Supplementary Material for "Dimensional Reduction in Quantum Dipolar Antiferromagnets"

P. Babkevich,^{1,*} M. Jeong,¹ Y. Matsumoto,² I. Kovacevic,¹ A. Finco,^{1,3}

R. Toft-Petersen,⁴ C. Ritter,⁵ M. Månsson,^{1,6,7} S. Nakatsuji,² and H. M. Rønnow¹

¹Laboratory for Quantum Magnetism, Institute of Condensed Matter Physics (ICMP), Ecole Polytechnique Féderale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

²Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

³ICFP, Département de physique, École normale supérieure, 45 rue d'Ulm, 75005 Paris, France

⁴Helmholtz-Zentrum Berlin für Materialien und Energie, D-14109 Berlin, Germany

⁵Institut Laue-Langevin, BP 156, F-38042, Grenoble Cedex 9, France

⁶Laboratory for Neutron Scattering, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

⁷Department of Materials and Nanophysics, KTH Royal Institute of Technology, SE-164 40 Kista, Sweden

Here we provide additional information on the structural refinement of $LiYbF_4$ and compare it to the isostructural $LiErF_4$ compound to show that the magnetic structures in the two materials appear to be different.



FIG. 1. (Color online) High-resolution neutron powder diffraction measurements using D2B diffractometer. Data collected at 10 K and refined to the structural model described in the text. Incident neutron wavelength was 1.594 Å.

CRYSTALLOGRAPHIC STRUCTURE

It is well known that systems of the Li RF_4 family crystallize in a scheelite CaWO₄ type structure. To verify our LiYbF₄ sample, we have performed careful measurements using D2B diffractometer in the paramagnetic phase at 10 K – well above magnetic ordering temperature. Our results are presented in Fig. 1. A good fit to the diffraction pattern was found using Rietveld method in the Fullprof package [1] which allows us to extract the atomic positions and B_{iso} isotropic Debye-Waller factors. In the case of ⁷Li, it was not possible to accurately refine the B_{iso} parameter and therefore it was fixed in the fitting. The detailed refinement, described in Table I, is in excellent agreement with that reported previously on the system in Ref. [2].

Atom	site	x	y	z	$B_{\rm iso}$ (Å ²)
$^{7}\mathrm{Li}$	4a	0.0000	0.2500	0.1250	0.80
Yb	4b	0.0000	0.2500	0.6250	0.09(3)
F	16f	0.2186(4)	0.4169(4)	0.4571(2)	0.43(4)

TABLE I. Nuclear structure refinement of LiYbF₄ shown in Fig. 1. The Bragg peaks were indexed by $I4_1/a$ space group with lattice parameters of a = 5.13435(8) Å and c =10.5918(2) Å. The fractional atomic positions using the second origin choice setting are listed in the table together with uncertainties given in brackets.

MAGNETIC STRUCTURE

Having confirmed the crystallographic structure of LiYbF₄ and the absence of impurities, we next consider the arrangement of the magnetic moments below $T_{\rm N}$. Previous study of LiErF₄ found that magnetic moments are arranged into a bilayer structure where the moments connected by *I*-centering are antiparallel [3]. Indeed, solving the Hamiltonian in the mean-field approximation quickly converges to this structure. Our previous mean-field simulations of LiYbF₄ and LiErF₄ indicate that the groundstate magnetic structures should be the same, with the only difference that the moment on Yb³⁺ ion is expected to be smaller than that on Er³⁺ [4].

Neutron diffraction data from studies of LiErF₄ is plotted in Figs. 2(a) and (b). Measurements were collected using DMC diffractometer with $\lambda = 2.457$ Å. Antiferromagnetic ordering in LiErF₄ sets in below 375 mK [3]. In order to obtain purely the magnetic contribution to the signal, we have subtracted measurements collected above 900 mK. Surprisingly, some of the stronger peaks are found to sit on broad humps which could indicate some short-range correlations in the system but could also be some artifacts related to the background. The origin of these cannot be elucidated further.

In comparison, data collected using D1B at $\lambda = 2.52$ Å



FIG. 2. (Color online) Neutron powder diffraction data recorded for (a,b) LiErF_4 and (c,d) LiYbF_4 plotted as a function of *d*-spacing. In each case measurements in the paramagnetic phase were used to subtract the nuclear contribution to the patterns leaving purely the magnetic Bragg peaks. Grey vertical lines under the patterns show the indexation of the reflection. Simulations assuming collinear magnetic structures with moments along [100] and [110] directions are plotted in panels (e,f).

examining LiYbF₄ show a slowly varying background with no signs of any additional features. We notice from the LiErF₄ and LiYbF₄ diffraction patterns shown in Figs. 2(b) and (d) that the relative intensities of (100) and (102), close to 5.1 and 3.7 Å, respectively, are clearly different for the two systems. The ratio of $\sigma(100)$ to $\sigma(102)$ intensity in LiErF₄ is 3.36(7) and in LiYbF₄ is 1.241(4).

Since the incident neutron wavelengths are very similar and the instrumental resolution is not very different for the two diffractometers we would have expected from mean-field simulations that the magnetic powder patterns are nearly the same. Intriguingly this does not appear to be the case. Performing Rietveld refinement of the magnetic structure for LiYbF₄ gives a better fit when the moments are allowed to rotate to be along the [110] direction. The simulations for the two different moment directions is shown in Figs. 2(e) and (f). In the model where the moments are along [100], the $\sigma(100)/\sigma(102) = 4.14$ – close to what we find for LiErF₄. Repeating this analysis for moments along [110], we find instead $\sigma(100)/\sigma(102) = 1.35$, viz LiYbF₄.

MAGNETIC REPRESENTATION ANALYSIS

The magnetic structures of LiYbF₄ and LiErF₄ can be described by the magnetic propagation wavevector $\mathbf{k} =$ (1,0,0). From the paramagnetic space group $I4_1/a$, the little group $G_{\mathbf{k}}$ contains 8 symmetry elements $(g_1 - g_8)$ listed in Table II. The magnetic representation Γ_{mag} of $G_{\mathbf{k}}$ reduces to $\Gamma_{\text{mag}} = 2\Gamma_1 + \Gamma_2$. Both Γ_1 and Γ_2 are two dimensional and their characters are given in Table II. Using Basireps [5], we obtain basis functions ψ , shown in Table III for two symmetry-related sites. The two sites create an extinction condition which makes is possible to distinguish between magnetic moment directions even in the tetragonal cell with powder averaging. In general, the *n*th moment \mathbf{m}_n can be expressed as a Fourier series,

$$\mathbf{m}_n = \sum_{\mathbf{k}} \mathbf{S}_n^{\mathbf{k}} e^{-\mathbf{i}\mathbf{k}\cdot\mathbf{t}},\tag{1}$$

where **t** is the real space translation vector. The vectors $\mathbf{S}_n^{\mathbf{k}}$ are a linear sum of the basis vectors such that,

$$\mathbf{S}_{n}^{\mathbf{k}} = \sum_{m,p} c_{mp} \psi_{\nu mp}^{\mathbf{k}},\tag{2}$$

TABLE II. Character table of the little group $G_{\mathbf{k}}$ showing how the irreducible representations Γ_{ν} transform according to symmetry operations g_1, \ldots, g_8 . Using the Seitz notation, the symmetry operations are defined as, $g_1 = \{1 \mid 0, 0, 0\}, g_2 = \{2_{00z} \mid 1/2, 0, 1/2\}, g_3 = \{4_{00z}^+ \mid 3/4, 1/4, 1/4\}, g_4 = \{4_{00z}^- \mid 3/4, 3/4, 3/4\}, g_5 = \{-1 \mid 0, 0, 0\}, g_6 = \{m_{xy0} \mid 1/2, 0, 1/2\}, g_7 = \{-4_{00z}^+ \mid 1/4, 3/4, 3/4\}$ and $g_8 = \{4_{00z}^- \mid 1/4, 1/4\}.$

ν	n	$(\psi^1_x,\psi^1_y,\psi^1_z)$	$(\psi_x^2,\psi_y^2,\psi_z^2)$
1	1	(1, 0, 0)	(0, 1, 0)
1	2	(0, 1, 0)	(-1, 0, 0)
1	3	(0, -1, 0)	(-1, 0, 0)
1	4	(1, 0, 0)	(0, -1, 0)
2	1	(1, 0, 0)	(0, 0, -i)
2	2	(0, 0, i)	(0, 0, -1)

TABLE III. Basis functions ψ of irreducible representation Γ_{ν} for ions situated at 1. (x, y, z) and 2. (-y + 3/4, x + 1/4, z + 1/4).

where coefficients c_{mp} can be complex. We label ν as the active irreducible representation Γ_{ν} , $m = 1 \dots n_{\nu}$, where n_{ν} is the number of times Γ_{ν} is contained in Γ_{mag} . The index p labels the component corresponding to the dimension of Γ_{ν} .

In the case of LiYbF₄, the moments lie in the *ab* plane, therefore Γ_1 is active (see Table III). However, the neutron data does not allow us to uniquely identify the magnetic ordering as any of the four basis vectors can refine the measured data. All four arrangements result in moments which rotate by 90° along *c*, as for example shown in Fig. 3(a). It is also possible to use a combination of two basis vectors, such as 1 and 3 or 2 and 4 to describe a collinear magnetic structure as shown in Figs. 3(b–d). However, it is not possible to refine the measured data for LiErF₄ using the same combination of basis vectors which appear to describe LiYbF₄. Indeed a combination of all four basis vectors, as depicted in Fig. 3(e), is needed to describe the best possible solution for LiErF₄ reported in Ref. [3] which sees the moments along the *a* axis

CRYSTAL FIELD INTERACTION

The in-plane anisotropy in LiErF₄ and LiYbF₄ is largely determined by the single-ion crystal field and dipolar interactions. We would expect that as the magnetic moment size is very similar in LiErF₄ and LiYbF₄, the dipolar interactions in the two systems do not differ significantly. One possible arrangement in LiYbF₄ is shown in Fig. 3(c) where the moments are all rotated by

ion	$10^{3}B_{2}^{0}$	$10^{3}B_{4}^{0}$	$10^{6}B_{6}^{0}$	$10^3 B_4^4(c)$	$10^3 B_6^4(c)$	$10^6 B_6^4(s) $
\mathbf{Er}	58.1	-0.536	-0.00625	-5.53	-0.106	23.8
	(3.4)	(0.032)	(0.00041)	(0.31)	(0.0061)	(1.5)
Yb	457	7.75	0	196	-9.78	0
	(5.2)	(0.12)	(0)	(0.65)	(0.0094)	(0)

TABLE IV. Crystal field parameters of LiYbF₄ and LiErF₄ compounds determine by inelastic neutron scattering. Typically, a coordinate system with $B_4^4(s) = 0$ is chosen, while two possible equivalent coordinations of R ion by F ions give different sign of $B_6^4(s)$. After [4].

 45° in the basal plane with respect to the LiErF₄ magnetic structure. This structure (amongst others) fits well the measured data. From the crystal field whose Hamiltonian for $\bar{4}$ point group symmetry at the *R* site is given by,

$$\mathcal{H}_{\text{CEF}} = \sum_{l=2,4,6} B_l^0 \mathbf{O}_l^0 + \sum_{l=4,6} B_l^4(c) \mathbf{O}_l^4(c) + B_l^4(s) \mathbf{O}_l^4(s).$$
(3)

The later B_l^4 terms play a role in the planar anisotropy where $B_4^4(c)$ term is found from experiments to be largest, see Table IV. Classically, one obtains the energy of rotating a moment of size J_0 in the plane by angle ϕ to be $E = J_0 B_4^4(c) \cos(4\phi)$. Hence, the minimum in energy for different signs of $B_4^4(c)$ is found to be 45° apart. While this appears to be a simple explanation for preferred moment direction, a strong crystal field interaction would result in an Ising-like system, which is not what we observe experimentally. Furthermore, dipolar interactions are not expected to favor such ordering. Therefore, further theoretical work is necessary to examine the mechanism by which the dipolar-coupled antiferromagnets order.

CONCLUSION

While it is entirely possible that the diffraction patterns can be also described by other models including ones where moments are non-collinear, qualitatively our experimental data appears to suggest that the groundstate magnetic structure of LiErF_4 is not the same as



FIG. 3. (Color online) Possible magnetic structures of Γ_1 irreducible representation. (a) Magnetic structure from just the first basis vector in Table III. (b) – (d) show arrangement of moments by combining two basis vectors. (e) Appropriate sum of all basis vectors to form magnetic structure which best describes LiErF₄.

 $LiYbF_4$. Thus, this highlights the universality of antiferromagnetism on a distorted diamond lattice found described in our Letter.

- * peter.babkevich@epfl.ch
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