. 6 together with the experimental curve. It can be observed that the experimental data saturate at the predicted value and they lie above the expression of Eq. (4.1) in the whole temperature range. Such a behavior clearly indicates that the predominant interaction, i.e., the Gd-Cu interaction through the oxamato bridge, is ferromagnetic.

Let us now discuss the magnetic specific heat data by presenting first the result for the Gd<sub>2</sub>Zn<sub>3</sub> compound (Fig. 7). A sharp increase appears when lowering the temperature below 1 K. Due to incomplete achievement of the ordering

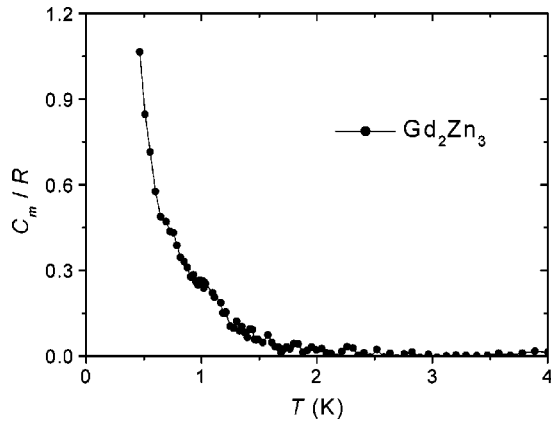


FIG. 7. Magnetic specific heat vs temperature for  $\text{Gd}_2\text{Zn}_3$ . Solid curve is a guide to the eye.

process in the temperature range of our experiments, an analysis of the experimental entropy is not possible.

Figure 8 shows the magnetic molar specific heat  $C_m/R$  versus the temperature  $T$  for  $\text{Gd}_2\text{Cu}_3$ . Two clear features can be observed: a distinct  $\lambda$  peak at  $T_C = (1.78 \pm 0.02)$  K confirming the assignment of a long-range ordering process, and a rounded maximum around 0.8 K. We note that the rounded anomaly occurs in the same temperature range as that observed in the susceptibility experiments (Fig. 5). Figure 8 shows also that the magnetic contribution at  $T > T_C$  is quite large and extends up to high temperatures, indicating the presence of important short-range ordering effects most probably related to the low dimensionality (no contributions from CF splittings are expected for Gd ions).

In order to calculate the entropy, we use the relation

$$S/R = \int_0^\infty [C_m(T)/RT] dT, \quad (4.2)$$

together with the experimental values of  $C_m$  in the temperature range  $0.2 \text{ K} < T < 5.7 \text{ K}$ . For the extrapolation down to

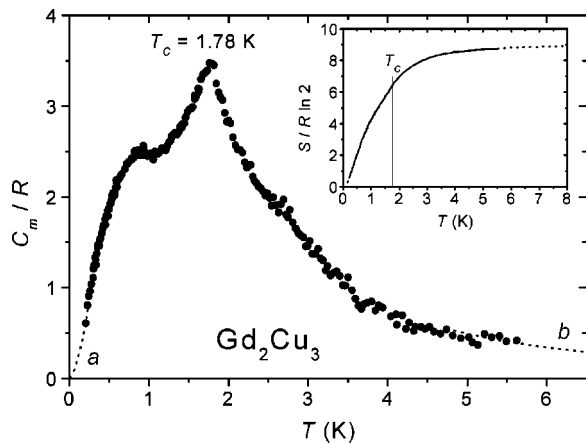


FIG. 8. Magnetic molar specific heat vs temperature for  $\text{Gd}_2\text{Cu}_3$ . Curve *a* is the ferromagnetic spin wave contribution ( $\propto T^{3/2}$ ); curve *b* is the high temperature limit ( $\propto T^{-2}$ ) of the magnetic anomaly tail. In the inset: temperature dependence of the magnetic entropy for  $\text{Gd}_2\text{Cu}_3$ .

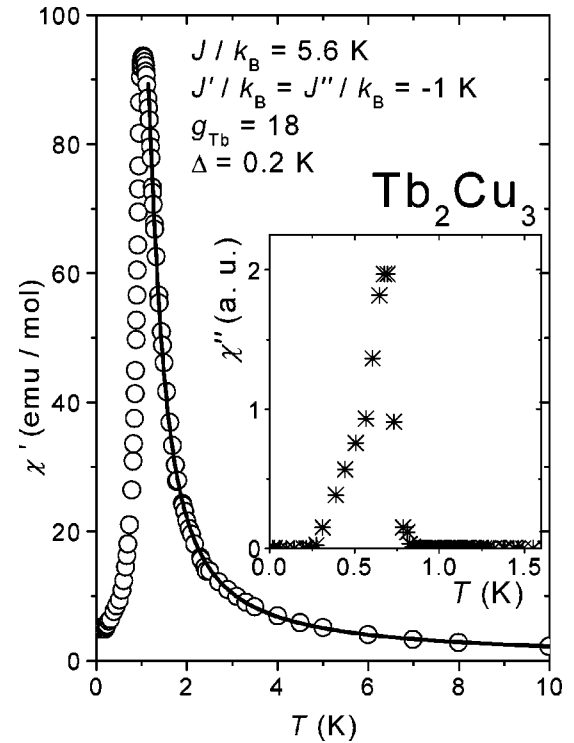


FIG. 9. Experimental low-temperature in-phase susceptibility vs temperature for  $\text{Tb}_2\text{Cu}_3$  together with the calculated susceptibility (for explanations see Sec. V B). In the inset: Experimental out-of-phase susceptibility.

0 K we assume a 3D ferromagnetic spin-wave type contribution ( $\propto T^{3/2}$ ) and on the high-temperature side a  $T^{-2}$  dependence for  $C_m$ . The calculated entropy gives a value of  $S/R \approx 9 \ln 2$ . This corresponds to the maximum expected value ( $= 3 \ln 2 + 2 \ln 8$ ) evidencing that both the Gd and Cu magnetic ions participate in the ordering process. As already said, the relatively large values of the specific heat above  $T_C$  may be associated with low-dimensional fluctuations within the ladders. This can be clearly seen by plotting the entropy variation as a function of the temperature (inset of Fig. 8). The calculated entropy variation above  $T_C$  gives  $(S_\infty - S_C) \approx 2.7 R \ln 2$ , which is a rather large fraction in comparison with theoretical values of three-dimensional models of ferromagnets.<sup>36</sup> All this agrees with the low-dimensional ladder-type magnetic structure of these materials.

### C. $\text{Tb}_2\text{Cu}_3$

The low-temperature susceptibility of  $\text{Tb}_2\text{Cu}_3$  is depicted in Fig. 9. The abrupt change of the in-phase susceptibility at 1 K is ascribed to a transition to a magnetically ordered state, which is obvious also from the specific heat curve shown in Fig. 10. The maximum value is 93.6 emu/mol at 1.0 K. This value is almost of the same order as expected for a ferromagnetic material in which demagnetization effects become important. In fact, an estimate of the demagnetizing factor gives the value of  $\approx 280$  emu/mol for the susceptibility of an isotropic ferromagnetic  $\text{Tb}_2\text{Cu}_3$  sample at the maximum, as-



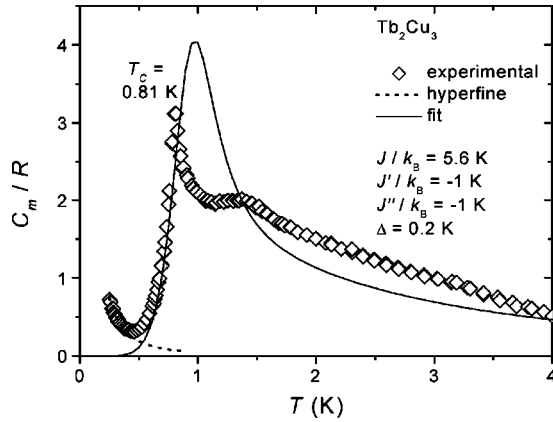


FIG. 10. Magnetic molar specific heat of  $\text{Tb}_2\text{Cu}_3$ . The dotted line is the calculated hyperfine contribution of the Tb ions. The solid line is the calculated specific heat due to the low-dimensionality of the ladder (for explanations see Sec. V B).

suming a cylindrical approximation of its shape. At the low temperature side of the anomaly, the susceptibility decreases sharply, reaching a value of 5.0 emu/mol at 10 mK. The specific heat data are plotted in Fig. 10 and indicate a transition temperature of  $T_C = (0.81 \pm 0.01)$  K. In the susceptibility data we see that fluctuations in the ordering process show up as a peak in the out-of-phase susceptibility  $\chi''$  centered at 0.7 K (inset of Fig. 9), whereas the in-phase susceptibility  $\chi'$  shows an inflection point (maximum in  $\partial\chi'/\partial T$ ) at that same temperature. The  $\chi''$  is in arbitrary units because it is null above 0.8 K and, thus, it was not possible to scale to data measured above 1.7 K with the commercial magnetometer. The observed behavior is not uncommon for a low-dimensional system which undergoes a phase transition to long-range magnetic order, for instance, to an antiferromagnetic arrangement of the ferromagnetic ladders, at  $T_C = 0.81$  K as deduced from the inflection point of  $\chi'$ . The relatively large value of the susceptibility at 1 K may suggest the presence of a dominating ferromagnetic interaction, probably associated with the intraladder Tb-Cu interaction. We will return to this point in Sec. V B. Moreover, the very low value reached by the in-phase susceptibility in the limit of very low temperature, clearly indicates the large anisotropy of the terbium ions in  $\text{Tb}_2\text{Cu}_3$ , as already pointed out in Sec. III A for  $\text{Tb}_2\text{Zn}_3$ . The anisotropy may also be responsible for the fact that the measured value of the  $\chi'$  at  $T_C$  is lower than the expected limit for an isotropic ferromagnetic sample. Since a powder is measured, the value is a directional average.

The main feature of the magnetic specific heat of  $\text{Tb}_2\text{Cu}_3$ , depicted in Fig. 10, is the  $\lambda$  peak at  $T_C = 0.81$  K indicating the transition to a long-range ordered state. The bump observed above  $T_C$  and centered around 1.5 K is probably associated with low-dimensional fluctuations within the ladders, since a contribution from excited CF levels is not expected in this temperature range (see Sec. III A). The data at the low-temperature side show a slight upward curvature. Below 0.4 K, the data obey the law  $C_m T^2/R = 0.05 \text{ K}^2$ . This contribution is probably coming from the hyperfine splitting of the magnetic levels of the Tb nuclei. Subtracting the cal-

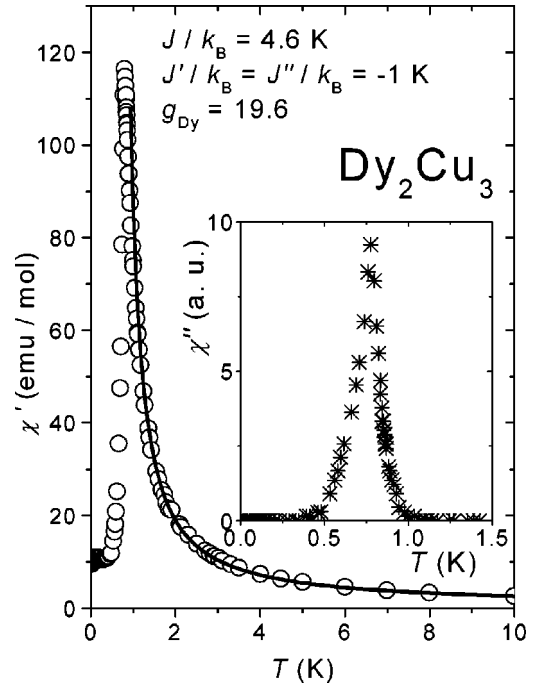


FIG. 11. Experimental low-temperature in-phase susceptibility vs temperature for  $\text{Dy}_2\text{Cu}_3$  together with the calculated susceptibility (for explanations see Sec. V B). In the inset: Experimental out-of-phase susceptibility.

culated hyperfine specific heat from the measured specific heat data, we estimate the remaining entropy. In order to calculate the magnetic entropy of  $\text{Tb}_2\text{Cu}_3$ , we carry out the integration in Eq. (4.2) using the experimental values of  $C_m/R$  in the temperature range  $0.1 \text{ K} < T < 5 \text{ K}$ . After extrapolation down to 0 K with an exponential function, the calculated entropy gives a value of  $S/R \approx 5 \ln 2$ . Taking into account that Cu has spin 1/2, which corresponds to  $S/R = \ln 2$  per atom, the experimental entropy content indicates that Tb has an effective spin 1/2, corresponding to a lowest lying doublet in the temperature region of the magnetic ordering process. In Sec. III A we have shown that for  $\text{Tb}_2\text{Zn}_3$  the lowest energy levels are two singlets with a separation of  $\Delta = 0.2$  K. For  $\text{Tb}_2\text{Cu}_3$  we expect a similar crystal environment and, as a consequence, a similar energy scheme. Nevertheless, the separation  $\Delta$  is relatively small in comparison with the thermal energy in the region of the magnetic ordering process. We thus conclude that we can apply the approximation of effective spin 1/2 for the Tb ion. In agreement with the pronounced high-temperature specific heat tail observed in Fig. 10, only about 15% of the entropy is left below  $T_C$ . This is another indication of the large amount of short-range magnetic order that is probably associated with the low-dimensionality of the ladder.

#### D. $\text{Dy}_2\text{Cu}_3$

Figure 11 shows the low-temperature ac susceptibility of  $\text{Dy}_2\text{Cu}_3$ . As in the case of  $\text{Tb}_2\text{Cu}_3$ , and as evidenced from the specific heat experiment presented in Fig. 12, clear evidence of a transition to a magnetically ordered phase is

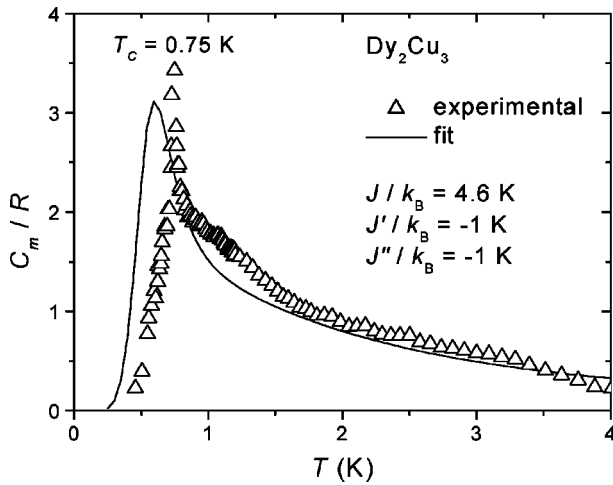


FIG. 12. Magnetic molar specific heat of  $\text{Dy}_2\text{Cu}_3$ . The solid line is the calculated specific heat due to the low-dimensionality of the ladder (for explanations see Sec. V B).

found. The in-phase susceptibility has a sharp peak centered at 0.8 K with a maximum value of 116.4 emu/mol. Below the peak, it decreases very sharply and remains almost constant at 10.0 emu/mol down to 10 mK. As for  $\text{Tb}_2\text{Cu}_3$ , the maximum of the experimental susceptibility is not far below the expected theoretical limiting value ( $\approx 280$  emu/mol) for an isotropic ferromagnetic sample. The out-of-phase susceptibility also shows a sharp peak centered at 0.77 K and it is zero below 0.4 K and above 1 K (inset of Fig. 11). At 0.77 K an inflection point occurs in the temperature dependence of the  $\chi'$ . The transition temperature deduced below from the specific heat is  $T_C = (0.75 \pm 0.01)$  K. Similar to  $\text{Tb}_2\text{Cu}_3$ , the data point toward a type of antiferromagnetic long-range ordering, with very small value for the antiferromagnetic coupling ( $J_{\text{AF}}$ ) between the ferromagnetic ladders. Since for an antiferromagnet the  $\chi$  at  $T_C$  is inversely proportional to  $J_{\text{AF}}$ , when the latter becomes small enough,  $\chi$  at  $T_C$  can reach the demagnetizing limit. It is then difficult to distinguish between ferromagnetic or antiferromagnetic coupling between the ferromagnetic chains. The peak in the  $\chi''$  found in both compounds may be due to a weak-ferromagnetic moment which arises when the antiferromagnetic ordering is accompanied by some degree of spin canting. Again, as for  $\text{Tb}_2\text{Cu}_3$ , the very low value of the in-phase susceptibility for  $T \rightarrow 0$  indicates large anisotropy of the Dy ions.

Figure 12 shows the magnetic specific heat, plotted as  $C_m/R$  versus  $T$ , for the  $\text{Dy}_2\text{Cu}_3$  compound, where  $C_m/R$  is the molar specific heat and  $T$  is the temperature. The prominent spike below 1 K is identified with the  $\lambda$  anomaly indicating the onset of a phase transition to a long-range ordered state. The peak is very sharp and allows an accurate determination of the critical temperature as  $T_C = (0.75 \pm 0.01)$  K. The analysis of the magnetic entropy content shows that only a very small portion (about 15%) is obtained below  $T_C$  and that, as for  $\text{Tb}_2\text{Cu}_3$ , the lanthanide has an effective spin 1/2 in the ground state, once more agreeing with the crystal field analysis (Sec. III A).

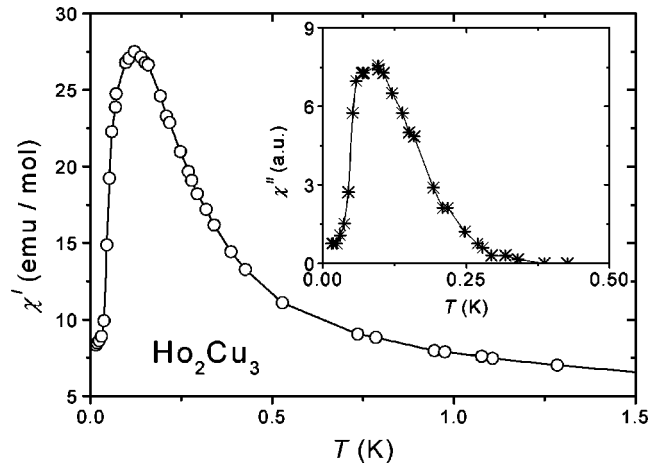


FIG. 13. Experimental molar in-phase and out-of-phase (inset) susceptibilities vs temperature for  $\text{Ho}_2\text{Cu}_3$ . Solid curves are guides to the eye.

### E. $\text{Ho}_2\text{Cu}_3$ and $\text{Ho}_2\text{Zn}_3$

The low-temperature susceptibility of  $\text{Ho}_2\text{Cu}_3$  is shown in Fig. 13. Also for this compound, evidence of an antiferromagnetic long-range ordering is observed. The in-phase susceptibility has a maximum of 27.5 emu/mol at 0.12 K (much lower than for  $\text{Tb}_2\text{Cu}_3$  and  $\text{Dy}_2\text{Cu}_3$ ). It sharply decreases down to 8.9 emu/mol at 30 mK, and remains nearly constant by further lowering the temperature down to 5 mK. The out-of-phase susceptibility shows a peak around 40–100 mK, in which temperature range also an inflection point, centered at  $(50 \pm 10)$  mK, is seen in the in-phase susceptibility.

The molar specific heat of  $\text{Ho}_2\text{Cu}_3$  is depicted in Fig. 14 together with that of  $\text{Ho}_2\text{Zn}_3$  for comparison. The specific heats of  $\text{Ho}_2\text{Cu}_3$  and  $\text{Ho}_2\text{Zn}_3$  are seen to overlap for  $T > 0.8$  K, showing a broad rounded anomaly with a maximum at 3.5 K (Fig. 14). This is probably due to crystal field splitting of the holmium levels. In Sec. III A we have seen that the susceptibility of  $\text{Ho}_2\text{Zn}_3$  down to 2 K may be ex-

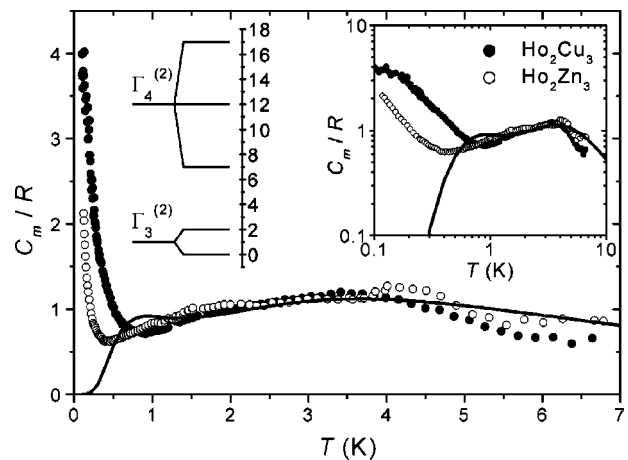


FIG. 14. Magnetic molar specific heat of  $\text{Ho}_2\text{Cu}_3$  ( $\bullet$ ) and  $\text{Ho}_2\text{Zn}_3$  ( $\circ$ ). The solid line is the calculated Schottky contribution due to the splitting of the  $\Gamma_3^{(2)}$  and  $\Gamma_4^{(2)}$  levels of the holmium ions as shown in the Figure. In the inset the same data in log-log scale.

plained in terms of a doublet ( $\Gamma_3^{(2)}$ ) ground state separated by 8.3 K from a triplet ( $\Gamma_4^{(2)}$ ) excited level. Taking into account a further splitting of these degenerate levels, the Schottky contribution arising from this configuration can be easily calculated. A nice agreement with the data is obtained for  $\Gamma_3^{(2)}$  further split by 2 K, and separated by 11 K from  $\Gamma_4^{(2)}$ , further split by 5 K each level (Fig. 14).

For  $\text{Ho}_2\text{Zn}_3$ , a sharp increase of the specific heat by lowering the temperature is observed below 0.3 K. This contribution is apparently coming from the hyperfine splitting of the magnetic levels of the Ho nuclei. In this temperature region, by fitting the data to  $C_m/R = aT^{-b}$ , we obtain  $a = 0.14$  and  $b = 1.3$ , and not the expected value of  $b = 2$ , for a magnetic anomaly high-temperature tail. The reason for that is probably related to problems of thermal contact between spin system and the lattice, since we found the specific heat at low temperature to become increasingly dependent on the measuring time we used in the experiments. In fact, both specific heats of  $\text{Ho}_2\text{Cu}_3$  and  $\text{Ho}_2\text{Zn}_3$  have been measured with the relaxation technique. If the measuring time is not long enough for the sample to achieve thermal equilibrium, between the spin system and the phonon bath, part of the electronic spin contribution will simply be missing. Also for  $\text{Ho}_2\text{Cu}_3$  an upward curvature is observed by lowering the temperature below 0.7 K. By comparison with the  $\text{Ho}_2\text{Zn}_3$  results, we see that in the specific heat of  $\text{Ho}_2\text{Cu}_3$  there is an extra contribution in addition to the hyperfine splitting of the Ho nuclei. This may readily be explained by a weak Ho-Cu coupling that, together with the dipole-dipole interladder interaction, shows up at very low temperature. Consequently, only the onset of a phase transition is observed. The low-temperature limit of our setup did not allow us to determine the ordering temperature that has to be below 0.1 K (judging from the  $\chi$  data). In combination with the susceptibility results (Fig. 13), we conclude that the ordering temperature  $T_C$  for  $\text{Ho}_2\text{Cu}_3$  is between 0.04 and 0.10 K. Due to the incomplete achievement of the magnetic ordering processes at the lowest temperature, the analysis of the entropy contents for  $\text{Ho}_2\text{Cu}_3$  and  $\text{Ho}_2\text{Zn}_3$  is not possible.

## V. COMPARISON WITH LADDER MODELS

### A. $\text{Gd}_2\text{Zn}_3$ and $\text{Gd}_2\text{Cu}_3$

For  $\text{Gd}_2\text{Zn}_3$ , the sharp increase of the specific heat below 1 K (Fig. 7) may reflect the onset of a 3D ordering process, which takes place at a temperature lower than obtained in the experiment. Even though the  $\text{Gd}_2\text{Zn}_3$  compound is more poorly crystallized than the Cu containing compounds,<sup>30</sup> its measured specific heat clearly underlines the relevance of the Gd-Cu interaction, when compared with the results found for  $\text{Gd}_2\text{Cu}_3$ . The absence of the copper at  $M$  sites reduces or inhibits the ordering temperature of the Gd sublattice below our lowest experimental temperature. It is clear that the Cu ion in  $\text{Gd}_2\text{Cu}_3$  is much more effective than the Zn ion in transmitting magnetic exchange interaction along the Gd-oxamato-Cu-oxamato-Gd superexchange pathway that gives rise to the net ferromagnetic coupling.

In order to explain the paramagnetic susceptibility of  $\text{Gd}_2\text{Cu}_3$ , let us consider the model proposed by Georges

*et al.*<sup>14</sup> for ladder-type double chains which has been successfully applied to describe the paramagnetic susceptibility of the  $\text{Gd}_2(\text{ox})[\text{Cu}(\text{pba})_3[\text{Cu}(\text{H}_2\text{O})_5] \cdot 20\text{H}_2\text{O}$  compound. This model, which is based on the standard transfer matrix method, takes into account the presence of copper quantum spins  $\sigma$  and gadolinium classical spins  $S$ , in a ladderlike arrangement similar to the  $L_2M_3$  compounds, where each gadolinium ion interacts isotropically with two neighboring copper ions. The approximation is the classical treatment of the gadolinium spin, which is allowed because of the high spin value of the ion.

With the aid of this model, we have analyzed the experimental thermal dependence of the susceptibility in the paramagnetic regime. The same Landé factor  $g = 2.00$ , determined in the high-temperature limit, has been attributed to all cations. A unique coupling constant  $J$  has been introduced for all the Gd-Cu isotropic interactions. We have thus used the Hamiltonian

$$\mathcal{H} = -J \sum_{(i,j)} (\sigma_i S_j) - \left( \sum_{i=1}^{N_\sigma} g \mu_B \sigma_i + \sum_{j=1}^{N_S} g \mu_B S_j \right) H_z, \quad (5.1)$$

where the Zeeman terms extend over all  $N_\sigma$  copper and  $N_S$  gadolinium ions. The best fitting of the experimental susceptibility results is obtained in the range  $2.5 \text{ K} < T < 20 \text{ K}$ . Figure 5 shows the calculated curve with  $J/k_B = 0.74 \text{ K}$ . As expected, the positive  $J$  value refers to a ferromagnetic exchange coupling, in agreement with the positive paramagnetic Curie temperature  $\theta = 2.3 \text{ K}$ . It is worthwhile to note that the  $J$  value obtained here does not differ substantially from the estimate of 0.5 K given in Sec. III A deduced by simple mean field analysis. At temperatures below 2.5 K, the three-dimensional ordering mechanism becomes apparent and, consequently, the experimental data can no longer be described with the above (paramagnetic) model.

It is well established that an array of isotropic spins with dimensionality two or less will not present long-range ordering.<sup>36</sup> The experimental specific heat data have shown the presence of short-range order for temperatures far above  $T_C$  already, and we have associated it with extended magnetic correlations along the spin ladders. The observed long-range ordering at  $T_C = 1.78 \text{ K}$  implies the existence of interactions between adjacent ladders. The structure of  $\text{Gd}_2\text{Cu}_3$  does not present any pathway between adjacent ladders that involve atomic contacts suitable for the propagation of magnetic exchange. Consequently, it seems reasonable to assume that the driving force for the magnetic long-range order is indeed the dipolar interaction.

Another interesting feature in  $\text{Gd}_2\text{Cu}_3$  is the maximum observed at about 0.8 K, and thus below  $T_C = 1.78 \text{ K}$ , in both the susceptibility (Fig. 5) and the specific heat (Fig. 8). To explain such a feature, we may consider the presence of two types of interchain coupled systems in  $\text{Gd}_2\text{Cu}_3$ , e.g., with slightly different packing of the ladders within the crystal structure. Then one polytype has  $T_C = 1.78 \text{ K}$  and the other has a lower critical temperature of 0.8 K. Unfortunately, due to the lack of a precise knowledge of the structure and to the

fact that the experiments have been performed on powdered samples, a detailed study of the ordering process could not be carried out.

For the sake of completeness we wish to mention briefly the nature of the mechanism of the Gd-Cu interaction. In preceding works,<sup>12,13</sup> the ferromagnetism of this interaction was attributed to the coupling between the  $4f-3d$  ground configuration and the excited configuration arising from the metal-metal charge transfer configurations. The latter is associated with the  $3d \rightarrow 5d$  process: an electron is transferred from the singly occupied orbital centered on copper toward an empty orbital centered on gadolinium. In such a mechanism,  $J$  is given by

$$J = \sum_{i=1}^5 [\beta_{5d-3d}^2 \delta / (4U^2 - \delta^2)]_i, \quad (5.2)$$

where  $\beta_{5d-3d}$  is the transfer integral of the  $3d \rightarrow 5d$  process,  $\delta$  is the energy gap between  $S=3$  and  $S=4$  excited states arising from the  $4f^7 5d^1$  electron-transfer configuration and  $U$  is the energy cost of such a transfer. The summation applies to the five  $5d$  gadolinium orbitals.

It is interesting to compare, qualitatively, the here obtained coupling constants  $J$  of  $\text{Gd}_2\text{Cu}_3$  ( $J/k_B = 0.74$  K) and of  $\text{Gd}_2(\text{ox})[\text{Cu}(\text{pba})]_3[\text{Cu}(\text{H}_2\text{O})_5] \cdot 20\text{H}_2\text{O}$ , which is a long-range ordered ferromagnet for  $T \leq 1.05$  K (Refs. 15,16) and has  $J/k_B = 0.40$  K.<sup>14</sup> The difference may in fact be understood on the basis of the above mechanism. In the latter compound, the Gd ions adopt a distorted capped square antiprism coordination of oxygen atoms; six out of a total of nine oxygen atoms are provided by the three bridging Cu(pba) groups, two by the oxalato ligand, and the last one by a water molecule.<sup>37</sup> In the former compound, due to the absence of the oxalato ligand, the  $5d$  orbitals of the gadolinium ions are distributed in a less distorted environment. This fact, together with slightly shorter Gd-Cu distances for  $\text{Gd}_2\text{Cu}_3$  (see Refs. 30 and 37 for comparison), gives higher values of  $\beta_{5d-3d}$  for  $\text{Gd}_2\text{Cu}_3$ . Consequently, according to Eq. (5.2), the coupling constant  $J$  should indeed be larger for  $\text{Gd}_2\text{Cu}_3$  than for  $\text{Gd}_2(\text{ox})[\text{Cu}(\text{pba})]_3[\text{Cu}(\text{H}_2\text{O})_5] \cdot 20\text{H}_2\text{O}$ , as found.

### B. $\text{Tb}_2\text{Cu}_3$ , $\text{Dy}_2\text{Cu}_3$ , and $\text{Ho}_2\text{Cu}_3$

Our measurements show  $\text{Tb}_2\text{Cu}_3$ ,  $\text{Dy}_2\text{Cu}_3$ , and  $\text{Ho}_2\text{Cu}_3$  to be strongly anisotropic systems with long-range order phase transitions below 1 K. As for  $\text{Gd}_2\text{Cu}_3$ , the low-dimensional structure of the compounds implies that the driving force for the long-range magnetic order is the dipolar interaction between the ferromagnetic chains. However, for  $\text{Tb}_2\text{Cu}_3$  and  $\text{Dy}_2\text{Cu}_3$ , evidence for an even larger amount of short-range order, associated with fluctuations within the ladder structure, is found above  $T_C$ . From the specific heat data, we have deduced that  $\text{Tb}_2\text{Cu}_3$  and  $\text{Dy}_2\text{Cu}_3$  may be described in terms of an effective spin 1/2 at low temperatures. We note that an effective spin 1/2, arising from a low-lying doublet, is often found for lanthanide compounds of dysprosium and terbium with low magnetic ordering temperature.<sup>38</sup> At higher

temperatures the behavior is strongly modified by the presence of low-lying excited states.

To explain the magnetic and thermal properties of  $\text{Tb}_2\text{Cu}_3$  and  $\text{Dy}_2\text{Cu}_3$ , a model has been developed, which is based on the standard transfer matrix technique, using the Ising approximation and assuming spin 1/2 for the  $L$  and the Cu ions. The details of the model can be found in the Appendix. As revealed from the susceptibility measurements, we have to expect a ferromagnetic coupling  $J$  for the  $L$ -Cu interaction. Next-nearest neighbor interactions are also taken into consideration. In fact, we have seen in Sec. III A that a weak antiferromagnetic interaction is acting between the copper ions in  $\text{La}_2\text{Cu}_3$ . Consequently, we may assume a similar Cu-Cu interaction to be present in  $L_2\text{Cu}_3$  for  $L = \text{Tb}$  and  $\text{Dy}$ . We shall denote by  $J'$  the Cu-Cu interaction. Similarly, we have also taken into account a weak antiferromagnetic coupling  $J''$  acting between the  $L$  ions, as suggested by the susceptibility data for  $\text{Gd}_2\text{Zn}_3$  (Sec. III A). According to our notation, a positive coupling constant implies a ferromagnetic coupling. The presence of next-nearest-neighbor interactions in 1D molecular systems based on lanthanide ions is not new and several examples can be found in the literature.<sup>39</sup> For the case of  $\text{Tb}_2\text{Cu}_3$ , the crystal field energy separation  $\Delta$  of the two lowest singlets of the non-Kramers Tb ion has also been included in the calculation. This contribution and the ones arising from next-nearest-neighbor interactions are then added to Eq. (5.1), where  $\sigma_i$  and  $S_j$  represent now the projections along the  $z$  axis of the Cu spins and the Tb or Dy effective spins, respectively, as explained in detail below in the Appendix.

To improve the reliability of the fits for  $\text{Tb}_2\text{Cu}_3$  and  $\text{Dy}_2\text{Cu}_3$ , we independently use the model in  $\text{La}_2\text{Cu}_3$  to get the estimate of  $J'$ , and in  $\text{Tb}_2\text{Zn}_3$  and  $\text{Dy}_2\text{Zn}_3$  to get the estimates of  $J''$ . We then fit the susceptibilities and specific heats of  $\text{Tb}_2\text{Cu}_3$  and  $\text{Dy}_2\text{Cu}_3$  with  $J'$  and  $J''$  fixed at the values obtained previously with only the coupling  $J$  and the effective gyromagnetic constant  $g$  as free parameters. The fits to the susceptibility and specific heat of  $\text{Tb}_2\text{Cu}_3$  are shown in Figs. 9 and 10, respectively. The fits provide the values of  $J/k_B = 5.6$  K,  $J'/k_B = -1.0$  K,  $J''/k_B = -1.0$  K,  $\Delta = 0.2$  K and an effective gyromagnetic constant of  $g = 18.0$  for the Tb ion. Similarly, the results for the susceptibility and specific heat of  $\text{Dy}_2\text{Cu}_3$  are shown in Figs. 11 and 12, respectively. In this case, the fits provide the values of  $J/k_B = 4.6$  K,  $J'/k_B = -1.0$  K,  $J''/k_B = -1.0$  K, and effective  $g = 19.6$ . It can be seen that the experimental behaviors above the 3D ordering temperatures are satisfactory reproduced. Only the specific heat of  $\text{Tb}_2\text{Cu}_3$  is not so well accounted for (Fig. 10). Probably, this comes from the influence of low-lying excited levels, making the Hamiltonian of this system less Ising-like than for  $\text{Dy}_2\text{Cu}_3$ . Moreover, the large  $g$  values found for both systems imply large magnetic moments which are moreover coupled ferromagnetically into chains, so that dipolar interactions may be strong enough to contribute also above the 3D ordering temperatures. Consequently, the model here presented may fail to give a detailed explanation in this temperature region. Nevertheless, the following conclusions can be drawn. The compounds  $\text{Tb}_2\text{Cu}_3$  and  $\text{Dy}_2\text{Cu}_3$  are very similar in behavior and are strongly anisotropic. We

TABLE II. Experimental results obtained for the Cu containing compounds.  $T_C$  is the long-range magnetic ordering temperature;  $\theta$  is obtained from the Curie-Weiss law (Sec. III);  $J$ ,  $J'$ , and  $J''$  are the exchange constants for the  $L$ -Cu, Cu-Cu, and  $L-L$  interactions, respectively (negative values stand for antiferromagnetic interactions);  $\Delta$  is the separation between the ground state and the first excited state (included also is the type of state:  $s$ =singlet;  $d$ =doublet;  $t$ =triplet);  $g_L$  is the Landé factor for the  $L$  ion; the models used are MF (mean field) or LLW (Sec. III B) or Georges (Sec. V A) or App. (Appendix and Sec. V B) or Schottky (Sec. IV E).

	La <sub>2</sub> Cu <sub>3</sub>	Gd <sub>2</sub> Cu <sub>3</sub>	Tb <sub>2</sub> Cu <sub>3</sub>	Dy <sub>2</sub> Cu <sub>3</sub>	Ho <sub>2</sub> Cu <sub>3</sub>
$T_C$ (K)		1.78(2)	0.81(1)	0.75(1)	0.04 ÷ 0.10
$\theta$ (K)	-0.2	2.3			
$J/k_B$ (K)		0.74	5.6	4.6	
$J'/k_B$ (K)	-0.2		-1.0	-1.0	
$J''/k_B$ (K)			-1.0	-1.0	
$\Delta$ (K)			0.2( $s-s$ )		$\approx 11$ ( $d-t$ )
$g_L$		2	18.0	19.6	
Model	MF	Georges	App.	App.	Schottky-LLW

note that large  $g$  values of order 20, found for both Tb<sub>2</sub>Cu<sub>3</sub> and Dy<sub>2</sub>Cu<sub>3</sub>, have been also reported for other Dy and Tb based compounds.<sup>40</sup> For both cases, the  $L$ -Cu interaction is predominant and ferromagnetic. This interaction is slightly stronger for Tb<sub>2</sub>Cu<sub>3</sub> than for Dy<sub>2</sub>Cu<sub>3</sub>, in line with the analysis reported in Ref. 18. Consequently, the 3D ordering temperature is also higher for Tb<sub>2</sub>Cu<sub>3</sub> ( $T_C=0.81$  K) than for Dy<sub>2</sub>Cu<sub>3</sub> ( $T_C=0.75$  K). For both compounds, the presence of next-nearest-neighbor interactions have to be taken into account. These interactions are much weaker than the  $L$ -Cu interaction and are antiferromagnetic in nature. In conclusion, the results here obtained suggest that Tb<sub>2</sub>Cu<sub>3</sub> and Dy<sub>2</sub>Cu<sub>3</sub> order ferromagnetically within the ladders. This ordering process is accompanied by weak dipolar and probably antiferromagnetic interladder interactions, that, together with strong crystal field effects, lower the susceptibility below  $T_C$ .

For Ho<sub>2</sub>Cu<sub>3</sub>, we have already reported that the Ho-Cu interaction has to be very weak. Indeed, crystal field effects and dipolar interactions are mainly responsible for the magnetic properties at low temperature (Sec. IV E). Consequently, also the 3D ordering temperature is the lowest one in comparison with Tb<sub>2</sub>Cu<sub>3</sub> and Dy<sub>2</sub>Cu<sub>3</sub>. The results obtained for the magnetic interaction parameters are summarized in Table II for the Cu containing compounds and in Table III for the Zn containing compounds.

## VI. CONCLUDING REMARKS

In the previous sections we have focused attention on the physical properties of spin-ladder molecular magnets containing lanthanide and transition metal ions. Together with the originality of their crystal structure, the  $L_2M_3$  compounds present interesting magnetic features such as the onset of long-range orderings for  $L=Gd, Tb, Dy, Ho$ , and

TABLE III. Experimental results obtained for the Zn containing compounds. The same notation of Table II is used.

	Gd <sub>2</sub> Zn <sub>3</sub>	Tb <sub>2</sub> Zn <sub>3</sub>	Dy <sub>2</sub> Zn <sub>3</sub>	Ho <sub>2</sub> Zn <sub>3</sub>
$\theta$ (K)	-0.1			
$J''/k_B$ (K)	$-6 \times 10^{-3}$	-1.0		
$\Delta$ (K)		0.2 ( $s-s$ )	13.7 ( $d-d$ )	8.3 ( $d-t$ )
Model	MF	LLW-App.	LLW	LLW

$M=Cu$ . To the best of our knowledge, Gd<sub>2</sub>Cu<sub>3</sub> is the lanthanide and transition metal ions based ferromagnet with the highest long-range ordering critical temperature  $T_C=(1.78 \pm 0.02)$  K so far reported. Moreover, as estimated from specific heat and susceptibility measurements, Tb<sub>2</sub>Cu<sub>3</sub> has a magnetic ordering temperature of  $T_C=(0.81 \pm 0.01)$  K, while Dy<sub>2</sub>Cu<sub>3</sub> orders at  $T_C=(0.75 \pm 0.01)$  K, and Ho<sub>2</sub>Cu<sub>3</sub> has a  $T_C$  between 0.04 and 0.10 K. These molecular based magnets are the first ones obtained with lanthanide ions other than gadolinium.

The very pronounced quasi-one-dimensionality of the magnetic structure implies that the 3D ordering is driven by the dipolar interaction acting between ladders together with the intraladder superexchange interaction. We have also reported that the intraladder  $L$ -Cu interaction is the dominant one and it is ferromagnetic for  $L=Gd, Tb$ , and  $Dy$ . The influence on the magnetic properties of the weaker antiferromagnetic next-nearest neighbor  $L-L$  and Cu-Cu interactions have also been analyzed. A remarkable point is the key role of the copper ions in these complex systems. They transmit the magnetic exchange interaction between the  $L$  ions across the ladder. As a proof of this, we have seen that, if Cu is substituted by the nonmagnetic Zn, the  $L-L$  interaction is inhibited and the critical temperature of the 3D ordering process is strongly diminished. Finally, the effects on the susceptibility and specific heat of the crystal field splittings of the magnetic energy levels of the lanthanide ions in  $L_2M_3$  have been discussed and rationalized, assuming the same symmetry and coordination for the lanthanide ion in each compound of the series.

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## APPENDIX: ISING MODEL FOR QUANTUM SPIN LADDER

The model here reported has been developed to explain the magnetic and thermal properties of the Tb<sub>2</sub>Cu<sub>3</sub> and Dy<sub>2</sub>Cu<sub>3</sub> compounds. As a first step, we assume only a coupling between the next-nearest copper (Cu) and lanthanide ( $L=Tb, Dy$ ) ions which is ferromagnetic (in the following notations, this means  $J>0$ ).

For Tb and Dy, we assume an effective low-temperature spin 1/2 and Ising coupling due to the crystal field anisotropy

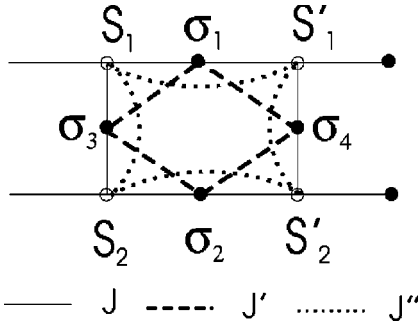


FIG. 15. Ladder structure considered by the model discussed in the Appendix.

of the lanthanide ion. For Cu, we assume spin 1/2 as well. The effective Hamiltonian is then

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} (\sigma_i S_j) - \left( \sum_{i=1}^{N_\sigma} g_\sigma \mu_B \sigma_i + \sum_{j=1}^{N_S} g_S \mu_B S_j \right) H_z, \quad (\text{A1})$$

where  $\sigma_i$  and  $S_j$  are the projections along the  $z$  axis of the spins of the copper and lanthanide ions, respectively (Fig. 15). The Landé factor of the copper ions is assumed to be  $g_\sigma = 2$ , while the one of the lanthanide ions is a fitting parameter. The Zeeman terms in Eq. (A1) extend over all  $N_\sigma$  copper and  $N_S$  lanthanide ions.

We build the transfer matrix on the unit cell

$$\begin{aligned} T(S_1, S_2; S'_1, S'_2) &= \sum_{\sigma_1, \sigma_2, \sigma_3, \sigma_4} \exp \left\{ \beta J \left[ \sigma_1 (S_1 + S'_1) + \sigma_2 (S_2 + S'_2) \right. \right. \\ &\quad \left. \left. + \frac{1}{2} \sigma_3 (S_1 + S'_2) + \frac{1}{2} \sigma_4 (S_1 + S'_2) \right] \right\} \\ &\times \exp \left\{ \frac{1}{2} \beta g_S \mu_B H_z (S_1 + S'_1 + S_2 + S'_2) + \beta g_\sigma \mu_B H_z \right. \\ &\quad \left. \times \left( \sigma_1 + \sigma_2 + \frac{1}{2} \sigma_3 + \frac{1}{2} \sigma_4 \right) \right\}, \end{aligned}$$

where  $\beta = 1/k_B T$ . The partition is expressed in terms of the  $4 \times 4$  transfer matrix

$$\begin{aligned} Z(T, H_z) &= \sum_{S_i} T(S_1, S_2; S'_1, S'_2) T(S'_1, S'_2; S''_1, S''_2) \\ &\quad \dots T(S_1^{(N)}, S_2^{(N)}; S_1, S_2) \\ &= \text{Tr} (T^N). \end{aligned}$$

Therefore, by defining

$$f(T, H_z) \equiv \lim_{N \rightarrow \infty} \frac{1}{N} \ln Z = \ln \lambda,$$

where  $\lambda$  is the largest eigenvalue of  $T$ , we obtain numerically the magnetic susceptibility and the molar specific heat by

$$\chi = k_B T \frac{\partial^2 f}{\partial H_z^2}, \quad C = k_B \beta^2 \frac{\partial^2 f}{\partial \beta^2}.$$

According to the susceptibility data of  $\text{La}_2\text{Cu}_3$  (Fig. 2), we assume a slight antiferromagnetic next-nearest-neighbor coupling  $J'$  between the copper ions. Similarly, according to the susceptibility data of  $\text{Gd}_2\text{Zn}_3$  (Fig. 2), we expect an antiferromagnetic next-nearest-neighbor coupling  $J''$  between the lanthanide ions. In both cases, the data are compatible with couplings not exceeding 1 K. By adding these second neighbors couplings we get the complete scheme depicted in Fig. 15.

The transfer matrix is now

$$\begin{aligned} T(S_1, \sigma_3, S_2; S'_1, \sigma_4, S'_2) &= \sum_{\sigma_1, \sigma_2} \exp \left\{ \beta J \left[ \sigma_1 (S_1 + S'_1) + \sigma_2 (S_2 + S'_2) \right. \right. \\ &\quad \left. \left. + \frac{1}{2} \sigma_3 (S_1 + S'_2) + \frac{1}{2} \sigma_4 (S_1 + S'_2) \right] \right\} \\ &\times \exp \left\{ \beta J' (\sigma_1 + \sigma_2) (\sigma_3 + \sigma_4) + \beta J'' \right. \\ &\quad \left. \times \left[ S_1 S'_1 + S_2 S'_2 + \frac{1}{2} (S_1 S_2 + S'_1 S'_2) \right] \right\} \\ &\times \exp \left\{ \frac{1}{2} \beta g_S \mu_B H_z (S_1 + S'_1 + S_2 + S'_2) + \beta g_\sigma \mu_B H_z \right. \\ &\quad \left. \times \left( \sigma_1 + \sigma_2 + \frac{1}{2} \sigma_3 + \frac{1}{2} \sigma_4 \right) \right\} \end{aligned}$$

with  $J > 0$ ,  $J' < 0$  and  $J'' < 0$ . This is now an  $8 \times 8$  matrix but the process is the same.

For the terbium case, that is a non-Kramers ion, we allow the spin states to be nondegenerate by adding to the Hamiltonian a term  $E(S_i)$  such that  $E(+\frac{1}{2}) = \Delta/2$  and  $E(-\frac{1}{2}) = -\Delta/2$ , where  $\Delta$  is the gap. The best fits for  $\text{Tb}_2\text{Cu}_3$  are displayed in Figs. 9, 10 and for  $\text{Dy}_2\text{Cu}_3$  in Figs. 11, 12.

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