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Effect of Exchange Interaction on the Low-Temperature Ordering of $GdCl_3$, Dysprosium Ethyl Sulfate, and Some Rare-Earth Hydroxides

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The low-temperature ordered states of Gd^{+++} ions in gadolinium trichloride and hydroxide lattices, Dy^{+++} ions in dysprosium ethyl sulfate and hydroxide lattices, and Tb^{+++}, Ho^{+++}, Nd^{+++}, and Er^{+++} ions in their respective hydroxide lattices are investigated taking into account both the dipole-dipole and exchange interactions. The method used is essentially that of Luttinger and Tisza for dipole-dipole interaction, later generalized by Niemeyer to include exchange interaction. A linear dependence of the energy eigenvalues upon the exchange-interaction constants is found. For $GdCl_3$ and $Gd(OH)_3$, which are the only cases where the values of the exchange-interaction constants are experimentally known, ferromagnetic and antiferromagnetic orderings, respectively, corresponding to the lowest energy are predicted in agreement with the experimental observations. For $Nd(OH)_3$, where a ferromagnetic low-temperature ordering is predicted by the dipole-dipole interaction, an antiferromagnetic ordering may prevail if antiferromagnetic exchange interactions of suitable values are considered. This is in accordance with the observation of Wolf, Meissner, and Catanese. For the remaining cases, a limit for the next-nearest-neighbor exchange constant is obtained which will yield the ferromagnetic ordered states as observed experimentally.

I. INTRODUCTION

Recently many papers have appeared dealing with the prediction of ordered states at 0 °K, taking into account the magnetic dipole-dipole interaction between the constituent ions.[1-4] An exception is the work of Niemeyer,[1] which not only takes into account the dipole-dipole interaction but also includes the exchange interaction in his calculation for the case of cerium magnesium nitrate crystals. The method used for such calculations is essentially that developed by Luttinger and Tisza in 1946,[5] based on classical considerations. Niemeyer, on the other hand, has presented a quantum-mechanical treatment which yields the same prescription as the classical method. He also shows that the exchange interaction between nearest neighbors can be simultaneously taken into account. The present paper deals with the investigation of the low-temperature ordered states of Gd^{+++} ions in $GdCl_3$ and $Gd(OH)_3$ lattices, Dy^{+++} ions in dysprosium ethyl sulfate (DyES) and $Dy(OH)_3$ lattices, Tb^{+++} ions in $Tb(OH)_3$ lattice, Ho^{+++} ions in $Ho(OH)_3$ lattice, Nd^{+++} ions in $Nd(OH)_3$ lattice, and Er^{+++} ions in $Er(OH)_3$ lattice, under the effect of both magnetic dipole-dipole and exchange interactions. The rare-earth ions in all these crystals lie on lattices which are similar to hexagonal close-packed except that the c/a ratio is much smaller. The motivation for this investigation is provided by the finding that the dipole-dipole interaction alone does not predict the observed antiferromagnetic low-temperature ordering of $Nd(OH)_3$ and $Gd(OH)_3$.[3,4] The exchange interaction may then play an important role in the settling of the crystal to the low-temperature ordered state, especially in view of the fact that for the case of dipole-dipole interaction alone the two lowest-lying energy eigenvalues of the relevant matrix are usually very close together, one of which corresponds to a ferromagnetic ordering while the other corresponds to an antiferromagnetic ordering. Thus inclusion of exchange interaction, however small, may be effective in reversing the order of these eigenvalues. Such is the situation, as will be seen in Sec. III. In Sec. II, an outline of the method used for calculation will be presented with generalization to take into account the division of the lattice into sixteen sublattices as required for all the cases considered in this paper. A discussion of the results of the application of the method to the various crystals considered will be given in Sec. III. The resulting conclusions will be summarized in Sec. IV.

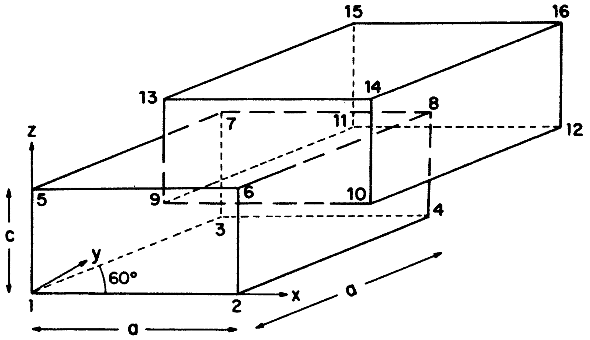

FIG. 1. Structure of the basic unit for the various crystals considered. Labeling of the various ion sites is indicated. Note that the triangle 123 (and other corresponding triangles) is equilateral. Site 9 is midway between the triangles 123 and 567, lying on the line joining their centers.

II. THEORY

The relevant interaction Hamiltonian can be written

$$\mathcal{H}=\sum_{i<j} \mathcal{H}_{ij} \;, \quad \mathcal{H}_{ij}=v_{ij}\Delta_{ij}\vec{S}_i\cdot\vec{S}_j+D_{ij}\;, \tag{2.1}$$

where the summation is over all the ions in the crystal. The first term in Eq. (2.1) represents the exchange interaction, with $\vec{S}$ standing for the ionic spin, and $\Delta_{ij}=1$ when i and j are nearest and next-nearest neighbors, 0 otherwise. v_{ij} is an exchange-interaction constant. An isotropic exchange interaction has been assumed for the calculations. The second term represents the dipole-dipole interaction, where

$$D_{ij}=\vec{\mu}_i\cdot\vec{\mu}_j/r_{ij}^3-3(\vec{\mu}_i\cdot\vec{r}_{ij})(\vec{\mu}_j\cdot\vec{r}_{ij})/r_{ij}^5 \;.$$

Here $\vec{r}_{ij}$ is the vector that joins ion i to ion j, with components r_{ij}^α, $\alpha=x, y, z$, and $\mu_i^\alpha=\mu_B g^\alpha S^\alpha$, where μ_B is the Bohr magneton and g^α is the g factor in the α direction (a coordinate system is chosen in which the g tensor has only the diagonal elements nonzero).

For all the cases under consideration the whole lattice can be generated by applying a group of translations $\vec{T}^2$ to the locations of the 16 ions sitting at the vertices of a basic unit (Fig. 1), where $\vec{T}=l_1\vec{a}+l_2\vec{b}+l_3\vec{c}$, is the group of translations with l_1, l_2, l_3 being integers. Now using a set of wave functions which are direct products of 16 one-spin wave functions, it is possible to write the expectation value of the energy per ion in the lattice as

$$E=\sum_{i,j=1}^{16}\sum_{\alpha,\beta} A_{ij}^{\alpha\beta}\xi_i^\alpha\xi_j^\beta \;, \tag{2.2}$$

where

$$A_{ij}^{\alpha\beta}=\sum_{l\in\{j\}} J_{il}^{\alpha\beta} \quad \text{for } i\neq j \;,$$

$$A_{jj}^{\alpha\beta}=\sum_{\substack{l\in\{j\}\\ \neq j}} J_{jl}^{\alpha\beta} \;, \tag{2.3}$$

$$J_{ij}^{\alpha\beta}=\tfrac{1}{2}S^2\{\mu_B^2[g^\alpha g^\beta\delta_{\alpha\beta}/r_{ij}^3-3g^\alpha g^\beta r_{ij}^\alpha r_{ij}^\beta/r_{ij}^5] +v_{ij}\Delta_{ij}\delta_{\alpha\beta}\}. \tag{2.4}$$

In Eq. (2, 3), i, j are the vertices of the basic unit, from which the whole lattice can be generated by the application of $\vec{T}^2$ as mentioned earlier and $\{j\}$ denotes the set of lattice sites generated by $\vec{T}^2$ from the jth vertex of the basic unit. In writing Eq. (2.4), a factor of $\frac{1}{2}$ has been included to take into account the fact that in its absence the interaction energy between two ions would have been counted twice, and a factor of S^2 accounts for the normalization expressed by Eq. (2.5) below. The quantities ξ_i^α in Eq. (2.2) represent the expectation value of the operator $\hat{S}_i^\alpha/S$. The quantities $\vec{\xi}_i$ further obey the constraint

$$\vec{\xi}_i\cdot\vec{\xi}_i=1 \;, \tag{2.5}$$

which is known as the "strong" condition.[5] The strong condition also implies the "weak" condition[5]

$$\sum_{i=1}^{16}\vec{\xi}_i\cdot\vec{\xi}_i=16 \;. \tag{2.6}$$

The lowest value of E, given by Eq. (2.2) under the constraint (2.6) is the lowest eigenvalue of the 48×48 matrix A (elements $A_{ij}^{\alpha\beta}$; $i, j=1$, 16 and α, $\beta=x, y, z$).[6] Niemeyer[1] shows that with his choice of eigenvectors the weak condition automatically satisfies the strong condition for any Bravais lattice. It can be easily shown that this is true for our hexagonal lattice as well. Thus the problem is reduced to finding the lowest eigenvalue of the matrix A.

The task of finding the eigenvalues can be further simplified by the following considerations.[1] If P_l

is the set of permutations acting on the 16 vertices of the basic unit (see Table I) such that

$$A^{\alpha\beta}_{P_t i, P_t j} = A^{\alpha\beta}_{ij} \quad \text{for all } i,\ j,\ \alpha,\ \beta \ ,$$

then the components of the eigenvectors of A can be expressed as

$$\eta^{\nu}_{j}(k,\gamma) = q_j(k)\Phi^{\nu}(\gamma) \ , \qquad k=1,\ 2,\ \ldots,\ 16; \quad \gamma = x,\ y,\ z \tag{2.7}$$

where the $\vec{q}(k)$ are the eigenvectors of the permutation operators P_t, given as column matrices with 16 elements each (for a listing see Table II). The $\Phi^{\nu}(l)$ are the solutions of the eigenvalue equation

$$\sum_{\nu} L^{\mu\nu}_{k}\Phi^{\nu}(\gamma) = \lambda^{l}_{k}\Phi^{\mu}(\gamma) \ ,$$

where

$$L^{\mu\nu}_{k} = \sum_{j} A^{\mu\nu}_{ij}\epsilon_{P(i,j)}(k) \ . \tag{2.8}$$

In Eq. (2.8), $\epsilon_{P(i,j)}(k)$ is the eigenvalue of the permutation operator $P(i,j)$ containing the cycle (i,j) with respect to the eigenvector $\vec{q}(k)$. A listing of ϵ_{P_t}'s relevant to our cases is given in Table III. The summation on the right-hand side of Eq. (2.8) is independent of the index i.

It is easily seen from Eq. (2.7) and the form of $\vec{q}(1)$ and $\vec{q}(2)$ that the eigenvalues of A for the eigenvectors $\eta(1,\gamma)$ and $\eta(2,\delta)$ would correspond to ferromagnetic and antiferromagnetic orderings, respectively, while the rest of the eigenvalues would correspond to layered antiferromagnetic orderings of spins on the lattice. Also, no configuration other than the ferromagnetic, antiferromagnetic, or layered antiferromagnetic arrangements of spins is possible as seen from the form of $\vec{q}(k)$'s.

TABLE I. Permutations P_t with the property $A^{\alpha\beta}_{P_t i, P_t j} = A^{\alpha\beta}_{ij}$. (It is easily seen that $[P_t, P_{t'}] = 0$.)

P_1 = identity
P_2 = (1, 2) (3, 4) (5, 6) (7, 8) (9, 10) (11, 12) (13, 14) (15, 16)
P_3 = (1, 3) (2, 4) (5, 7) (6, 8) (9, 11) (10, 12) (13, 15) (14, 16)
P_4 = (1, 4) (2, 3) (5, 8) (6, 7) (9, 12) (10, 11) (13, 16) (14, 15)
P_5 = (1, 5) (2, 6) (3, 7) (4, 8) (9, 13) (10, 14) (11, 15) (12, 16)
P_6 = (1, 6) (2, 5) (3, 8) (4, 7) (9, 14) (10, 13) (11, 16) (12, 15)
P_7 = (1, 7) (2, 8) (3, 5) (4, 6) (9, 15) (10, 16) (11, 13) (12, 14)
P_8 = (1, 8) (2, 7) (3, 6) (4, 5) (9, 16) (10, 15) (11, 14) (12, 13)
P_9 = (1, 9) (2, 10) (3, 11) (4, 12) (5, 13) (6, 14) (7, 15) (8, 16)
P_{10} = (1, 10) (2, 9) (3, 12) (4, 11) (5, 14) (6, 13) (7, 16) (8, 15)
P_{11} = (1, 11) (2, 12) (3, 9) (4, 10) (5, 15) (6, 16) (7, 13) (8, 14)
P_{12} = (1, 12) (2, 11) (3, 10) (4, 9) (5, 16) (6, 15) (7, 14) (8, 13)
P_{13} = (1, 13) (2, 14) (3, 15) (4, 16) (5, 9) (6, 10) (7, 11) (8, 12)
P_{14} = (1, 14) (2, 13) (3, 16) (4, 15) (5, 10) (6, 9) (7, 12) (8, 11)
P_{15} = (1, 15) (2, 16) (3, 13) (4, 14) (5, 11) (6, 12) (7, 9) (8, 10)
P_{16} = (1, 16) (2, 15) (3, 14) (4, 13) (5, 12) (6, 11) (7, 10) (8, 9)

TABLE II. Eigenvectors of operators P_t corresponding to the permutations of the 16 vertices of the basic unit shown in Fig. 1. Since all P_t's commute they have a common set of eigenvectors.

$$\vec{q}(1) = \begin{pmatrix}\alpha\\ \alpha\\ \alpha\\ \alpha\end{pmatrix}, \quad \vec{q}(2) = \begin{pmatrix}\alpha\\ \alpha\\ -\alpha\\ -\alpha\end{pmatrix}, \quad \vec{q}(3) = \begin{pmatrix}\beta\\ -\beta\\ \beta\\ -\beta\end{pmatrix}, \quad \vec{q}(4) = \begin{pmatrix}\beta\\ -\beta\\ -\beta\\ \beta\end{pmatrix},$$

$$\vec{q}(5) = \begin{pmatrix}\gamma\\ \gamma\\ \gamma\\ \gamma\end{pmatrix}, \quad \vec{q}(6) = \begin{pmatrix}\gamma\\ \gamma\\ -\gamma\\ -\gamma\end{pmatrix}, \quad \vec{q}(7) = \begin{pmatrix}\alpha\\ -\alpha\\ \alpha\\ -\alpha\end{pmatrix}, \quad \vec{q}(8) = \begin{pmatrix}\alpha\\ -\alpha\\ -\alpha\\ \alpha\end{pmatrix},$$

$$\vec{q}(9) = \begin{pmatrix}\delta\\ \delta\\ \delta\\ \delta\end{pmatrix}, \quad \vec{q}(10) = \begin{pmatrix}\delta\\ \delta\\ -\delta\\ -\delta\end{pmatrix}, \quad \vec{q}(11) = \begin{pmatrix}\gamma\\ -\gamma\\ \gamma\\ -\gamma\end{pmatrix}, \quad \vec{q}(12) = \begin{pmatrix}\gamma\\ -\gamma\\ -\gamma\\ \gamma\end{pmatrix},$$

$$\vec{q}(13) = \begin{pmatrix}\beta\\ \beta\\ \beta\\ \beta\end{pmatrix}, \quad \vec{q}(14) = \begin{pmatrix}\beta\\ \beta\\ -\beta\\ -\beta\end{pmatrix}, \quad \vec{q}(15) = \begin{pmatrix}\delta\\ -\delta\\ \delta\\ -\delta\end{pmatrix}, \quad \vec{q}(16) = \begin{pmatrix}\delta\\ -\delta\\ -\delta\\ \delta\end{pmatrix},$$

where,

$$\alpha = \begin{pmatrix}1\\ 1\\ 1\\ 1\end{pmatrix}, \quad \beta = \begin{pmatrix}1\\ -1\\ -1\\ 1\end{pmatrix}, \quad \gamma = \begin{pmatrix}1\\ 1\\ -1\\ -1\end{pmatrix}, \quad \delta = \begin{pmatrix}1\\ -1\\ 1\\ -1\end{pmatrix}.$$

III. APPLICATIONS

All the cases considered in this paper, namely, $GdCl_3$, $Gd(OH)_3$, DyES, $Dy(OH)_3$, $Tb(OH)_3$, $Ho(OH)_3$, $Nd(OH)_3$, and $Er(OH)_3$, have the same structure.[7,8] The basic unit is shown in Fig. 1. In Table IV a listing of the values of a, c, $g_{\parallel}(=g^z)$, and $g_{\perp}(=g^x=g^y)$ are given for the various cases considered. In order to construct the matrix A, as given by Eq. (2.3), one requires the lattice sums and the exchange-interaction constants. The lattice sums for the present considerations are presented in Tables V–XI, where the unit of length is $2a$ in each case and the sums are evaluated within a sphere of radius 500 Å (for larger radii there is negligible difference in the lattice sums). Only the sums from the sublattices generated by ions 1, 3, 5, 7, 9, and 12 to ion 1 are given as the sums from the remaining sublattices can be easily obtained from these.

Since the lattice sums have been evaluated over a sphere, rather than over a long, thin needle, one needs the demagnetization contributions to the eigenvalues E_i of the matrix A corresponding to the ferromagnetic configuration of spins, namely, to the eigenvalues E_1, E_2, and E_3. The demagnetization factors are listed in Table IV and a discussion of how to evaluate them is presented in the Appendix.

Although by using Eq. (2.7), the task of finding the eigenvalues of the matrix A is reduced to diagonalization of sixteen 3×3 matrices and can be

TABLE III. Eigenvalues of the vectors $\vec{q}(k)$ under the operations P_t.

	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}	P_{12}	P_{13}	P_{14}	P_{15}	P_{16}
$\vec{q}(1)$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\vec{q}(2)$	1	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1
$\vec{q}(3)$	1	−1	−1	1	−1	1	1	−1	1	−1	−1	1	−1	1	1	−1
$\vec{q}(4)$	1	−1	−1	1	−1	1	1	−1	−1	1	1	−1	1	−1	−1	1
$\vec{q}(5)$	1	1	−1	−1	1	1	−1	−1	1	1	−1	−1	1	1	−1	−1
$\vec{q}(6)$	1	1	−1	−1	1	1	−1	−1	−1	−1	1	1	−1	−1	1	1
$\vec{q}(7)$	1	1	1	1	−1	−1	−1	−1	1	1	1	1	−1	−1	−1	−1
$\vec{q}(8)$	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1	1	1	1	1
$\vec{q}(9)$	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1
$\vec{q}(10)$	1	−1	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1	−1	1
$\vec{q}(11)$	1	1	−1	−1	−1	−1	1	1	1	1	−1	−1	−1	−1	1	1
$\vec{q}(12)$	1	1	−1	−1	−1	−1	1	1	−1	−1	1	1	1	1	−1	−1
$\vec{q}(13)$	1	−1	−1	1	1	−1	−1	1	1	−1	−1	1	1	−1	−1	1
$\vec{q}(14)$	1	−1	−1	1	1	−1	−1	1	−1	1	1	−1	−1	1	1	−1
$\vec{q}(15)$	1	−1	1	−1	−1	1	−1	1	1	−1	1	−1	−1	1	−1	1
$\vec{q}(16)$	1	−1	1	−1	−1	1	−1	1	−1	1	−1	1	1	−1	1	−1

done manually, this task was done on a computer. The dipole-dipole contributions E_i^{dd} to the eigenvalues of A for the various cases considered are given in Table XII.

As far as the contributions of the exchange interaction are concerned, only the nearest and the next-nearest neighbors have been taken into account; the latter being included in view of the experimental results of Clover and Wolf for $GdCl_3$,[9] who found that the magnitude of the exchange-interaction constant for the next-nearest neighbor is of the same order and somewhat greater than that for the nearest neighbor. A reference to Fig. 1 shows that nearest neighbors to ion 1 are ions 5, 5′ at a distance c (~0.56a for our cases), whereas the next-nearest neighbors are the ions 9, 10′, 11′, 13′, 14′, and 15′ at a distance $a(\frac{1}{3}+c^2/4a^2)^{1/2}$ (~0.64a for our cases). The prime denotes the ion obtained by a $\vec{T}^2$ translation to an ion on the basic unit. The relevant exchange-interaction constants will be denoted by v_{nn} and v_{nnn}, respectively, where the subscripts nn and nnn stand for nearest neighbor and next-nearest neighbor, respectively. Using the technique described in Sec. II the contribution E_i^{ex} of the exchange interaction to the eigenvalues E_i of the matrix A can be readily

TABLE IV. Values of a, c/a, and the demagnetization factors for the various lattices and the $g_\parallel$, $g_\perp$, and S values of the ions located on their sites (as indicated). The values of a, c, $g_\parallel$, and $g_\perp$ for all cases, except for $GdCl_3$ and DyES, are taken from Ref. 11. For the values of $GdCl_3$ refer to Ref. 8 and for the values for DyES refer to Ref. 7 (Ketelaar *et al.*) and Ref. 12 (Cooke *et al.*).

Crystal	Effective spin (S)	a(Å)	c/a	$g_\parallel$	$g_\perp$	Demagnetization contribution (°K) x,y	z
$GdCl_3$ (Gd^{+++})	$\frac{7}{2}$	7.363	0.5575	1.991	1.991	−0.65764	−0.65764
$Gd(OH)_3$ (Gd^{+++})	$\frac{7}{2}$	6.265	0.566	1.992	1.992	−1.0526	−1.0526
DyES (Dy^{+++})	$\frac{1}{2}$	13.906	0.506	10.8	0	0	−0.06459
$Dy(OH)_3$ (Dy^{+++})	$\frac{1}{2}$	6.27	0.563	19.0	0	0	−1.9600
$Tb(OH)_3$ (Tb^{+++})	$\frac{1}{2}$	6.27	0.563	17.8	0	0	−1.7202
$Ho(OH)_3$ (HO^{+++})	$\frac{1}{2}$	6.26	0.564	15.2	0	0	−1.2582
$Nd(OH)_3$ (Nd^{+++})	$\frac{1}{2}$	6.27	0.561	3.63	1.95	−0.02072	−0.0718
$Er(OH)_3$ (Er^{+++})	$\frac{1}{2}$	6.25	0.5645	1.69	8.75	−0.4186	−0.015615

TABLE V. Lattice sums for $GdCl_3$. The variables r, x, y, and z are the displacements and its components, from an origin situated at a given ion in sublattice 1 of Fig. 1 to each ion in one of the various sublattices. The unit of length is $2a$, $a = 7.363$ Å.

Sublattice summed	A $[\equiv \sum (3z^2 - r^2)/r^5]$	B $[\equiv \sum (x^2 - y^2)/r^5]$	C $[\equiv \sum xy/r^5]$	D $[\equiv \sum xz/r^5]$	E $[\equiv \sum yz/r^5]$
1	19.0602	0	0	0	0
3	−12.1220	−7.8311	6.7819	0	0
5	185.6040	0	0	0	0
7	−5.3002	−6.2917	5.4488	0	0
9	−6.0604	13.5287	11.7162	7.7257	4.4604
12	−8.6639	0	0	0	0

written down since the matrix corresponding to this interaction is already diagonal. Explicitly,

$$2S^{-2}E_i^{ex} = 2v_{nn} + 6v_{nnn} \quad i = 1,\ 2,\ 3$$

$$2S^{-2}E_i^{ex} = 2v_{nn} - 6v_{nnn}\ , \quad i = 4,\ 5,\ 6$$

$$2S^{-2}E_i^{ex} = -2v_{nn}\ , \quad i = 7\text{–}12,\ 19\text{–}24,\ 31\text{–}36,\ 43\text{–}48$$

$$2S^{-2}E_i^{ex} = 2v_{nn} + 2v_{nnn}\ ,$$

$$i = 13,\ 14,\ 15,\ 25,\ 26,\ 27,\ 40,\ 41,\ 42$$

$$2S^{-2}E_i^{ex} = 2v_{nn} - 2v_{nnn}\ ,$$

$$i = 16,\ 17,\ 18,\ 28,\ 29,\ 30,\ 37,\ 38,\ 39\ .$$

A discussion of the various cases will now be presented.

A. $GdCl_3$

The following values of the constants v_{nn} and v_{nnn} have been deduced for this salt from experimental measurements[8]:

$$v_{nn} = +(0.078 \pm 0.004)\ ^\circ\mathrm{K}\ ,$$

$$v_{nnn} = -(0.096 \pm 0.004)\ ^\circ\mathrm{K}\ .$$

The lowest eigenvalue of the matrix A then turns out to be $E_3 = -3.6978\ ^\circ\mathrm{K}$ corresponding to a ferromagnetic configuration in agreement with the experimental observation, with all the spins pointing in the z direction. The next-lying eigenvalue, $-1.8965\ ^\circ\mathrm{K}$, is threefold degenerate ($= E_{15} = E_{27} = E_{42}$). The same ferromagnetic configuration is also predicted to be the lowest lying by a consideration of dipole-dipole interaction alone.

B. $Gd(OH)_3$

The measurements of Cochrane, Wu, and Wolf[10] yield $v_{nn} = 0.1822\ ^\circ\mathrm{K}$ and $v_{nnn} = -0.0119\ ^\circ\mathrm{K}$ for Gd^{+++}-Gd^{+++} exchange interaction in $Gd(OH)_3$. The lowest eigenvalue then turns out to be sixfold degenerate ($= E_i = -3.1593\ ^\circ\mathrm{K}$; $i = 9,\ 12,\ 33,\ 36,\ 45,\ 48$) corresponding to antiferromagnetic orderings in agreement with the experimental finding.[11]

C. DyES, $Dy(OH)_3$, $Tb(OH)_3$, and $Ho(OH)_3$

There are similarities in all these cases in that all these salts have been observed to undergo ferromagnetic low-temperature orderings,[11,12] have $g_\perp = 0$, have E_3^{dd} (ferromagnetic) as the lowest-lying eigenvalue due to the dipole-dipole interaction, and have a threefold degenerate eigenvalue ($E_{15}^{dd} = E_{27}^{dd} = E_{42}^{dd}$) as the next-lowest dipole-dipole eigenvalue (antiferromagnetic). The difference $\Delta E (\equiv E_3 - E_{15})$ between these two lowest-lying eigenvalues, taking into account the exchange interaction also, is given as follows:

DyES: $\Delta E = (0.0028 - \frac{1}{2} v_{nnn})\ ^\circ\mathrm{K}$,

$Dy(OH)_3$: $\Delta E = (0.151 - \frac{1}{2} v_{nnn})\ ^\circ\mathrm{K}$,

$Tb(OH)_3$: $\Delta E = (0.133 - \frac{1}{2} v_{nnn})\ ^\circ\mathrm{K}$,

$Ho(OH)_3$: $\Delta E = (0.098 - \frac{1}{2} v_{nnn})\ ^\circ\mathrm{K}$.

From these values it is clear that a ferromagnetic low-temperature ordering would prevail in all these cases when v_{nnn} is less than 0.0056, 0.302, 0.266, and 0.196 °K for DyES, $Dy(OH)_3$, $Tb(OH)_3$, and $Ho(OH)_3$, respectively. The mag-

TABLE VI. Lattice sums for $Gd(OH)_3$. For an explanation of notation refer to Table V. The unit of length is $2a$, $a = 6.265$ Å.

Sublattice summed	A	B	C	D	E
1	17.9486	0	0	0	0
3	−12.1555	−7.7646	6.7243	0	0
5	177.1197	0	0	0	0
7	−5.0182	−6.1473	5.3237	0	0
9	−5.7706	13.2783	11.4993	7.8142	4.5115
12	−8.5319	0	0	0	0

TABLE VII. Lattice sums for DyES. For an explanation of notation refer to Table V. The unit of length is $2a$, $a = 13.906$ Å.

Sublattice summed	A	B	C	D	E
1	27.5628	0	0	0	0
3	−12.0166	−8.3154	7.2014	0	0
5	250.2611	0	0	0	0
7	−7.1356	−7.2351	6.2658	0	0
9	−7.8323	15.1711	13.1386	7.0482	4.0693
12	−9.5559	0	0	0	0

TABLE VIII. Lattice sums for Dy$(OH)_3$ and Tb$(OH)_3$. For an explanation of notation refer to Table V. The unit of length is $2a$, a=6.27 Å.

Sublattice summed	A	B	C	D	E
1	18.3335	0	0	0	0
3	−12.1389	−7.7886	6.7451	0	0
5	180.0552	0	0	0	0
7	−5.1228	−6.1981	5.3677	0	0
9	−5.8740	13.3663	11.5755	7.7835	4.4938
12	−8.5845	0	0	0	0

TABLE X. Lattice sums for Nd$(OH)_3$. For an explanation of notation refer to Table V. The unit of length is $2a$, a=6.27 Å.

Sublattice summed	A	B	C	D	E
1	18.5956	0	0	0	0
3	−12.1362	−7.8034	6.7580	0	0
5	182.0394	0	0	0	0
7	−5.1873	−6.2315	5.3966	0	0
9	−5.9406	13.4248	11.6262	7.7622	4.4815
12	−8.6114	0	0	0	0

nitudes of these limiting values of v_{nnn} are quite small.

This will be true for $v_{nn} < 0$. On the other hand, when $v_{nn} > 0$, the exchange contributions to the eigenvalues numbered 7–12, 19–24, 31–36, 43–48 (namely, $-\frac{1}{4}v_{nn}$) may play an important role. However, for $v_{nn} < 2\delta E - 1.5v_{nnn}$ ($v_{nnn} < \frac{4}{3}\delta E$) the ferromagnetic low-temperature ordering (corresponding to E_3) would still prevail. [Here δE is the difference between the lowest-lying eigenvalue of E_i^{dd} (i= 7–12, 19–24, 31–36, 43–48) and E_3^{dd}.]

D. Nd$(OH)_3$

This is another interesting case since the consideration of dipole-dipole interaction predicts a ferromagnetic low-temperature ordering,[3] while an antiferromagnetic low-temperature ordering has been observed experimentally.[11] This case is different from the cases considered in Secs. III A, III B, and III C, in that here one has neither $g_{\parallel} = g_{\perp}$ nor $g_{\perp} = 0$. Here again, considering only the dipole-dipole interaction, the lowest-lying eigenvalue turns out to be E_3^{dd} ($= -0.1217$ °K) corresponding to a ferromagnetic ordering and the next-lowest eigenvalue is threefold degenerate ($= E_{15}^{dd} = E_{27}^{dd} = E_{42}^{dd} = -0.1162$ °K). Using the same definition of ΔE as in Secs. III B and III C, one has

$$\Delta E = (0.0055 - \tfrac{1}{2}v_{nnn})\ °\mathrm{K}\ .$$

Obviously, an antiferromagnetic low-temperature ordering would result for a value of v_{nnn} greater than 0.011 °K in agreement with the experimental observation.[11] As in Gd$(OH)_3$, this is consistent with the observation of Wolf *et al.*[11] that antiferromagnetic nondipolar interaction is important in this salt.

In addition to the possibility of antiferromagnetic low-temperature orderings for $v_{nnn} > 0.011$ °K (for $v_{nn} < 0$) it can be shown using the same arguments as in Sec. III C that such low-temperature orderings would also be possible for $v_{nn} > 0$ as long as $v_{nn} > (0.2048 - 1.5v_{nnn})$ °K. (This requires $v_{nnn} < 0.1365$ °K.)

E. Er$(OH)_3$

For this case no experimental observation is available as to what kind of low-temperature ordering takes place. This case is different from Nd$(OH)_3$ in that here $g_{\parallel} < g_{\perp}$. The dipole-dipole interaction alone predicts an antiferromagnetic low-temperature ordering (lowest eigenvalue $= E_{13}^{dd} = E_{26}^{dd} = E_{41}^{dd} = -0.4087$ °K). The lowest-lying eigenvalue corresponding to ferromagnetic configurations is $E_1^{dd} = E_2^{dd} = -0.2766$ °K. Between E_1^{dd} and E_{13}^{dd} there is one eigenvalue corresponding to an antiferromagnetic configuration. Using an analysis similar to the one used in Secs. III B–III D, it can be inferred that a ferromagnetic low-temperature ordering would be improbable for very small values of v_{nn} and v_{nnn}. On the other hand, a set of values for v_{nn} and v_{nnn} with suitably large magnitudes may force the nature of the low-temperature ordering to change from antiferromagnetic to ferromagnetic one.

IV. CONCLUDING REMARKS

The analysis presented in this paper clearly reveals the fact that the exchange interaction may play an important role in effecting the low-temperature ordering—ferromagnetic or antiferromagnetic—of the salts considered here. The measured values of the exchange-interaction constants are available only for GdCl$_3$ and Gd$(OH)_3$ for which it is found that the consideration of both the dipole-

TABLE IX. Lattice sums for Ho$(OH)_3$. For an explanation of notation refer to Table V. The unit of length is $2a$, a=6.26 Å.

Sublattice summed	A	B	C	D	E
1	18.2047	0	0	0	0
3	−12.1484	−7.7799	6.7376	0	0
5	179.0783	0	0	0	0
7	−5.0850	−6.1811	5.3530	0	0
9	5.8377	13.3370	11.5502	7.7943	4.5000
12	−8.5640	0	0	0	0

TABLE XI. Lattice sums for Er$(OH)_3$. For an explanation of notation refer to Table V. The unit of length is $2a$, a=6.25 Å.

Sublattice summed	A	B	C	D	E
1	18.1455	0	0	0	0
3	−12.1535	−7.7763	6.7344	0	0
5	178.5765	0	0	0	0
7	−5.0674	−6.1726	5.3456	0	0
9	−5.8199	13.3221	11.5373	7.7994	4.5030
12	−8.5567	0	0	0	0

TABLE XII. Eigenvalues (in °K) for the various cases considered. The demagnetization factors as given in Table IV should be added to the eigenvalues numbered 1, 2, and 3 corresponding to the ferromagnetic orderings in each case. [Corresponding to the eigenvector $\vec{q}(k)$, the three eigenvalues (x, y, z) are denoted with the numbers $(3k-2)$, $(3k-1)$, and $3k$, respectively.]

Eigenvalue number	DyES	Dy(OH)$_3$	Tb(OH)$_3$	Ho(OH)$_3$
3	−0.0650	−1.343	−1.179	−0.8567
6	−0.1210	−2.838	−2.491	−1.813
9, 12, 33, 36, 45, 48	0.0920	2.206	1.936	1.410
15, 27, 42	−0.1269	−3.152	−2.767	−2.017
18, 30, 39	−0.1239	−2.998	−2.631	−1.917
21, 24	0.1002	2.606	2.287	1.670
$(3n+1)$, $(3n+2)$, $n=0, 1, 2, \cdots, 15$	0	0	0	0
	GdCl$_3$	Gd(OH)$_3$	Nd(OH)$_3$	Er(OH)$_3$
1, 2	0.2338	0.3536	0.0072	0.1420
3	−0.4677	−0.7072	−0.0499	−0.0106
4, 5	0.4882	0.7515	0.0151	0.3009
6	−0.9764	−1.503	−0.1049	−0.0225
7, 10, 32, 35, 43, 46	0.9560	1.514	0.0904	0.0345
8, 11, 44, 47	−0.4221	−0.6599	−0.0132	−0.2217
9, 12, 45, 48	−0.5339	−0.8538	−0.0193	−0.2635
13, 26, 41	−0.6322	−1.031	−0.0201	−0.4087
14, 25, 40	1.709	2.708	0.0536	1.079
15, 27, 42	−1.077	−1.676	−0.1162	−0.0250
16, 28, 37	0.8815	1.380	0.0275	0.5508
17, 29, 38	0.1461	0.2116	0.0044	0.0857
18, 30, 39	−1.028	−1.591	−0.1107	−0.0238
19, 20, 22, 23	−0.4430	−0.6951	−0.0138	−0.2774
21, 24	0.8860	1.390	0.0959	0.0207
31, 34	−0.4221	−0.6599	−0.0132	−0.2635
33, 36	−0.5339	−0.8538	−0.0193	−0.2217

dipole and exchange interactions together predicts ferromagnetic and antiferromagnetic low-temperature ordered states, respectively, in agreement with the experimental results. For the case of Nd(OH)$_3$ the inclusion of exchange interaction may correctly predict the experimentally observed antiferromagnetic ordering in contrast to the ferromagnetic low-temperature ordering prediction based on the dipole-dipole interaction alone. Furthermore, it is found that only $v_{\rm nnn}$, rather than both $v_{\rm nn}$ and $v_{\rm nnn}$, is decisive in the low-temperature ordering. It is due to the fact that the contribution of $v_{\rm nn}$ to at least the three lowest-lying eigenvalues is the same in each case considered.

The analysis presented here has been confined to small magnitudes only of $v_{\rm nn}$ and $v_{\rm nnn}$. A consideration of altogether different magnitudes of these quantities than considered here would not, however, vitiate the conclusion that the exchange interaction may play an important decisive role in the low-temperature ordering of the crystals containing paramagnetic ions.

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APPENDIX

According to Kittel[13] a formation of long, thin needle ferromagnetic domains is expected for dipolar ordering. Formation of such long, thin needle domains takes place since it only requires very small energy changes compared to the total interaction energy.[13,14] The ferromagnetic energy is dependent upon the shape of the sample over which the lattice sums are evaluated. When the sample is long needle shaped and the dipoles lie in the direction of the needle then the ferromagnetic energy is lower than its counterpart for a spherical sample by a value which is dependent upon the "demagnetization factor" $-\frac{4}{3}\pi$.[15] [The field due to the magnetization of a sphere is $-(\frac{4}{3}\pi)n_0\mu$, where n_0 is the number of dipoles per unit volume and μ is the dipole moment per ion.] It is easily established that when the dipoles lie along the direction of the needle (say α direction; $\alpha = x, y, z$) the demagnetization energy per ion (in °K) is

$$\tfrac{1}{2}\mu^\alpha(-\tfrac{4}{3}\pi)n_0\mu^\alpha/k\,, \quad \mu^\alpha = g^\alpha \mu_B S\,,$$

where S is the effective spin of the ion, g^α is the α component of the g tensor (in a coordinate system in which it is diagonal), μ_B is the Bohr magneton, and k is the Boltzmann constant. A factor of $\frac{1}{2}$ in the above expression corrects for the counting twice of the dipole-dipole interaction energy.

Instead of evaluating the lattice sums over a sphere and then adding the demagnetization correction for a sphere, one could alternatively evaluate lattice sums over an ellipsoid with a very large major to minor axis ratio, for which case the demagnetization correction is zero.

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Magnetic Structure of DySb†

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A neutron-diffraction study of a single crystal of DySb has shown that at about 9.5 K the compound has a crystallographic as well as a magnetic transition. Below the transition DySb is monoclinic (almost tetragonal) with type-II antiferromagnetic ordering. The direction of the magnetic moment is close to the tetragonal axis at low temperature and tilts away with increasing temperature. The extrapolated saturation moment is $(9.8 \pm 0.2)\mu_B$/dysprosium atom.

I. INTRODUCTION

DySb is an antiferromagnetic substance with its Néel temperature (T_N) at about 9.5 K.[1] Above T_N the crystal structure of the antimonide is strictly of NaCl type. At T_N the lattice undergoes a slight contraction along one of the cubic axes.[2] A neutron-diffraction study on powder sample[3] indicated an antiferromagnetic ordering compatible with a type-II structure: a rhombohedral spin arrangement in which + spins and − spins are assigned alternatively to every other (111) plane of cations. Magnetic measurements at[4] 1.5 K indicated that the easy axis for the magnetic moments is along one of the [100] axes of the distorted cube. The ordered magnetic moment for dysprosium is close[3-5] to the expected saturation value for the free ion. The rhombohedral symmetry of the type-II magnetic structure seems to contrast with the tegragonal nature of the distortion. The present neutron-diffraction study on a single crystal of DySb was undertaken in order to resolve the problem. Additional results obtained, e.g., the direction of the magnetic moments and the details of the transition, will also be presented.

II. MAGNETIC MODELS

The treatment of the magnetic models follows closely that of the isostructural CoO on which there exists an extensive body[6-9] of work in the past years.

It is convenient to discuss the structure of DySb in terms of the cubic symmetry which it has above the Néel temperature. The crystallographic distortion observed by x rays at T_N introduces tetragonal domains (t domains) in the crystal. If the magnetic structure is indeed type II, magnetic domains of rhombohedral character (r domains) should appear throughout the crystal. The type-II antiferromagnetic structure is represented in Fig. 1(a). The antiferromagnetic sheets are stacked along the [111] direction. The other three r domains are obtained by stacking the antiferromagnetic sheets along another of the equivalent [111] directions.

The magnetic cell can be obtained simply by doubling all the edges of the pseudocubic crystal cell. In this expanded cell, the allowed magnetic lines have the index relations presented in Table I. A characteristic of the type-II structure is that within one t domain each magnetic reflection belongs to one and only one r domain. As a result the relative orientation of the magnetic reflections is very sensitive to a rhombohedral distortion that might accompany the magnetic ordering. On the other hand the nuclear reflections, each composed of four r domains, are rather insensitive to such a distortion. If no distortions were detectable, but