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Magnetic order of RBa$_2$Cu$_4$O$_8$ (R = rare earth) due to dipole-dipole and exchange interactions

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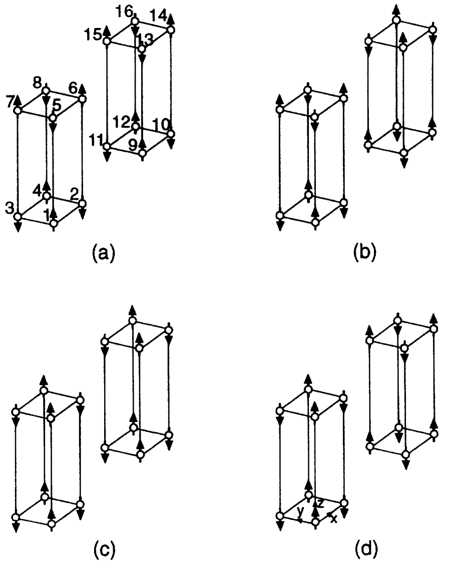
The Luttinger-Tisza method has been applied, taking into account both the dipole-dipole and exchange interactions, to calculate the low-temperature ordered states of the magnetic rare-earth ions in the various RBa$_2$Cu$_4$O$_8$ (R = rare earth) compounds. Dipolar interaction alone has been found to explain the observed orderings in ErBa$_2$Cu$_4$O$_8$ and DyBa$_2$Cu$_4$O$_8$, the only materials whose low-temperature magnetic orderings have been determined by neutron diffraction. The expected low-temperature orderings for the other RBa$_2$Cu$_4$O$_8$ compounds based on purely dipolar interactions have also been calculated.

The magnetic properties of the copper oxide superconductors RBa$_2$Cu$_3$O$_{6+x}$ (hereafter called R123 where R = rare earth) have been studied extensively in the last several years.[1] The subsequently discovered copper oxide superconductors RBa$_2$Cu$_4$O$_8$ (R124) possess stable oxygen content unlike the R123 compounds; as well, they are much less susceptible to twinning.[2] The structure of the R124 compounds differs from that of the R123 compounds in that in R124 successive planes of rare-earth ions are displaced half a lattice spacing along the b axis relative to the corresponding planes in R123. However, there are the following features which are common to both R123 and R124: (i) The magnetic rare-earth ions have little effect on the superconducting properties 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. (ii) The rare-earth sublattice undergoes magnetic ordering at low temperatures. (iii) 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. (iv) There is a coexistence of superconductivity and magnetic ordering at characteristic temperatures.

The superconducting R123 and R124 systems are both nearly tetragonal with a slight orthorhombic distortion, the unit-cell parameter b being slightly greater than a. While in R123 one has $c \approx 3a$, with only one rare-earth ion per unit cell, for R124 $c \approx 7a$, there being two rare-earth ions per unit cell. Thus the c-axis spacing of the rare-earth ions is ~ 3 times the a-b spacing for both the R123 and R124 compounds.

As for the magnetic ordering of the rare-earth sublattice of R124 compounds, only two compounds—Er124 and Dy124—have been investigated by neutron scattering,[3] undergoing antiferromagnetic orderings in the ab plane ($T_N = 0.49$ K) and along the c axis ($T_N = 0.9$ K), respectively. (Here T_N is the magnetic transition temperature.) These orderings closely resemble those of the corresponding Er123 and Dy123 compounds.[1] The observed rare-earth magnetic structures in Dy124 and Er124 are shown in Figs. 1 and 2, respectively. In Gd124, a canted spin structure has been found using magnetization and Mössbauer measurements.[4] However, the technique of neutron scattering to predict unequivo-



(a) (b)

(c) (d)

FIG. 1. Predicted lowest-energy ordered magnetic structures of RBa$_2$Cu$_4$O$_8$ compounds when the moments are aligned along the z direction satisfying the condition $g_{\parallel} > 1.39 g_{\beta\beta}$, where $g_{\beta\beta}$ represents the smaller of g_{xx}, g_{yy}: (a) $q(3z)$, (b) $q(4z)$, (c) $q(13z)$, and (d) $q(14z)$. Each arrangement is assumed to be characterized by 16 sublattices; all the dipole moments on a given sublattice are parallel to one another. The numbering of the ions belonging to the various sublattices is indicated in (a), while the orientations of the x,y,z axes in (d). The coordinates of the ions 1, 2, 3, 5, 9, 10, 11, and 13 are, respectively, (0,0,0), (a,0,0), (0,b,0), (0,0,c), (0,b/2,c/2), (a,b/2,c/2), (0,3b/2,c/2), and (0,b/2,3c/2). This completely specifies the positions of all the 16 ions looking at (a). Arrangements (a) and (b) fit the ordering measured for R = Dy (Refs. 1 and 3).

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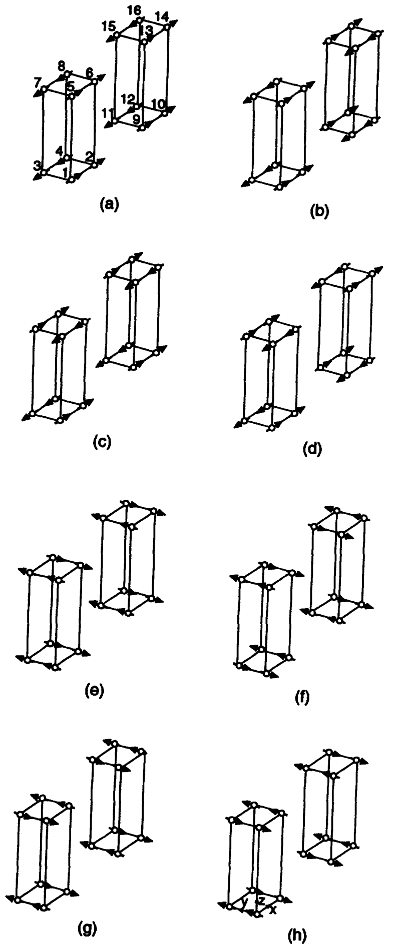

FIG. 2. Predicted lowest-energy orderings for R124 compounds when the moments are aligned along the x/y direction satisfying the condition $g_{\parallel} < 1.39 g_{\beta\beta}$, where $g_{\beta\beta}$ represents the smaller of g_{xx}, g_{yy}: (a) $q(5x)$, (b) $q(6x)$, (c) $q(11x)$, (d) $q(12x)$, (e) $q(9y)$, (f) $q(10y)$, (g) $q(15y)$, and (h) $q(16y)$, ignoring the small difference in the energies of these configurations with the moments pointing in the x/y directions. 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 (h). The arrangement (f) corresponds to the ordering measured for R = Er (Refs. 1 and 3).

cally the spin structure has not been used to confirm this structure due to the large neutron-absorption cross section of Gd.

Recently,[5,6] the expected low-temperature ordered states of the rare-earth sublattices in R123 compounds have been calculated on the basis of dipolar and exchange interactions between the R^{3+} ions using the Luttinger-Tisza (LT) method.[7] The purpose of the present paper is to report a similar study of the low-temperature ordered states in the R124 compounds.

A brief outline of the general LT method as applicable to the R123 compounds was given in Ref. 5. However, the present case of R124 is somewhat more complicated since there exist two rare-earth ions per unit cell in R124 instead of one in R123. A detailed account of the LT method for the case of two magnetic ions per unit cell, employing permutation groups, can be found in Refs. 8 and 9. In the present case, the lattice sites occupied by R^{3+} ions are divided into 16 sublattices instead of only 8 sublattices for R123. All the magnetic moments located on any one of the 16 sublattices are assumed to be parallel to one another. It is then possible for the entire rare-earth lattice to have either a ferromagnetic, an antiferromagnetic, or a layered-antiferromagnetic configuration. The eigenvectors corresponding to these configurations and the required eigenvalues of these eigenvectors under a permutation group of 16 objects are listed in Eq. (10) and Table V of Ref. 8. The lattice sums used in the LT method for the orthorhombically distorted tetragonal crystal structure of Gd124 are listed in Table I. The same lattice sums will be used for all the other R124 compounds since their unit-cell parameters are quite close to those of Gd124.

It is to be noted that when calculating the energy of a ferromagnetic configuration, the demagnetization contribution should also be taken into account since the lattice sums have been presently evaluated over a sphere.[10] This contribution is given by

$$-(4\pi/3)[S(S+1)/2]n_0 g_{\alpha\alpha}^2, \quad \alpha=x,y,z \;, \tag{1}$$

where S is the effective spin, $n_0 = 2/abc$ is the number of rare-earth ions per unit volume, and $g_{\alpha\alpha}$ is the αth diagonal element of the g tensor.

Experimental values of the g factors are not available for any R124 compound, while they are available only for three R^{3+} ions in R123 compounds, namely, Er^{3+}

TABLE I. Lattice sums over a sphere of 500 Å for the lattice of Gd^{3+} ions in Gd124. 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 and the orientations of the x,y,z axes in Fig. 1 or 2). The unit of length is 2 Å. All of the required lattice sums can be calculated from the sums listed here. (The z axis is parallel to the c axis, and the x,y axes are coincident with the **a**,**b** vectors of the unit cell, respectively.) It is noted that all $\sum xy/r^5 = \sum yz/r^5 = \sum zx/r^5 = 0$. The values of the unit-cell parameters used are $a = 3.863$ Å, $b = 3.881$ Å, and $c = 27.26$ Å (Refs. 2 and 4).

Sublattice summed	$\sum \frac{3z^2-r^2}{r^5}$	$\sum \frac{x^2-y^2}{r^5}$
1	−0.135 11	0.000 47
2	−0.383 68	0.257 74
3	−0.380 11	−0.253 70
4	−0.264 03	−0.000 77
5	0.020 50	0.000 00
6	0.020 50	0.000 00
7	0.020 50	0.000 00
8	0.020 50	0.000 00
9	0.020 52	−0.000 01
10	0.020 48	0.000 01
11	0.020 52	−0.000 01
12	0.020 48	0.000 01
13	0.020 52	−0.000 01
14	0.020 48	0.000 01
15	0.020 52	−0.000 01
16	0.020 48	0.000 01

($g_{\parallel}=4.5$, $g_{\perp}=8.0$),[11] Nd^{3+} ($g_{\parallel}=3.60$, $g_{\perp}=2.13$),[12] and Dy^{3+} ($g_{\parallel}=14.2$, $g_{xx}=1.8$, $g_{yy}=1.2$).[13] (Here $g_{\parallel}=g_{zz}$ and $g_{\perp}=g_{xx}=g_{yy}$ unless otherwise stated.) The latter will here be used for the calculation of the lowest-energy configurations of R 124 compounds, because both R 123 and R 124 have the same symmetry, about the same c-axis spacing relative to the spacing in the ab plane, and are thus expected to have similar values of the crystal electric field parameters, which determine the g factors.

The lowest and next-lowest energies (in units of K) and the corresponding configurations $q(k\alpha)$ of the various orthorhombically distorted tetragonal R 124 compounds, where $q(k\alpha)$ stand for the relative directions of moments of the various sublattices given by $q(k)$ (listed in Ref. 8) with the moments oriented in the α ($=x,y,z$) direction, as calculated using the LT method, are

$$\begin{aligned}
&E_{q(3z)}=E_{q(4z)}=E_{q(13z)}=E_{q(14z)}=-0.0107g_{zz}^2-2v_{n'}-2v_{n''}+4v_{nn}\ ,\\
&E_{q(9z)}=E_{q(10z)}=E_{q(15z)}=E_{q(16z)}=-0.0039g_{zz}^2-2v_{n'}+2v_{n''}-4v_{nn}\ ,\\
&E_{q(5z)}=E_{q(6z)}=E_{q(11z)}=E_{q(12z)}=-0.0037g_{zz}^2+2v_{n'}-2v_{n''}-4v_{nn}\ ,\\
&E_{q(5x)}=E_{q(6x)}=E_{q(11x)}=E_{q(12x)}=-0.0206g_{xx}^2+2v_{n'}-2v_{n''}-4v_{nn}\ ,\\
&E_{q(7x)}=E_{q(8x)}=-0.0183g_{xx}^2+2v_{n'}+2v_{n''}+4v_{nn}\ ,\\
&E_{q(9y)}=E_{q(10y)}=E_{q(15y)}=E_{q(16y)}=-0.0204g_{yy}^2-2v_{n'}+2v_{n''}-4v_{nn}\ ,\\
&E_{q(7y)}=E_{q(8y)}=-0.0180g_{yy}^2+2v_{n'}+2v_{n''}+4v_{nn}\ .
\end{aligned}\tag{2}$$

In Eqs. (2), the $v_{n'}$, $v_{n''}$, and v_{nn} terms represent the contribution of the exchange interaction, assumed to be isotropic, while the terms in g_{xx}, g_{yy}, and g_{zz} represent the contribution of the dipolar interaction. $v_{n'}$, $v_{n''}$, and v_{nn} are the (isotropic) exchange-interaction constants of ion 1 with the two nearest-neighbor ions (distance $=3.863$ Å) which lie on sublattice 2, the two next-nearest-neighbor ions (distance $=3.881$ Å) which lie on sublattice 3, and the four next-next-nearest-neighbor ions (distance $=5.476$ Å) which lie on sublattice 4, respectively. Since because of the close proximity of the nearest- and next-nearest ions, $v_{n'}\sim v_{n''}$, the next-next-nearest-neighbor interaction v_{nn} has also been included. The values of these exchange constants have not been experimentally determined. It is noted from Eqs. (2) that all the specified different arrangements in any one of these equations possess the same dipolar energy; the exchange interaction cannot distinguish between their energies.

From Eqs. (2), it is seen that when the moments orient in the z direction (parallel to the c axis), the dipolar interactions alone lead to four states $q(3z)$, $q(4z)$, $q(13z)$, and $q(14z)$, which possess the same lowest energies, as shown in Fig. 1. When the moments point in the x direction, the four configurations possessing the same lowest dipolar energies are $q(5x)$, $q(6x)$, $q(11x)$, and $q(12x)$, shown in Fig. 2. When the moments point in the y direction, the four lowest dipolar energy configurations are $q(9y)$, $q(10y)$, $q(15y)$, and $q(16y)$, also shown in Fig. 2. It is seen from Eqs. (2) that for the same values of g_{xx} and g_{yy}, the lowest dipolar energy corresponding to the four y configurations is very slightly higher than that of the four x configurations as a result of the slight orthorhombic distortion from tetragonal symmetry of the R 124 lattice.

To summarize, the ordering with lowest dipolar energy will be of the $q(3z)$, $q(4z)$, $q(13z)$, or $q(14z)$ type if $g_{\parallel}>1.39g_{\beta\beta}$, while it will be $q(5x)$, $q(6x)$, $q(11x)$, $q(12x)$, $q(9y)$, $q(10y)$, $q(15y)$, or $q(16y)$ if $g_{\parallel}<1.39g_{\beta\beta}$, where $g_{\beta\beta}$ represents the smaller of g_{xx} and g_{yy}, ignoring the small difference between the x/y orderings as given by Eqs. (2). The exchange interactions cannot distinguish between choices within each group; however, they could be important for the case $g_{\parallel}\sim 1.39g_{\beta\beta}$.

When $g_{xx}^2>0.99g_{yy}^2$, for the case $g_{\parallel}<1.39g_{\beta\beta}$, the antiferromagnetic configurations $q(5x)$, $q(6x)$, $q(11x)$, and $q(12x)$ with the moments pointing in the x direction will be favored since these configurations have a lower energy than that of the configurations $q(9y)$, $q(10y)$, $q(15y)$, and $q(16y)$ with the moments pointing in the y direction; otherwise, these antiferromagnetic configurations with the moments pointing in the y direction will be energetically favored.

When the contributions of the exchange interactions to the energies of the configurations included in Eqs. (2) are also taken into account, the relative order of the energies of these antiferromagnetic configurations may be significantly modified from those predicted by the dipolar interaction alone if the exchange interactions are sufficiently large. The exact relative order will, of course, depend on the actual values of the exchange interactions and will be determined by the use of Eqs. (2). Further, if the exchange interaction is, in fact, anisotropic, it could also change the relative order of energies. However, this information is not available at present.

The experimentally determined g values for Dy^{3+}, Nd^{3+}, and Er^{3+} in R 123 compounds satisfy the condition for the $g_{\parallel}/g_{\beta\beta}$ ($\beta=x,y$) ratio in such a way that the present calculations predict, on the basis of the LT method, that as a result of dipolar interactions alone Dy^{3+} and Nd^{3+} should order antiferromagnetically (layered) with the moments in the z direction, while Er^{3+} should order antiferromagnetically (layered) with the moments in the x/y direction, with the configurations given by Eqs. (2), ignoring the small difference in energy of the x/y configurations. This is in complete agreement with the experimental results on Dy124 and Er124, the only R124 compounds investigated experimentally by neutron scattering. The g values for the various R124 or R123 compounds, where R is different from Dy, Nd, and Er, are not available. If one were to use the same values as those calculated for $R\mathrm{Rh}_4\mathrm{B}_4$,[5,14] which are characterized by the same symmetry as that of the R124 compounds, the following configurations will be favored, on the basis of purely dipolar interactions, using the conditions derived presently for the lowest energies based on the ratios of $g_{\parallel}/g_{\perp}$: $q(3z)$, $q(4z)$, $q(13z)$, and $q(14z)$ for R =Ce, Pr, Gd, Tb, and Tm and $q(5x)$, $q(6x)$, $q(11x)$, $q(12x)$ or $q(9y)$, $q(10y)$, $q(15y)$, and $q(16y)$ for R =Sm and Yb. These are similar to those predicted for the corresponding R123 compounds.[5]

The present investigation indicates that it is possible to account for the observed orderings, i.e., those of the R124 (R =Dy and Er) compounds, on the basis of purely dipolar interactions, using the same g values as those of the corresponding R123 compounds. This is the same result as that found previously for the R123 compounds.[5] Further, based on the measured g values for Nd123, for which experimental data are not available, it is predicted that for R124 the Nd^{3+} moments should orient along the z direction corresponding to the antiferromagnetic configurations $q(3z)$, $q(4z)$, $q(13z)$, and $q(14z)$.

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[1] See, e.g., J. W. Lynn, J. Alloys Compounds **181**, 419 (1992), and references therein.

[2] D. E. Morris, J. H. Nickel, J. Y. T. Wei, N. G. Asmar, J. S. Scott, U. M. Scheven, C. T. Hultgren, A. G. Markelz, J. E. Post, P. J. Heaney, D. R. Veblen, and R. M. Hazen, Phys. Rev. B **39**, 7347 (1989); R. M. Hazen, L. W. Finger, and D. E. Morris, Appl. Phys. Lett. **54**, 1057 (1989).

[3] H. Zhang, J. W. Lynn, W.-H. Li, T. W. Clinton, and D. E. Morris, Phys. Rev. B **41**, 11 229 (1990).

[4] H. J. Bornemann, D. E. Morris, C. Steinleitner, and G. Czjzek, Phys. Rev. B **44**, 12 567 (1991).

[5] S. K. Misra and J. Felsteiner, Phys. Rev. B **46**, 11 033 (1992).

[6] A. G. Anders and S. V. Volotskii, Superconductivity **5**, 575 (1992).

[7] J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946).

[8] S. K. Misra, Phys. Rev. B **8**, 2026 (1973).

[9] J. Felsteiner and S. K. Misra, Phys. Rev. **8**, 253 (1973).

[10] M. Redi and P. W. Anderson, Proc. Natl. Acad. Sci. USA **78**, 27 (1981).

[11] J. A. Hodges, P. Bonville, P. Imbert, and G. Jéhanno, Physica C **184**, 283 (1991).

[12] N. Guskos, M. Calamiotou, S. M. Paraskevas, A. Koufoudakis, C. Mitros, H. Gamari-Seale, J. Kuriata, L. Sadlowski, and M. Wabia, Phys. Status Solidi B **162**, K101 (1990).

[13] P. Allenspach, A. Furrer, and F. Hulliger, Phys. Rev. B **39**, 2226 (1989). According to P. Allenspach (private communication), the g values quoted in this reference were smaller by a factor of 2. The values quoted in the present paper are therefore twice as much as those mentioned in this reference. This does not change our conclusions since the ratios of the various g values, which decide which energies lie the lowest, still remain the same.

[14] S. K. Misra and H. Postma, Phys. Rev. B **30**, 1285 (1984).