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Low-temperature ordered states of lithium rare-earth tetrafluorides (LiRF$_4$)

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The low-temperature ordered states of lithium rare-earth tetrafluorides (LiRF$_4$) are investigated using a generalization of the Luttinger-Tisza method. It is found that for those LiRF$_4$ for which the ratio $g_{\parallel}/g_{\perp}$ is greater than 1.017748 ferromagnetic ordering in the c direction corresponds to the configuration with the lowest energy, otherwise the lowest-energy configuration is the layered antiferromagnetic ordering in the ab plane. These predictions are in agreement with the experimental observations for LiTbF$_4$ and LiHoF$_4$, the only materials in the family of LiRF$_4$ experimentally investigated so far.

I. INTRODUCTION

Considerable interest has been expressed recently in the magnetic properties of LiR_xY$_{1-x}$F$_4$ (R is a rare earth); absorption and fluorescence,[1] and EPR[2] spectra have been obtained for these materials. They are efficient laser materials[3] and can be used for frequency conversion in the infrared-visible region.[4] These materials are simple for theoretical treatment, owing to their high point symmetry, as well as the rare earths being fairly ionic atoms, which are coupled predominantly by the dipole-dipole interaction.

Of the various LiRF$_4$, the orderings of only LiTbF$_4$ and LiHoF$_4$ have been observed experimentally.[5,6] (Hansen *et al.*[6] concluded by extrapolation that below 0.5 K LiErF$_4$ will order ferromagnetically, with the magnetic moments in the crystalline ab plane.) Both LiTbF$_4$ and LiHoF$_4$ are found to order ferromagnetically, with the transition temperatures (T_c) being[5] 2.874 and[6] 1.30 K, respectively. The LiRF$_4$ possess a body-centered-tetragonal crystal structure, containing four R^{+++} ions per unit cell. The Luttinger-Tisza (LT) method,[7] as originally proposed for the calculation of the energies of magnetic configurations, is not, in general, applicable to the case of more than two ions per unit cell.[8] In view of the recently proposed generalization of the LT method[9] for the case of highly anisotropic dipole-dipole interaction, it is possible to treat the cases of LiTbF$_4$ and LiHoF$_4$, since for these materials the g tensor is highly anisotropic, as well as the conditions for the applicability of the LT method using permutation groups are satisfied for configurations characterized by $\vec{T}$ periodicity ($\vec{T} = l\vec{a} + m\vec{b} + n\vec{c}$; l, m, n are positive or negative integers, or zero, and $\vec{a}, \vec{b}, \vec{c}$ are unit-cell vectors). For those LiRF$_4$, for which the g tensors of the R^{+++} ion are not highly anisotropic it turns out (Sec. II) that the extended LT method using permutation groups is still applicable to the configurations characterized by $\vec{T}$ periodicity because of the particular crystal symmetry of LiRF$_4$. It is then possible to calculate the energies of the various configurations (ferromagnetic, antiferromagnetic, and layered antiferromagnetic) and thus predict the kind of low-temperature ordering (corresponding to the lowest energy) expected for a given $g_{\parallel}/g_{\perp}$ ratio, where $g_{\parallel}$ and $g_{\perp}$ are the principal values of the effective g tensor of the lowest-lying Kramers doublet of the particular rare-earth ion considered.

It is the purpose of this paper to calculate the low-temperature orderings of the various LiRF$_4$ by proposing an extension of the LT method using permutation groups for configurations characterized by $\vec{T}$ periodicity. This extension is discussed in Sec. II. Only the dipole-dipole interaction is considered; the exchange interaction is neglected.[5,6] In Sec. III relevant details of the crystal structure of LiRF$_4$ are presented. Section IV deals with the calculation of energies of the various configurations. The conclusions are summarized in Sec. V.

II. CRYSTAL STRUCTURE OF LiRF$_4$

Figure 1 shows the positions of R^{+++} ions in the unit cell of LiRF$_4$. The crystal structure for these salts is the same as that for the mineral scheelite (CaWO$_4$).[10-12] The ionic positions are $\vec{r}_1 = (0, 0, \frac{1}{2}c)$, $\vec{r}_2 = (0, \frac{1}{2}a, \frac{3}{4}c)$, $\vec{r}_3 = (\frac{1}{2}a, \frac{1}{2}a, 0)$, $\vec{r}_4 = (\frac{1}{2}a, 0, \frac{1}{4}c)$. Positions 3 and 4 are obtained from 1 and 2 by the body-centering translation $(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}c)$. In the primitive unit cell, which has a volume of half the tetragonal unit cell, only sites 1 and 2 need be included. All R^{+++} sites, however, are magnetically equivalent; the point symmetry is S_4 in the absence

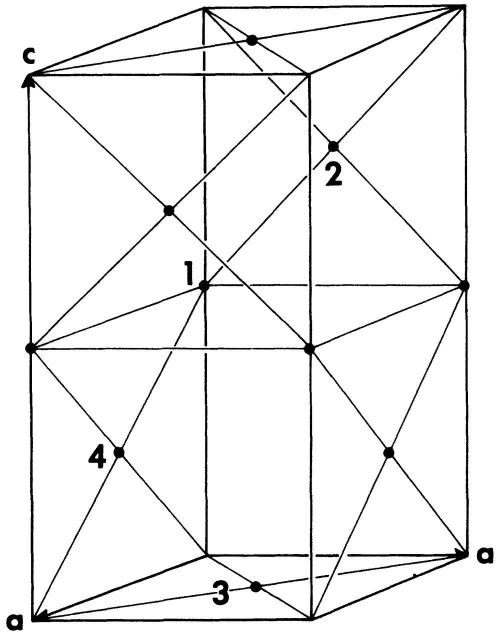

FIG. 1. Positions of Tb^{+++} ions in the body-centered-tetragonal unit cell of $LiTbF_4$.

of an applied field. The unit-cell parameters for the various $LiRF_4$ are listed in Table I.

In the following discussion the z axis is chosen parallel to the c axis.

III. EXTENSION OF THE LT METHOD

The LT method using permutation groups is now briefly reviewed. In this method one calculates the energies corresponding to various ferro-, antiferro-, and layered antiferromagnetic configurations, wherein the whole lattice is divided into $8n$ sublattices (n is the number of magnetic ions per unit cell); within each sublattice (characterized by $\vec{T}^2 = 2l\vec{a} + 2n\vec{b} + 2n\vec{c}$ translations) all spins point in the same direction. It then follows that the LT method is applicable (i.e., the "weak" condition also satisfies the "strong" condition) provided that

$$A^{\alpha\beta}_{P_t i,\, P_t j} = A^{\alpha\beta}_{ij}\,, \qquad (\alpha\beta = x, y, z;\ i, j = 1, 2, \ldots, 8n)\,, \tag{1}$$

where P_t are the groups of permutation of $8n$ elements (listed in Ref. 8). The $A^{\alpha\beta}_{ij}$ in Eq. (1) are defined (assuming the existence of dipole-dipole interaction only) by

$$A^{\alpha\beta}_{ij} = \sum_{l\in\{j\}} J^{\alpha\beta}_{il} \quad \text{for } i \neq j\,, \qquad A^{\alpha\beta}_{jj} = \sum_{l\in\{j\},\, l\neq j} J^{\alpha\beta}_{jl}\,, \tag{2a}$$

TABLE I. Unit-cell parameters a and c for the various $LiRF_4$.

Compound	c (Å)	a (Å)	c/a
$LiTbF_4$[a]	10.873	5.181	2.099
$LiYbF_4$[b]	10.59	5.132	2.064
$LiLuF_4$[c]	10.55	5.13	2.057
$LiTmF_4$[c]	10.64	5.15	2.066
$LiErF_4$[b]	10.70	5.162	2.073
$LiYF_4$[b]	10.74	5.175	2.075
$LiHoF_4$[b]	10.75	5.175	2.077
$LiDyF_4$[b]	10.83	5.189	2.088
$LiGdF_4$[b]	10.97	5.219	2.102
$LiEuF_4$[b]	11.03	5.228	2.110

[a] Reference 5.

[b] Reference 11.

[c] J. D. H. Donnay, G. Donnay, O. Kennard, and O. King, *Crystal Data Determinative Tables* (American Crystallographic Association, Washington, D. C., 1963), Vol. 2, 3rd ed.

$$J^{\alpha\beta}_{ij} = \frac{S^2 \mu_B^2 g^{\alpha\alpha} g^{\beta\beta}}{r^3_{ij}} \left(\delta_{\alpha\beta} - \frac{3 r^{\alpha}_{ij} r^{\beta}_{ij}}{r^2_{ij}} \right). \tag{2b}$$

In Eq. (2a), $\{j\}$ denotes the set of lattice sites generated by the application of $\vec{T}^2$ to spin j. In Eq. (2b) the $g^{\alpha\alpha}$ represent the diagonal elements of the effective g tensor (a coordinate system in which the g tensor is diagonal is chosen), $\vec{r}_{ij}$ is the vector drawn from spin i to spin j, μ_B is the Bohr magneton, S is the ionic spin, and $\delta_{\alpha\beta}$ is the Kronecker delta.

The case of $LiRF_4$, while it does not satisfy the condition represented by Eq. (1) for $\vec{T}^2$ sublattices, is, nevertheless, amenable to treatment by the LT method using permutation groups provided the $\{j\}$ in Eq. (2a) denote the set of lattice sites generated by the application of $\vec{T}$ to spin j [i.e., then Eq. (1) is satisfied]. This can be easily seen from Fig. 1 showing the positions of the R^{+++} ions in the unit cell. Thus, for this case, all those ionic spins which are related by $\vec{T}$ translations (T sublattices) point in the same direction.

IV. ENERGIES OF VARIOUS CONFIGURATIONS

Specifically for $LiRF_4$, four types of magnetic orderings with $\vec{T}$ periodicity corresponding to each of the X, Y, Z, directions can be considered—one ferromagnetic configuration, one antiferromagnetic

TABLE II. Permutations P_t of four objects.

P_1 = Identity
$P_2 = (1,2)(3,4)$
$P_3 = (1,3)(2,4)$
$P_4 = (1,4)(2,3)$

TABLE III. Eigenvalues $\epsilon_{P_i}(k)$ of the vectors $q(k)$ under the permutations P_t.

	P_1	P_2	P_3	P_4
$q(1)$	1	1	1	1
$q(2)$	1	−1	1	−1
$q(3)$	1	1	−1	−1
$q(4)$	1	−1	−1	1

configuration (spins 1, 2 parallel, spins 3, 4 antiparallel), and two layered antiferromagnetic configurations [(a) spins 1, 2 parallel, spins 3, 4 antiparallel; (b) spins 1, 4 parallel, spins 2, 3 antiparallel]. The eigenvectors of the various configurations are[8] $\phi(k,\alpha)=q(k)\phi_k(\alpha)$ $(k=1,2,3,4;$ $\alpha=x,y,z)$, where the $q(k)$ are as follows:

Ferromagnetic antiferromagnetic

$$q(1)=\begin{bmatrix}1\\1\\1\\1\end{bmatrix}, \qquad q(2)=\begin{bmatrix}1\\-1\\1\\-1\end{bmatrix},$$

layered antiferromagnetic
(a) (b)

$$q(3)=\begin{bmatrix}1\\1\\-1\\-1\end{bmatrix}, \quad q(4)=\begin{bmatrix}1\\-1\\-1\\1\end{bmatrix}.$$

The $\phi_k(\alpha)$ are the eigenvalues of the matrix L_k whose elements are defined as

$$L_k^{\mu\nu}=\sum_{j=1}^{4} A_{ij}^{\mu\nu}\epsilon_{P(i,j)}(k)\,, \tag{3}$$

$$(i,j=1,2,3,4;\ \ \mu,\nu=x,y,z)\,.$$

In Eq. (3) the sum is independent of i, $P(i,j)$ is the permutation of four objects containing the cycle (i,j) (listed in Table II), and $\epsilon_{P(i,j)}(k)$ is the eigenvalue of permutation $P(i,j)$ with respect to $q(k)$, listed in Table III. The lattice sums required for $A_{ij}^{\mu\nu}$ are listed in Table IV, using the parameters for $\mathrm{LiTbF_4}$. (These lattice sums are also used for other $\mathrm{Li}R\mathrm{F_4}$, owing to small differences in the unit-cell parameters for $\mathrm{Li}R\mathrm{F_4}$).

The lowest energies corresponding to orientations of the spins in the X, Y, and Z directions are as follows in terms of $g_\parallel$ and $g_\perp$, the components of the g tensor parallel and perpendicular to the c axis.

Z direction: $-0.005\,370(g_\parallel)^2$ °K (ferromagnetic), taking into account the demagnetization factor of $(-\frac{4}{3}\pi n_0)(\frac{1}{2}g_\parallel^2 S^2\mu_B^2)$, where n_0 is the number of ions per unit volume.[13]

X direction: $-0.005\,562(g_\perp)^2$ °K [layered antiferromagnetic ordering (a)].

Y direction: $-0.005\,562(g_\perp)^2$ °K [layered antiferromagnetic ordering (b)].

Thus when $g_\parallel/g_\perp > (0.005\,562/0.005\,370)^{1/2} = 1.017\,748$, a ferromagnetic ordering along the c direction will be favored. Otherwise, a layered antiferromagnetic ordering of spins in the ab plane is favored, constituted by equal mixtures of layered antiferromagnetic orderings (a) and (b) in the X and Y directions, respectively.

Table V contains the experimentally measured values of $g_\parallel$ and $g_\perp$ for the various $\mathrm{Li}R\mathrm{F_4}$, the lowest energies, and the corresponding expected low-temperature orderings. (Note that $S=\frac{1}{2}$ for Kramers doublets.)

TABLE IV. Lattice sums over a sphere of radius 500 Å for $\mathrm{LiTbF_4}$. 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 $\vec{\mathrm{T}}$ sublattices. The unit of length is 1 Å.

Sublattice summed	$\sum(3z^2-r^2)/r^5$	$\sum(x^2-y^2)/r^5$	$\sum(xy/r^5)$	$\sum(yz/r^5)$	$\sum(zx/r^5)$
1	−0.036 245	0	0	0	0
2	0.016 724	0.013 451	0	0	0
3	0.025 877	0	0	0	0
4	0.016 724	−0.013 451	0	0	0

TABLE V. g factors, the lowest energies E_0 of the various LiRF$_4$, and the corresponding configurations. (FM, ferromagnetic along c direction; LAFM, layered antiferromagnetic in the ab plane.)

Ion	$g_\parallel$	$g_\perp$	$g_\parallel/g_\perp$	E_0 (°K)	Configuration
Tb^{+++}	17.7^a	0	∞	−1.6824	FM
Ho^{+++}	13.3^b	0	∞	−0.9499	FM
Nd^{+++}	1.987^a	2.554	0.778	−0.0363	LAFM
Dy^{+++}	1.112^a	9.219	0.121	−0.4727	LAFM
Er^{+++}	3.137^a	8.105	0.387	−0.3654	LAFM
Yb^{+++}	1.331^a	3.917	0.340	−0.0853	LAFM

[a] Reference 2.
[b] Reference 6.

V. CONCLUSIONS

From Table V it is clear that the calculated lowest-energy orderings are ferromagnetic orderings for LiTbF$_4$ and LiHoF$_4$; this is in complete agreement with the experimental results.[5,6] For LiErF$_4$, whose low-temperature ordering has *not* been established experimentally, our calculations predict a layered antiferromagnetic ordering in the ab plane in contrast with the ferromagnetic ordering in the ab plane predicted by Hansen *et al.*[6]

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