

Low-temperature ordered states of $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($R = \text{rare earth}$) due to dipole-dipole and exchange interactions

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Low-temperature ordered states of the various $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($R = \text{rare earth}$) compounds have been calculated using the Luttinger-Tisza method, taking into account both the dipole-dipole and exchange interactions among the rare-earth ions. It is found that dipolar interactions alone can explain all the observed orderings of these materials. As for the Ho compound below 0.1 K, its observed ordering can also be explained with appropriate values of exchange interactions and/or an appropriate g_{\parallel}/g_{\perp} ratio.

I. INTRODUCTION

Recently, an extremely large number of papers have appeared in the literature, dealing with theoretical and experimental aspects of the high- T_c superconductors of the type $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (hereafter called the Y 1:2:3 compound).^{1,2} It is generally possible to replace completely the Y^{3+} ion in the Y 1:2:3 compound by a rare-earth ion, R^{3+} , to form $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (hereafter called the R 1:2:3 compound), without appreciable modification of the superconducting transition temperature, T_c .³ Substitution of the trivalent Y^{3+} ion, in general, has little effect on superconductivity, since the $4f$ electrons of the R^{3+} ions are effectively isolated from the Cu-O superconducting layers, as well as from each other, thereby making dipolar interactions quite important in these compounds.⁴ For this reason, the rare-earth sublattice generally undergoes magnetic ordering only at very low temperatures (≤ 2 K), just like "magnetic superconductor" systems.⁵ On the other hand, the tetravalent rare-earth ions Ce^{4+} , Pr^{4+} , Tb^{4+} in the R 1:2:3 compounds are more strongly coupled to the rest of the electronic system. For the Pr 1:2:3 compounds, the magnetic ordering temperatures are much higher than those for the trivalent rare-earth ions,⁶ and the superconducting transition temperature is found to decrease strongly with increasing substitution by these elements.⁷ It should be noted that, in the Pr 1:2:3 compound, there may also be present Pr^{3+} ions, being in a mixed-valent state.⁷ Hereafter, for the consideration of magnetic ordering of Pr 1:2:3, it will be assumed that there exist Pr^{3+} ions.

Pr 1:2:3 is not superconducting; as well, it has the highest transition temperature (~ 17 K) (Ref. 2) to the magnetically ordered Pr^{3+} sublattice, as compared to those of the magnetically ordered R^{3+} lattices of the various R 1:2:3 compounds. On the other hand, Gd 1:2:3 has the highest transition temperature to the superconducting state of the various R 1:2:3 compounds.¹ The Pr 1:2:3 system forms the same orthorhombic structure as Y 1:2:3; however, the Pr ion is strongly mixed valent, close

to the tetravalent ionic state. The superconductivity becomes increasingly suppressed as the Pr concentration increases,⁷ ultimately disappearing for a Pr concentration greater than 60%. The inelastic-neutron-scattering spectrum led to the conclusion that the f electrons in tetravalent materials are strongly hybridized, playing an important role in the electronic properties.⁴

The R 1:2:3 compounds with $6.5 < (7-\delta) < 7.0$ all become superconducting at appropriate temperatures with the exception of $R = \text{Ce}, \text{Pr}, \text{Tb}$. Their crystal structure is tetragonal, with a slight orthorhombic distortion. In these compounds, the Cu^{2+} sublattice does not undergo any magnetic ordering. On the other hand, the R 1:2:3 compounds with $6.0 < (7-\delta) < 6.5$ do not become superconducting; they possess tetragonal crystal structure. The sublattice of Cu^{2+} ions in these compounds also undergoes magnetic ordering at low temperatures. However, there occurs no interaction between the Cu^{2+} sublattice and the sublattice formed by the rare-earth ions, since the field due to the R^{3+} (Cu^{2+}) sublattice at the site of a Cu^{2+} (R^{3+}) ion is zero because of symmetry. Finally, there is coexistence of superconductivity and magnetic ordering in the R 1:2:3 compounds at characteristic temperatures. In the R 1:2:3 systems, which are either tetragonal or nearly tetragonal (orthorhombic distortion), the unit-cell parameters are such that $a \sim b$, $c \sim 3a$, there being only one rare-earth ion per chemical unit cell. Because $c \gg a, b$, the interactions are expected to be much stronger in the ab plane.

As for the magnetic ordering of the rare-earth sublattice of R 1:2:3 compounds, those which order magnetically at low temperatures have been found to undergo antiferromagnetic orderings, either in the ab plane or along the c axis. The rare-earth magnetic structure which has been observed in R 1:2:3 ($R = \text{Nd}, \text{Gd}, \text{Dy}, \text{and Pr}$) is exhibited in Fig. 1(a), while that in Er 1:2:3 is exhibited in Fig. 2(a). In R 1:2:3 ($R = \text{Nd}, \text{Gd}, \text{Dy}, \text{and Pr}$) systems, a simple antiferromagnetic structure, as shown in Fig. 1(a), has been determined. For the Gd 1:2:3 system, a chain-like structure similar to the Er 1:2:3 system has also been

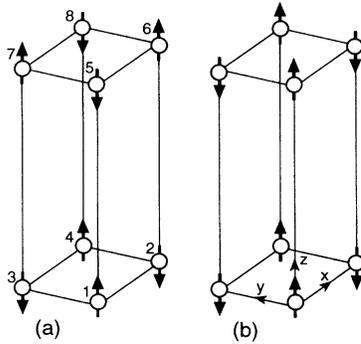


FIG. 1. Predicted low-temperature (lowest-energy) ordered magnetic structures of $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds when the moments are aligned along the z direction satisfying the condition $g_{\parallel} > 1.40g_{\perp}$: (a) corresponding to configuration $q(2z)$, which is the same as that given in Table I, for $R = \text{Nd, Gd, Dy, and Pr}$; (b) $q(7z)$. The numbering of the ions generating the eight sublattices by \mathbf{T}^2 translations, as used in the Luttinger-Tisza method employing permutation groups, is also indicated. Each arrangement is assumed to be characterized by eight sublattices; all the dipole moments on a given sublattice are parallel to each other. The ions belonging to the various sublattices are indicated in (a), while the orientations of the x, y, z axes are in (b).

determined.⁸ The Er 1:2:3 structure consists of chains of moments which are aligned ferromagnetically along the b axis while adjacent chains are aligned antiparallel to each other to form an overall antiferromagnetic configuration.⁹ In some samples, however, the spins along the c axis are found to be parallel, rather than antiparallel, forming ferromagnetic sheets of spins.¹⁰ (For more details, see Sec. IV.)

As regards the origin of magnetic ordering in R 1:2:3 compounds, there is no evidence that it is due to a Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, mediated by conduction electrons, since ^{155}Gd Mössbauer spectroscopy results of Alp *et al.*¹¹ provided direct evidence for an absence of conduction electrons at Gd^{3+} sites in the Gd 1:2:3 compound. Thus, the low-temperature ordering in R 1:2:3 compounds is most likely due to dipole-dipole interactions between rare-earth ions, which may be influenced by the superexchange interaction with ligands. To this end, Felsteiner¹² applied the Luttinger-Tisza¹³ method to analyze the low-temperature magnetic ordering in the Gd 1:2:3 compound, taking into account the dipolar interactions between Gd^{3+} ions. He concluded that the observed ordering in this compound may be explained provided that a certain condition on relative values of g_{zz} and g_{xx} ($g_{zz} > \alpha g_{xx}$; $\alpha = 1.388$ for tetragonal phase and $\alpha = 1.400$ for orthorhombically distorted tetragonal phase) can be satisfied, with perhaps the inclusion of a weak superexchange interaction.

It is the purpose of the present paper to investigate what kind of low-temperature ordered states of the rare-earth sublattice can be expected in R 1:2:3 compounds on the basis of dipolar and exchange interactions between R^{3+} ions using the Luttinger-Tisza (LT) method.¹³ A brief outline of the general LT method, as applicable to the present study, is provided in Sec. II. The specific ap-

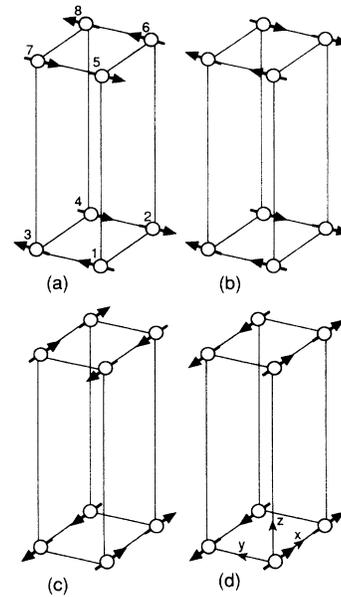


FIG. 2. Predicted low-temperature (lowest-energy) orderings for R 1:2:3 compounds in both orthorhombic and tetragonal phases when the moments are aligned along the x/y direction satisfying the condition $g_{\parallel} < 1.40g_{\perp}$: (a) corresponding to configuration $q(8y)$, as given in Table I, for $R = \text{Er}$; (b) $q(5y)$; (c) $q(6x)$; (d) $q(3x)$. The other details are the same as those given in the caption of Fig. 1. The orientations of the x, y, z axes are indicated here in (d).

plication to the R 1:2:3 compounds is made in Sec. III. The results, taking into account experimental data, are discussed in Sec. IV. Concluding remarks are made in Sec. V.

II. A BRIEF OUTLINE OF THE LUTTINGER-TISZA METHOD USING PERMUTATION GROUPS

The details of the LT method, as applied to the present study of magnetic ordering of R 1:2:3 compounds, are described in this section; for more details, see Ref. 14. The lattice sites occupied by R^{3+} ions are divided into eight sublattices by the application of the double translation vectors $\mathbf{T}^2 = 2l\mathbf{a} + 2m\mathbf{b} + 2n\mathbf{c}$, where $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are unit-cell vectors ($a = b$ for tetragonal, $a < b$ for orthorhombic structure) and l, m, n are zero, positive, or negative integers, to the eight vertices of a parallelepiped which are situated at $p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$; $p, q, r = 0, 1$, having chosen the origin at one of the rare-earth sites. The ferromagnetic and antiferromagnetic configurations whose energies can be calculated by the LT method are such that all magnetic moments located on any one of the eight sublattices are parallel to each other, and the relative directions of the magnetic moments of the various sublattices render the entire rare-earth lattice ferromagnetic, antiferromagnetic, or layered antiferromagnetic. The eigenvectors corresponding to these configurations are expressed as $q(k)\phi_k(\alpha)$ ($k = 1, 2, \dots, 8$; $\alpha = x, y, z$). The elements of the unnormalized eight-dimensional eigenvectors $q(k)$

TABLE I. Unnormalized eigenvectors $q(k)$ of group of permutations P_i ($i=1,2,\dots,8$).

$q(1)$	$q(2)$	$q(3)$	$q(4)$	$q(5)$	$q(6)$	$q(7)$	$q(8)$
1	1	1	1	1	1	1	1
1	-1	1	1	-1	1	-1	-1
1	-1	-1	1	1	-1	-1	1
1	1	-1	1	-1	-1	1	-1
1	-1	1	-1	1	-1	1	-1
1	1	1	-1	-1	-1	-1	1
1	1	-1	-1	1	1	-1	-1
1	-1	-1	-1	-1	1	1	1

are listed in Table I, wherein +1 and -1, respectively, represent parallel and antiparallel directions of the rare-earth magnetic moments on a sublattice. The energies and corresponding cosines of the directions in the physical space along which the spins of these configurations are oriented are respectively given by the eigenvalues and the eigenvectors $[\phi_k(\alpha); \alpha=x,y,z]$ of the 3×3 matrix L_k , whose components are given by

$$L_k^{\mu\nu} = \sum_{j=1}^{16} A_{ij}^{\mu\nu} \epsilon_{P(i,j)}(k), \quad i=1,2,\dots,8, \quad (2.1)$$

where $\epsilon_{P(i,j)}$ are the eigenvalues of $q(k)$ under a permutation group of eight objects, listed in Table II, and $P(i,j)$ is the permutation containing the cycle (i,j) (listed in Ref. 14). The summation in Eq. (2.1) is independent of i .¹⁴ The matrix elements $A_{ij}^{\mu\nu}$, appearing in Eq. (2.1), represent the dipole-dipole and exchange interactions between an ion situated on sublattice i , and all ions on sublattice j , as follows:

$$A_{ij}^{\mu\nu} = \begin{cases} \sum_{l \in \{j\}} J_{il}^{\mu\nu} & \text{for } i \neq j, \\ \sum_{l \in \{j\}, l \neq i} J_{il}^{\mu\nu} & \text{for } i = j. \end{cases} \quad (2.2)$$

In Eq. (2.2), $\{j\}$ represents all ions on sublattice j , and

$$J_{ij}^{\mu\nu} = \frac{\langle \mathbf{S}^2 \rangle}{2} \mu_B^2 \left[g_{\mu\mu} g_{\nu\nu} \frac{r_{ij}^2 \delta_{\mu\nu} - 3r_{ij}^\mu r_{ij}^\nu}{r_{ij}^5} + v_{ij} \Delta_{ij} \delta_{\mu\nu} \right]. \quad (2.3)$$

In Eq. (2.3), S is the effective ionic spin [$=\frac{1}{2}$ for all cases considered presently; quantum mechanically $\langle \mathbf{S}^2 \rangle = S(S+1)$], μ_B is the Bohr magneton, $g_{\mu\mu}$ is the

TABLE II. Eigenvalues, $\epsilon_{P(i,j)}$, of the vector $q(k)$ for the permutations $P_{(i,j)}$ ($j=1,2,\dots,8$).

	$P_{(1,1)}$	$P_{(1,2)}$	$P_{(1,3)}$	$P_{(1,4)}$	$P_{(1,5)}$	$P_{(1,6)}$	$P_{(1,7)}$	$P_{(1,8)}$
$q(1)$	1	1	1	1	1	1	1	1
$q(2)$	1	-1	-1	1	-1	1	1	-1
$q(3)$	1	1	-1	-1	1	1	-1	-1
$q(4)$	1	1	1	1	-1	-1	-1	-1
$q(5)$	1	-1	1	-1	1	-1	1	-1
$q(6)$	1	1	-1	-1	-1	-1	1	1
$q(7)$	1	-1	-1	1	1	-1	-1	1
$q(8)$	1	-1	1	-1	-1	1	-1	1

μ th diagonal element of the g tensor (assumed to be diagonal for the present choice of coordinate axes), r_{ij} is the vector that joins the ionic position i to j with r_{ij}^μ as its μ th component, $\delta_{\mu\nu}$ is the Kronecker δ function, v_{ij} represents the (isotropic) exchange interaction between the ions i and j , $\Delta_{ij}=1$ if i and j are nearest or next-nearest neighbors, 0 otherwise. The factor $\frac{1}{2}$ in Eq. (2.3) is introduced so that the energy of interaction is not counted twice. The first term in Eq. (2.3) describes the dipolar interaction, while the second term describes the exchange interaction, the latter being confined presently to the nearest and next-nearest neighbors.

The eigenvalues corresponding to the various configurations, represented by $q(k)$, are those of the 3×3 matrices $L_k^{\mu\nu}$, given by Eq. (2.1). The one that corresponds to the lowest of these energies represents the low-temperature ordered state. In calculating energies, one should also take into account the demagnetization contribution if the lattice sums are evaluated over a sphere, as described in Ref. 14, for the case of ferromagnetic orderings $q_1 \phi_1(\alpha)$, $\alpha=x,y,z$. For the present case of a diagonal g tensor, this contribution is given by

$$-(4\pi/3) \langle \mathbf{S}^2 \rangle / 2 n_0 g_{\alpha\alpha}^2, \quad \alpha=x,y,z, \quad (2.4)$$

where $n_0=1/(abc)$ is the number of rare-earth ions per unit volume, and $\langle \mathbf{S}^2 \rangle = S(S+1)$.

III. APPLICATION OF THE LT METHOD TO THE LOW-TEMPERATURE ORDERED STATES OF R 1:2:3 COMPOUNDS

A. Lattice sums

The required lattice sums in Eq. (2.3) for the tetragonal and orthorhombically distorted tetragonal crystal structures of Gd 1:2:3 compound are listed in Table III. (The same lattice sums will be used for the other R 1:2:3 compounds due to close proximity of their unit-cell parameters to those for Gd 1:2:3.) The coordinate system chosen is such that the z axis is parallel to the c axis and the x and y axes are coincident with the a and b vectors of the unit cell.

B. Crystalline electric-field parameters and the g factors

The experimental values of the g factors of the various R^{3+} ions in R 1:2:3 compounds are generally not available. They can, however, be calculated from a knowledge of the crystalline electric-field (CEF) parameters. The CEF Hamiltonian relevant to R 1:2:3 compounds, characterized by tetragonal symmetry, can be expressed as follows:¹⁵

$$H_{\text{CEF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4. \quad (3.1)$$

In Eq. (3.1), the O_l^m are spin operators as defined by Abragam and Bleaney.¹⁶ For the present case of assumed isotropic exchange interaction, the CEF determines the anisotropy.

When the values of CEF parameters B_l^m in Eq. (3.1) are known, the g values for the various R^{3+} ions in R 1:2:3 compounds can be estimated from the Hund-rule ground

TABLE III. Lattice sums over a sphere of 500 Å for the lattice of Gd^{3+} ions in Gd 1:2:3. The variables r , x , y , and z are the displacements and their components from an origin situated at a given ion in sublattice 1 to each ion in one of the various sublattices [see, e.g., numberings in Fig. 1(a) or 2(a) and the orientations of the x, y, z axes in Fig. 1(b) or 2(d)]. The unit of length is 2 Å. All of the required lattice sums can be obtained from the following listed sums. (The z axis is parallel to the c axis, and the x/y axis is coincident with the a/b vector of the unit cell.) It is noted that all $\sum xy/r^5 = \sum yz/r^5 = \sum zx/r^5 = 0$. The values of unit-cell parameters used are $a = 3.8397$ Å, $b = 3.8987$ Å, $c = 11.703$ Å for the orthorhombically distorted tetragonal phase and $a = b = 3.8770$ Å, $c = 11.810$ Å for the tetragonal phase (Ref. 3).

Sublattice summed	Tetragonal		Orthorhombic	
	$\sum \frac{3z^2 - r^2}{r^5}$	$\sum \frac{x^2 - y^2}{r^5}$	$\sum \frac{3z^2 - r^2}{r^5}$	$\sum \frac{x^2 - y^2}{r^5}$
1	-0.107 814	0.000 000	-0.108 155	0.001 538
2	-0.353 638	0.254 719	-0.361 414	0.263 020
3	-0.353 638	-0.254 719	-0.349 689	-0.249 731
4	-0.236 233	0.000 000	-0.237 320	-0.002 522
5	0.047 576	0.000 000	0.048 233	0.000 009
6	0.047 178	0.000 127	0.047 827	0.000 135
7	0.047 178	-0.000 127	0.047 777	-0.000 136
8	0.046 813	0.000 000	0.047 421	-0.000 009

state.¹⁷ The values of B_l^m for the Er 1:2:3 compound have been estimated by Simizu *et al.*¹⁵ by scaling from inelastic-neutron-scattering data on Ho 1:2:3 (Refs. 18–20) to be (in K) $B_2^0 = 0.0328$, $B_4^0 = -0.0144$, $B_6^0 = 0.00075$, $B_4^4 = 0.00211$. The value of the largest parameter B_2^0 here is of the same order of magnitude as that for $ErRh_4B_4$ ($= 0.07$ K),²¹ whose CEF's have been used to estimate the g factors of the R^{3+} ions in the various RRh_4B_4 compounds, also characterized by tetragonal symmetry, and listed by Misra and Postma.¹⁷ (For more details, see Ref. 17.) These factors are listed in Table IV along with the Hund-rule ground state for the various R^{3+} ions. They will be used for the calculation of the lowest-energy configurations of R 1:2:3 compounds because of the same symmetry and the same order of magnitude of the CEF parameter B_2^0 as for RRh_4B_4 compounds.

C. Lowest-lying energies

The same g factors g_{\parallel} ($=g_{zz}$) and g_{\perp} ($=g_{xx} = g_{yy}$), will be assumed for both the tetragonal and orthorhombically distorted tetragonal phases because the orthorhombic phase exhibits only a very small distortion from tetragonal phase. (The lattice sums employed are, of course, those calculated using the correct unit-cell dimensions for the tetragonal and orthorhombically distorted tetragonal phases.) The two lowest-lying energies (in units of K) and the corresponding configurations $q(k\alpha)$ of the various R 1:2:3 compounds, where $q(k\alpha)$ stand for the relative directions of moments of the various sublattices given by $q(k)$ (listed in Table I) with the moments oriented in the α ($=x, y, z$) direction, as calculated using the LT method employing permutation groups, are given by Eqs. (3.2) and (3.3) below.

Tetragonal R 1:2:3 compounds:

$$\begin{aligned}
 q(7z): E_{L'} &= -0.010610g_{\parallel}^2 - 4v_n + 4v_{nn}, \\
 q(2z): E_{L''} &= -0.010608g_{\parallel}^2 - 4v_n + 4v_{nn}, \\
 q(3z) = q(5z): E_{NL} &= -0.003773g_{\parallel}^2 - 4v_{nn}, \\
 q(3x) = q(5y) = q(6x) = q(8y): \\
 E_L &= -0.020444g_{\perp}^2 - 4v_{nn}, \\
 q(1x) = q(1y) = q(4x) = q(4y): \\
 E_{NL} &= -0.018111g_{\perp}^2 + 4v_n + 4v_{nn}.
 \end{aligned} \tag{3.2}$$

Orthorhombically distorted tetragonal R 1:2:3 compounds:

$$\begin{aligned}
 q(7z): E_{L'} &= -0.010681g_{\parallel}^2 - 2v_n - 2v_{n''} + 4v_{nn}, \\
 q(2z): E_{L''} &= -0.010678g_{\parallel}^2 - 2v_n - 2v_{n''} + 4v_{nn}, \\
 q(5z): E_{NL'} &= -0.004138g_{\parallel}^2 - 2v_n + 2v_{n''} - 4v_{nn}, \\
 q(3z): E_{NL''} &= -0.003455g_{\parallel}^2 + 2v_n - 2v_{n''} - 4v_{nn}, \\
 q(3x) = q(6x): E_{L'} &= -0.020927g_{\perp}^2 + 2v_n - 2v_{n''} - 4v_{nn}, \\
 q(5y) = q(8y): E_{L''} &= -0.020229g_{\perp}^2 - 2v_n + 2v_{n''} - 4v_{nn}, \\
 q(1x) = q(4x): \\
 E_{NL'} &= -0.018763g_{\perp}^2 + 2v_n + 2v_{n''} + 4v_{nn}, \\
 q(1y) = q(4y): \\
 E_{NL''} &= -0.017685g_{\perp}^2 + 2v_n + 2v_{n''} + 4v_{nn}.
 \end{aligned} \tag{3.3}$$

In Eqs. (3.2), when the moments are oriented along the z direction, the subscripts (L', L'') and NL stand for the lowest (there are two which are not exactly equal in energy, but extremely close to each other) and the next-lowest energies; on the other hand, when the moments are oriented along the x/y direction, the subscripts L and NL stand for the lowest and next-lowest energies. It is

noted that the degeneracies for the tetragonal phase, as given by Eqs. (3.2), of the groups of configurations $\{q(3z), q(5z)\}$, $\{q(3x), q(5y), q(6x), q(8y)\}$, and $\{q(1x), q(1y), q(4x), q(4y)\}$, whose energies are denoted as E_{NL} , E_L , and E_{NL} , respectively, are (partially) lifted when the symmetry is reduced to the orthorhombically distorted tetragonal phase, according to Eqs. (3.3), as follows: $\{q(5z)\}$, $\{q(3z)\}$, $\{(3x), q(6x)\}$, $\{q(5y), q(8y)\}$, $\{q(1x), q(4x)\}$, and $\{q(1y), q(4y)\}$; these energies are denoted as $E_{\text{NL}'}$, $E_{\text{NL}''}$, $E_{L'}$, $E_{L''}$, $E_{\text{NL}'}$, and $E_{\text{NL}''}$. [It is noted that, in Eqs. (3.2) and (3.3), the energies of the ferromagnetic configurations $q(1x)$ and $q(1y)$ are extremely slightly lower than those of the antiferromagnetic configurations $q(4x)$ and $q(4y)$, respectively (of the order of 1 part in 20 000).]

In Eqs. (3.2), for the case of tetragonal phase, v_n and

v_{nn} represent the exchange interactions of ion 1 with the four nearest-neighbor ions, which lie on sublattices 2 and 3, and four next-nearest ions, which lie on sublattice 4, respectively. On the other hand, in Eqs. (3.3), for the case of orthorhombically distorted tetragonal phase, v_n' , v_n'' , and v_{nn} represent the exchange interactions of ion 1 with the two nearest-neighbor ions which lie on sublattice 2, two next-nearest-neighbor ions which lie on sublattice 3, and four next-next-nearest-neighbor ions which lie on sublattice 4, respectively. Because of the close proximity of nearest and next-nearest ions for the orthorhombically distorted tetragonal phase $v_n' \sim v_n''$; for this reason, for the orthorhombically distorted tetragonal phase and the next-next-nearest-neighbor interaction, v_{nn} , has also been included. It should be noted, upon taking into account the distances of nearest neighbors in the tetragonal and

TABLE IV. Calculated values of g_{\parallel} and g_{\perp} factors (the same as for RRh_4B_4 compounds) as well as the (only) reported measured values of g_{\parallel} and g_{\perp} for Dy^{3+} and Er^{3+} , Hund-rule ground state for the various R^{3+} ions, predicted low-temperature orderings (more details in Sec. III) on the basis of dipolar interactions, and experimentally observed orderings for the various R 1:2:3 compounds. AF and NS stand, respectively, for antiferromagnetic and nonsuperconducting. (If nothing is indicated, it means that the compound becomes superconducting at a characteristic temperature.)

R^{3+}	Hund-rule ground state $2S+1L_J$	g_{\parallel}	g_{\perp}	Predicted ordering	Observed ordering
$^{58}\text{Ce}^{3+}(4f^1)$	$^2F_{5/2}$	4.28	0.126	z axis AF	NS ^{a,b}
$^{59}\text{Pr}^{3+}(4f^2)$	3H_4	4.80	0	z axis AF	z axis AF ^c , NS
$^{60}\text{Nd}^{3+}(4f^3)$	$^4I_{9/2}$	6.51	0.073	z axis AF	z axis AF ^d
$^{61}\text{Pm}^{3+}(4f^4)$	5I_4	0	0		^b
$^{62}\text{Sm}^{3+}(4f^5)$	$^6H_{5/2}$	0.286	0.857	x,y axis AF	AF ^{d,e}
$^{63}\text{Eu}^{3+}(4f^6)$	7F_0	0	0		
$^{64}\text{Gd}^{3+}(4f^7)$	$^8S_{7/2}$	14.0	0	z axis AF	z axis AF ^f
$^{65}\text{Tb}^{3+}(4f^8)$	7F_6	18.0	0	z axis AF	NS ^b
$^{66}\text{Dy}^{3+}(4f^9)$	$^9H_{5/2}$	20.0	0	z axis AF	z axis AF ^g
		7.1 ^h	(0.9, 0.6) ^h		
$^{67}\text{Ho}^{3+}(4f^{10})$	5I_8	20.0	0	z axis AF	z axis AF ⁱ
$^{68}\text{Er}^{3+}(4f^{11})$	$^4I_{15/2}$	0.937	9.219	x,y axis AF	x,y axis AF ^j
		4.5 ^h	8.0 ^h		
$^{69}\text{Tm}^{3+}(4f^{12})$	3H_6	1.318 ^k	0 ^k	z axis AF	No ordering (above 0.5 K) ^l
$^{70}\text{Yb}^{3+}(4f^{13})$	$^2F_{7/2}$	1.142	4.571	x,y axis AF	AF ^{e,m}

^aThe experimental ordering has not been determined.

^bThe particular rare-earth ion does not form an R 1:2:3 compound.

^cReference 6.

^dK. N. Yang, J. M. Ferreira, B. W. Lee, M. B. Maple, W. H. Li, J. W. Lynn, and R. W. Erwin, Phys. Rev. B **40**, 10 963 (1989); P. Fischer, B. Schmid, P. Brüesch, F. Stucki, and P. Unternährer, Z. Phys. B **74**, 183 (1989).

^eThe direction of ordering has not been determined.

^fH. A. Mook, D. McK. Paul, B. C. Sales, L. A. Boatner, and L. Cussen, Phys. Rev. B **38**, 12 008 (1988); see also, Ref. 8.

^gA. I. Goldman, B. X. Yang, J. Tranquada, J. E. Crow, and C.-S. Jee, Phys. Rev. B **36**, 7234 (1987).

^hExperimental g factors as determined (i) for Dy^{3+} by Allenspach *et al.* (Ref. 22); the g_{\perp} column contains (g_{xx}, g_{yy}) values, respectively, and (ii) for Er^{3+} by Hodges *et al.* (Ref. 23).

ⁱOrdering changes to x,y axis AF below 0.1 K; see P. Birrer, F. N. Gygax, B. Hitti, E. Lippelt, A. Schenck, M. Weber, S. Barth, F. Hulliger, and H. R. Ott, Phys. Rev. B **39**, 11 449 (1989).

^jReferences 9 and 10.

^kThe doublet that lies just above the lowest-lying singlet has been used for the calculation of g factors.

^lJ. M. Ferreira, B. W. Lee, Y. Dalichaouch, M. S. Torikachvili, K. N. Yang, and M. B. Maple, Phys. Rev. B **37**, 1580 (1988); S. H. Liu, *ibid.* **37**, 7470 (1988).

^mJ. A. Hodges, P. Imbert, and G. Jéhanno, Solid State Commun. **64**, 1209 (1987).

TABLE V. The predicted ground-state energies $E_L(z)$ and $E_L(xy)$, in units of K, for the orderings in the z and x/y directions, respectively, as calculated on the basis of dipolar interactions alone for the tetragonal phase, and the magnetic ordering temperatures T_N (as listed by Lynn in Ref. 1) for the various R 1:2:3 compounds.

R	T_N	$E_L(z)$	$E_L(xy)$
Ce		-0.1943	-0.0003
Pr	17	-0.2445	0.0000
Nd	0.52,1.5	-0.4497	-0.0001
Pm			
Sm	0.6	-0.0009	-0.0150
Eu			
Gd	2.2,2.24,2.6	-2.0796	0.0000
Tb		-3.4377	0.0000
Dy	0.8,0.95	-4.2441	0.0000
		-0.5349 ^a	-0.0115 ^a
Ho	0.15	-4.2441	0.0000
Er	0.6,0.87	-0.0093	-1.7375
		-0.2149 ^a	-1.3084 ^{a,b}
Tm		-0.0184	0.0000
Yb	0.35	-0.0138	-0.4272

^aCalculated using the experimental g factors as referred to in footnote (h) of Table IV.

^bFor g_{\perp} the average value of g_{xx} and g_{yy} has been used here.

orthorhombically distorted tetragonal phases, that $v_n \sim v_n' \sim v_n''$. The values of these exchange constants have not been experimentally determined and it is rather difficult to estimate them theoretically.

Equations (3.2) and (3.3) are so close to each other that, within experimental error, they predict the same low-temperature ordering independent of the structure. From Eqs. (3.2) and (3.3), it is clear that, for both the tetragonal and orthorhombically distorted tetragonal phases, when the moments orient in the z direction (parallel to the c axis), the dipolar interactions alone lead to two states, $q(2z)$ and $q(7z)$, which possess the lowest energies (i.e., their energies are extremely close to each other), the lower one of these, e.g., $q(7z)$ [Fig. 1(b)], corresponds to antiferromagnetic ordering in the x (parallel to the a axis) and y (parallel to the b axis) directions, with ferromagnetic ordering along the z direction, while the higher one of these, i.e., $q(2z)$ [Fig. 1(a)], has the same configuration of moments in the x and y directions but antiferromagnetic ordering of moments in the z direction. The exchange-interaction contribution, being the same for these two states, does not alter their relative order in energy. On the other hand, when the moments are pointed in the x/y direction, it is seen from Eqs. (3.2) that the four configurations for the tetragonal phase, which possess the lowest energy, are such that when the moments point in the x direction the ordering is ferromagnetic in the x direction, antiferromagnetic in the y direction, and either ferromagnetic [$q(3x)$, Fig. 2(d)] or antiferromagnetic [$q(6x)$, Fig. 2(c)] in the z direction, and when the moments point in the y direction the ordering is antiferromagnetic in the x direction, ferromagnetic in the y direction, and either ferromagnetic [$q(5y)$, Fig. 2(b)] or

antiferromagnetic [$q(8y)$, Fig. 2(a)] in the z direction; the exchange-interaction contribution, being the same for these four states, does not remove their degeneracy in energy. The degeneracy of these four configurations for the x/y orientation of moments for the tetragonal phase is partially lifted to yield two doublets when the symmetry is reduced to that of the orthorhombically distorted tetragonal phase, such that the doublet $\{q(3x), q(6x)\}$ lies somewhat lower in energy than the doublet $\{q(5y), q(8y)\}$, as seen from Eqs. (3.3). Finally, when only the dipolar interactions are taken into account, the lowest-energy configuration with the moments oriented in the z direction will be favored, as long as $g_{\parallel} > \alpha g_{\perp}$, where $\alpha = 1.3883$ and 1.3999 for the tetragonal and orthorhombically distorted tetragonal phases, respectively. However, this condition will be somewhat modified when the exchange interactions are taken into account, according to Eqs. (3.2) and (3.3).

To summarize, the ordering will be of the $q(2z)$ or $q(7z)$ type if $g_{\parallel} > 1.40g_{\perp}$, while it will be $q(3x)$, $q(5y)$, $q(6x)$, $q(8y)$ [or, perhaps $q(1x)$, $q(1y)$, $q(4x)$, $q(4y)$] if $g_{\parallel} < 1.40g_{\perp}$. The exchange interactions cannot distinguish between choices within each group; however, they could play a decisive role for the case $g_{\parallel} \sim 1.40g_{\perp}$.

IV. DISCUSSION OF PREDICTED ORDERINGS AND EXPERIMENTAL RESULTS

In Table IV are listed the Hund-rule ground states of the various rare-earth ions and the calculated g_{\parallel} and g_{\perp} values using CEF parameters as discussed in Sec. III, along with the theoretically predicted orderings on the basis of dipolar interactions alone, as well as the experimentally observed orderings. (For Dy 1:2:3, the g_{xx} , g_{yy} , and g_{zz} factors have been determined by Allenspach, Furrer, and Hulliger²² to be 0.9, 0.6, and 7.1, respectively, while for Er 1:2:3 the values are $g_{zz} = 4.5$, $g_{xx} = g_{yy} = 8.0$ as reported by Hodges *et al.*,²³ these experimentally determined g values satisfy the same conditions for the g_{\parallel}/g_{\perp} ratios as those by the theoretically calculated g values for the magnetic orderings, discussed in Sec. III.) An inspection of Table IV reveals that, for R 1:2:3 compounds with $R = \text{Pr}$, Nd , Gd , Dy , Ho ($T > 0.1$ K), and Er , there is complete agreement of the prediction with the experiment. On the other hand, for $R = \text{Sm}$ and Yb , the predicted and observed orderings are both antiferromagnetic; however, the precise directions of moments have not been experimentally determined. The compound Tm 1:2:3 is not found to order magnetically down to 0.5 K. Further, the compounds with $R = \text{Ce}$ and Pm cannot be produced experimentally. On the other hand, Eu 1:2:3 can be produced, but it is not interesting, since Eu^{3+} is a nonmagnetic ion. Finally, it should be pointed out that the experimentally observed orderings are, in most cases, as those given in Figs. 1(a) and 2(a) for the various cases. These do not cover the four theoretically predicted configurations given in Figs. 1(b) and 2(b)–2(d). However, there have been published some reports of observing all the theoretically predicted orderings, as those given in Table IV.²

The only disagreement between the theoretically predicted and experimentally observed ordering^{1,8-10} is for the Ho 1:2:3 compound below 0.1 K. The two may be brought into agreement if, either the values of exchange interactions below 0.1 K become sufficiently strong, or the relative strength of the g_{\parallel} and g_{\perp} values changes, as dictated by Eqs. (3.2) and (3.3).

Finally, we note that there does not appear to be any correlation between the ground-state energies (E_L) and the ordering temperatures (T_N), as listed in Table V; of course, these energies are computed, in most cases, using theoretically calculated g values rather than experimentally determined ones. The only noteworthy point is the rather large value of T_N for Pr 1:2:3 (~ 17 K) as compared to those of the other R 1:2:3 compounds, which are much smaller.

V. CONCLUDING REMARKS

The present investigation indicates that it is possible to account for the observed orderings of the R 1:2:3 compounds on the basis of purely dipolar interactions. For the case of the Ho 1:2:3 compound, the observed ordering below 0.1 K can also be explained with appropriate values of exchange interactions between the Ho^{3+} ions and/or with an appropriate g_{\parallel}/g_{\perp} ratio.

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- ¹C. P. Poole, Jr., T. Datta, and H. A. Farach, *Copper Oxide Superconductors* (Wiley, New York, 1988); *High Temperature Superconductivity*, edited by J. W. Lynn (Springer-Verlag, New York, 1990).
- ²J. W. Lynn, *Physica B* **163**, 69 (1990); his paper gives a brief review of magnetic orderings and spin fluctuations in oxide superconductors.
- ³K. N. Yang, Y. Dalichaouch, J. M. Ferreira, R. W. Lee, J. J. Neumeier, M. S. Torikachvili, H. Zhou, M. B. Maple, and R. Hake, *Solid State Commun.* **63**, 515 (1987); J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, *Phys. Rev. B* **36**, 226 (1987).
- ⁴K. N. Yang, J. M. Ferreira, B. W. Lee, Y. Dalichaouch, M. S. Torikachvili, and M. B. Maple, *Chin. J. Phys.* **26**, 5130 (1988); S. Skanthkumar, W.-H. Lee, J. W. Lynn, A. Kebede, J. E. Crow, and T. Mihalisin, *Physica B* **163**, 239 (1990); W.-H. Li, J. W. Lynn, S. Skanthkumar, T. W. Clinton, A. Kebede, C.-S. Jee, J. E. Crow, and T. Mihalisin, *Phys. Rev. B* **40**, 5300 (1989); J. W. Lynn and W. H. Li, *J. Appl. Phys.* **64**, 6065 (1988); B. W. Lee, J. M. Ferreira, Y. Dalichaouch, M. S. Torikachvili, K. N. Yang, and M. B. Maple, *Phys. Rev. B* **37**, 2368 (1988); F. Nakamura, K. Senoth, T. Tamura, Y. Ochiai, and Y. Narahara, *ibid.* **39**, 12283 (1989); H. Sakamoto, M. Tei, K. Mizoguchi, and K. Kumar, *ibid.* **41**, 9513 (1990).
- ⁵For a review, see *Topics in Current Physics*, edited by Ø. Fischer and M. B. Maple (Springer-Verlag, New York, 1982), Vols. 32 and 34.
- ⁶Li, Lynn, Skanthkumar, Clinton, Kebede, Jee, Crow, and Mihalisin (Ref. 4).
- ⁷L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. U. Segre, and I. K. Shuller, *Nature* **328**, 604 (1987); J. K. Liang, X. T. Xu, S. S. Xie, G. H. Rao, X. Y. Shao, and Z. G. Duan, *Z. Phys. B* **69**, 137 (1987); Y. Dalichaouch, M. S. Torikachvili, E. A. Early, B. W. Lee, C. L. Seaman, K. N. Yang, H. Zhou, and M. B. Maple, *Solid State Commun.* **65**, 1001 (1988).
- ⁸T. Chattopadhyay, H. Maletta, W. Wirgen, K. Fischer, and P. J. Brown, *Phys. Rev. B* **38**, 838 (1988).
- ⁹J. W. Lynn, T. W. Clinton, W.-H. Li, R. W. Erwin, J. Z. Liu, R. N. Shelton, and P. Klavins, *Phys. Rev. Lett.* **63**, 2606 (1989).
- ¹⁰T. Chattopadhyay, P. J. Brown, B. C. Sales, L. A. Boatner, H. A. Mook, and H. Maletta, *Phys. Rev. B* **40**, 2624 (1989).
- ¹¹E. E. Alp, L. Solderholm, G. K. Shenoy, D. G. Hinks, D. W. Capone, II, K. Zhang, and B. D. Dunlap, *Phys. Rev. B* **36**, 8910 (1987); H. H. A. Smit, M. W. Dirken, R. C. Thiel, and L. J. de Jong, *Solid State Commun.* **64**, 695 (1987).
- ¹²J. Felsteiner, *Phys. Rev. B* **39**, 7248 (1989).
- ¹³J. M. Luttinger and L. Tisza, *Phys. Rev.* **70**, 954 (1946).
- ¹⁴S. K. Misra, *Phys. Rev. B* **8**, 2026 (1973); J. Felsteiner and S. K. Misra, *ibid.* **8**, 253 (1973).
- ¹⁵S. Simizu, G. H. Bellesis, J. Lukin, S. A. Friedberg, and H. S. Lessure, *Phys. Rev. B* **39**, 9099 (1989).
- ¹⁶A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Metal Ions* (Clarendon, Oxford, 1970).
- ¹⁷S. K. Misra and H. Postma, *Phys. Rev. B* **30**, 1285 (1984).
- ¹⁸A. Furrer, P. Brüesch, and P. Unternährer, *Solid State Commun.* **67**, 69 (1988).
- ¹⁹A. Furrer, P. Brüesch, and P. Unternährer, *Physica C* **153-155**, 164 (1988).
- ²⁰A. Furrer, P. Brüesch, and P. Unternährer, *Phys. Rev. B* **38**, 4616 (1988).
- ²¹H. B. Radousky, B. D. Dunlap, G. S. Knapp, and D. G. Niarchos, *Phys. Rev. B* **27**, 5526 (1983).
- ²²P. Allenspach, A. Furrer, and F. Hulliger, *Phys. Rev. B* **39**, 2226 (1989).
- ²³J. A. Hodges, P. Bonville, P. Imbert, and G. Jéhanno, *Physica C* **184**, 283 (1991).