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NEUTRON SCATTERING DETERMINATION OF THE CRYSTAL FIELD PARAMETERS IN 
ErCu$_4$Al$_8$ AND ErFe$_4$Al$_8$ INTERMETALLICS

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An inelastic neutron scattering experiment has been performed in order to determine the crystal field potential acting at the rare earth site in the paramagnetic phase of ErCu$_4$Al$_8$ and ErFe$_4$Al$_8$ intermetallic compounds. The profile refinement of the spectra measured at different temperatures, and experimental information on the electric field gradient available in the literature, allow a reliable estimate of the parameters for the tetragonal crystal field. Positive values of the lowest order term $B_2$ suggest an easy plane magnetic anisotropy of the Er sublattice, but the higher order terms could play an important role in determining the magnetisation direction.

Keywords: A. magnetically ordered materials, D. crystal fields, E. neutron scattering.

1. INTRODUCTION

THE SEARCH for new magnetic materials has recently turned to ternary rare-earth (RE) systems, and Fe-rich intermetallic compounds, with the tetragonal ThMn$_{12}$ type of crystal structure and general formula REFe$_{12-x}$M$_x$ (M = Ti, V, Cr, W, Si, C), have aroused considerable interest due to their promising properties for permanent magnet applications [1–8]. In these systems, both the 3$d$ and the RE sublattices contribute to the magnetocrystalline anisotropy. The Fe sublattice favours an easy magnetisation direction parallel to the $c$ axis, whilst the rare-earth contribution varies with RE and can be conveniently described by the crystal field (CF) theory, once the parameters defining the CF Hamiltonian have been determined [9]. However, a direct observation by neutron spectroscopy of the single-ion electronic excitations in REFe$_{12-x}$M$_x$ is difficult due to the strong molecular field produced by the transition metal (T) sublattice, and the CF potential can only be deduced from fitting the values experimentally obtained for bulk properties, such as the magnetisation or the anisotropy field, once the RE–T exchange field is known.

The situation is different for the isostructural series of compounds with formula RET$_4$Al$_8$ which are characterised by a weaker exchange interaction and remain paramagnetic down to low temperatures [10, 11], where they exhibit a wide variety of magnetic
phenomena [12-14]. Thus, the magnetic properties which are due to the interaction of the \( f \)-electrons with the CF can be studied in isolation. We have therefore performed inelastic neutron scattering (INS) experiments on some members of the \( \text{RE}T_4\text{Al}_8 \) family in order to obtain detailed information about the CF potential by measuring the energies and dipole matrix elements of transitions between CF levels. Preliminary results on \( \text{REMn}_4\text{Al}_8 \) (\( E = \text{Tb}, \text{Ho}, \text{Er} \)) have been published earlier [15, 16]. The present article reports an INS determination of the CF parameters in \( \text{ErCu}_4\text{Al}_8 \) and \( \text{ErFe}_4\text{Al}_8 \).

The crystallographic structure is body centred tetragonal with space group \( \text{I}4/\text{mmm} \) [17] and two formula units per unit cell \( (a = 8.712(3) \text{Å} \text{ and } c = 5.130(3) \text{Å} \text{ for } T = \text{Cu}; \ a = 8.700(4) \text{Å} \text{ and } c = 5.028(3) \text{Å} \text{ for } T = \text{Fe}) \) [10]. The Er atoms occupy the 2(a) sites of point symmetry 4/\text{mmm}, at the corners and the centres of tetragonal prisms. They are surrounded by four Al atoms at 3.0 Å (8(i) sites), eight Al at 3.2 Å (8(j) sites) and by eight transition metal atoms located at the 8(f) sites at 3.4 Å. Neutron diffraction experiments on \( \text{RE}T_4\text{Al}_8 \) revealed only small deviations from the ideal site occupations [18].

In \( \text{ErCu}_4\text{Al}_8 \), an antiferromagnetic order develops at \( T_N = 6 \text{ K} \). Magnetic susceptibility and Mössbauer spectroscopy data clearly indicate that the Cu sublattice is nonmagnetic and that only the Er ions contribute to the effective paramagnetic moment \( (\mu_{\text{eff}} = 9.6 \mu_B) \) [10]. On the other hand, two magnetic transitions are exhibited by \( \text{ErFe}_4\text{Al}_8 \), with the Er sublattice ordering at 25 K and the Fe sublattice at 111 K. The iron paramagnetic effective moment deduced from the susceptibility curves is \( 4.3(2) \mu_B \) per Fe ion [10]. Neutron diffraction experiments show that Er orders antiferromagnetically with a ferromagnetic component and an helical component incommensurate with the lattice, whilst the Fe sublattice has both ferromagnetic and antiferromagnetic components [11].

2. EXPERIMENTAL DETAILS AND RESULTS

The \( \text{ErCu}_4\text{Al}_8 \) and \( \text{ErFe}_4\text{Al}_8 \) polycrystalline samples were prepared by melting stoichiometric amounts of the elements (of at least 99.9% purity) in an arc furnace under a reduced argon atmosphere. They were then wrapped in a tantalum foil, sealed in a quartz tube in argon atmosphere and annealed for six weeks at 1073 K. Both samples were subsequently characterised by X-ray diffraction, showing that they were single phase with all Bragg peaks consistent with the \( \text{ThMn}_{12} \) structure. About 40 g of each compound were mounted in an aluminium can onto a liquid He cryostat for the INS experiments. A sample of \( \text{YMn}_4\text{Al}_8 \) was also measured in order to identify contributions to the neutron spectra arising from vibrational scattering.

The neutron spectroscopy experiments were performed on the direct-geometry time-of-flight spectrometer IN4 at the Institut Laue-Langevin in Grenoble, France, by using neutrons with an incident energy of 17 meV. For both compounds, data were collected at different scattering angles \( \phi \) between 10 and 74 degrees at \( T = 5, 50, 100 \text{ and } 150 \text{ K} \). The scattering functions obtained for \( \text{ErCu}_4\text{Al}_8 \) at
Energy Transfer (meV)

$T = 5, 50$ and $100$ K, with full scattering angle $\phi = 10^\circ$ are shown in Fig. 1. No peaks are observable in the same energy transfer region for YMn$_4$Al$_8$ ruling out the possibility that the excitations arise from vibrational scattering. This is confirmed by the reduction in intensity observed for the spectra measured at larger scattering angles up to $\phi = 74^\circ$. In Fig. 2 is shown the magnetic scattering function obtained for ErFe$_4$Al$_8$ in the paramagnetic phase at $T = 150$ K.

The magnetic response in the ordered phase is not presented here because, in the absence of detailed information on the magnetic structure, we are not able to analyze it. Low temperature neutron diffraction experiments are planned to address this problem.

3. DATA ANALYSIS AND DISCUSSION

The magnetic scattering function $S(Q, \hbar \omega)$ for unpolarized neutrons and small values of the momentum transfer $Q$ is given, in the case of a system of $N$ non-interacting ions, by [19]:

$$S(Q, \hbar \omega) = \frac{N}{4} (g_N r_e)^2 f^2(Q)g^2 \sum_{i,j} p_i$$

$$\times (|\langle f | J_\perp | i \rangle|^2 P(\hbar \omega - \Delta_f, \Gamma_f)),$$

where $(g_N r_e)^2 / 4 = 0.0724$ barn str$^{-1}$, $\Delta_f = E_f - F_i$, $\hbar \omega$ is the neutron energy transfer, $|i\rangle$ are the $4f$-electron eigenstates with energies $E_i$ and thermal occupation probabilities $p_i = \exp(-\beta E_i) / \Sigma_i \exp(-\beta E_i)$ ($\beta = 1/k_B T$), $J_\perp$ is the total angular momentum component perpendicular to $Q$ and $f(Q)$ is the single ion magnetic form factor. $P(\hbar \omega - \Delta_f, \Gamma_f)$ is the line-shape function for a peak of full width at half maximum $\Gamma_f$ and energy transfer centred at $\Delta_f$. The INS cross-section is therefore composed of peaks corresponding to dipole-allowed magnetic excitations the energies of which give the eigenvalues of the CF Hamiltonian, while their intensities provide information about the CF wave functions through the matrix elements of $J_\perp$.

Equation (1) shows that CF transitions may be identified by the manner in which their intensities vary with both temperature $T$ and scattering vector $Q$.

The matrix elements and the energies can be obtained by diagonalization of the CF Hamiltonian given by (for a system of $p$-fold symmetry)

$$H_{\text{CF}} = \sum_{n>0} \sum_{m=0}^n B_n^m \hat{O}_n^m$$

with $n = 2k$, $m = pk$, $k$ being an integer, and $l = 2, 3$ for $d$- and $f$-electrons, respectively. The $B_n^m$ are the CF parameters and the $\hat{O}_n^m$ are the Stevens operator equivalents built up of the total angular momentum operators. For a RE ion ($l = 3$) in tetragonal symmetry ($p = 4$) and the z-axis as the quantization axis, the hamiltonian (2) is

$$H_{\text{CF}} = B_0^0 \hat{O}_2^0 + B_2^2 \hat{O}_4^2 + B_4^4 \hat{O}_4^4 + B_6^6 \hat{O}_6^6 + B_8^8 \hat{O}_8^8.$$

The degeneracy of the $4I_{15/2}$ ground state multiplet of the Er$^{3+}$ ions is partly removed by the CF into 8 Kramers doublets and this splitting is directly measured in the INS experiment.

The lowest-order term can be written as $B_0^0 = \alpha_f (r^2) A_0^0$, where $\alpha_f$ is the second-order Stevens constant, $\langle r^2 \rangle$ is the second moment of the $4f$ radial wavefunction and $A_0^0$ is a CF parameter which is independent of the RE. For Er$^{3+}$ ions, $\alpha_f (r^2) = 5.06 \times 10^4 \text{Å}^2$. Experimental information on $A_0^0$ can be obtained from $^{155}$Gd Mössbauer spectroscopy data for GdT$_4$Al$_8$ ($T = \text{Cu, Fe}$) available in the literature. In fact, from the measured nuclear quadrupole splitting one may derive $A_2^0$ through the relation [20]

$$A_2^0 = -2021 \frac{e^2 q Q}{Q(1 - \gamma_\infty)} \text{meV a}_0^{-2}.$$

The quadrupole coupling constant $e^2 q Q$ is given in mm s$^{-1}$ and $Q$ in barn. In equation (4) $a_0$ is the Bohr radius, $Q$ is the quadrupole moment of the nucleus, $eq$ is the field gradient and $\gamma_\infty$ is the Sternheimer anti-shielding factor. For $^{155}$Gd it is $Q(1 - \gamma_\infty) = 121$ barn [21]; moreover, the values $e^2 q Q = -1.182$ mm s$^{-1}$ and $e^2 q Q = -3.425$ mm s$^{-1}$ have been reported for the GdCu$_4$Al$_8$ and the GdFe$_4$Al$_8$ compounds, respectively [10].
Table 1. Crystal field parameters for ErCu₄Al₈ and ErFe₄Al₈ as obtained from the present experiment. The $B_n^m$ parameters are in meV units, the $A_n^m$ in meV $a_0^{-n}$ ($n = 2, 4, 6$), $a_0$ being the Bohr radius

<table>
<thead>
<tr>
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<th>$10^2 B_2^2$</th>
<th>$10^4 B_4^2$</th>
<th>$10^5 B_6^0$</th>
<th>$10^5 B_4^4$</th>
<th>$10^4 B_6^4$</th>
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<tr>
<td>ErCu₄Al₈</td>
<td>0.20(4)</td>
<td>0.2(1)</td>
<td>-0.69(2)</td>
<td>-0.3(2)</td>
<td>-0.44(5)</td>
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<tr>
<td>ErFe₄Al₈</td>
<td>0.40(4)</td>
<td>2.1(2)</td>
<td>-0.27(3)</td>
<td>0.2(1)</td>
<td>-0.06(2)</td>
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<th>$A_4^2$</th>
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<th>$A_4^4$</th>
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<tbody>
<tr>
<td>ErCu₄Al₈</td>
<td>11(6)</td>
<td>4(2)</td>
<td>-0.69(2)</td>
<td>-5(3)</td>
<td>-4.4(5)</td>
</tr>
<tr>
<td>ErFe₄Al₈</td>
<td>22(2)</td>
<td>37(6)</td>
<td>-0.27(3)</td>
<td>4(2)</td>
<td>-0.6(2)</td>
</tr>
</tbody>
</table>

Table 2. Largest components of the ground state CF wave functions in (a) ErCu₄Al₈ and (b) ErFe₄Al₈

(a) $-0.018[\mp 9/2] - 0.095[\mp 1/2] + 0.847[\pm 7/2] + 0.524[\pm 15/2]$
(b) $0.059[\mp 15/2] + 0.993[\mp 7/2] - 0.095[\pm 1/2] + 0.028[\pm 9/2]$

The $A_2^0$ parameter in the two compounds and, subsequently, the $B_2^0$ values for the Er ions can then be calculated from equation (4). One obtains $B_2^0 = 0.036\text{meV}$ for $T = \text{Cu}$ and $B_2^0 = 0.10\text{meV}$ for $T = \text{Fe}$. These values have been taken as starting points in a least-squares fitting procedure of the measured profiles based on the diagonalization of the Hamiltonian (3). The use of equation (4) has to be taken with reservation because it has become clear from band structure calculations that this equation lacks a sound physical basis [22]. The reason for this is that antishielding effects are based on radial excitations of core electron states that play only a minor role in determining the electric field gradient at the nuclear site. The main contribution to the electric field gradient comes from on-site valence electron asphericities. However, the 5d electron asphericities contribute mainly to $A_2^0$, whereas the 6p electron asphericities contribute mainly to $e^2qQ$. Although both on-site valence electron asphericities need not be the same, there are strong indications that an empirical relation between $A_2^0$ and $e^2qQ$ still exists. For instance, the change in sign and magnitude of $A_2^0$ found by means of single crystal measurements and inelastic neutron scattering experiments in the series REGd₂₋ₓAlₓ could be accurately followed (within 3%) by a similar behaviour of $e^2qQ$ determined from Gd Mössbauer spectroscopy on the corresponding Gd compounds [23].

It must be noticed that the relation given in [23], namely $A_2^0 = -6.8e^2qQ$, leads to an $A_2^0$ value smaller than obtained by equation (4). The disagreement is only apparent, since equation (4) gives the "bare" $A_2^0$, which does not include the modification of the CF on the 4f electrons due to the polarization of the outer 5s^25p^2 electron shells. This effect reduces the second order CF parameters by a factor $(1 - \sigma_2)$, with $\sigma_2 \approx 0.6$ for the ions of the RE series [24].

The results of the fitting procedure for the $B_n^m$ coefficients (and for the related $A_n^m$'s) are reported in Table 1. As expected from the previous considerations, the final $B_2^0$ are smaller than the starting ones.

The calculated magnetic scattering profile is shown as a solid line in Figs. 1 and 2; the individual excitations contributing to the spectra are shown by dashed lines.

The agreement between calculated and experimental observations is particularly good. In the case of the Cu compound, attention must be paid to the...
fact that at $T = 5$ K the system is magnetically ordered. Even though the molecular field is expected to be small ($T_N = 6$ K), nevertheless it should be taken into account. In fact, the splitting of the Kramers doublets that is produced could justify the extra intensity observed around 5 meV. A quantitative analysis of the ordered phase is, however, not possible, until the details of the magnetic structure are known.

The ground state in ErFe$_4$Al$_8$ is a doublet which mainly contains $|J_z = \pm 7/2\rangle$ wavefunctions, the next level being an almost pure $|J_z = \pm 9/2\rangle$ doublet lying at only 0.85 meV above the ground state; the total splitting is of about 11 meV. In the case of ErCu$_4$Al$_8$, the ground state is an admixture of mainly $|J_z = \pm 7/2\rangle$ and $|J_z = \pm 15/2\rangle$, with a second doublet at 3.6 meV and a total splitting of 27 meV (Table 2). The energy level scheme for both compounds is reported in Fig. 3.

For both compounds, the second order term $A_2^S$ is positive and, therefore, the CF induced anisotropy should favour an easy-plane magnetic arrangement of the Er sublattice. On the other hand, the Fe contribution in ErFe$_4$Al$_8$ tends to favour an easy magnetisation direction along the $c$-axis and spin reorientation transitions are likely to appear.

We have to mention that, in a first approach to interpret our experimental data, we tried to use a different point of view, namely to reduce the number of independent parameters in the Hamiltonian (3) by fixing the order of magnitude and the sign of the ratios $B_i / B_4$ following the ideas of the Newman Superposition Model [25]. However, we failed to find a unifying picture for these compounds and for the other of the series, REMn$_4$Al$_8$ (RE = Tb, Ho, Er). On the contrary, the use of equation (4) has been the key for a consistent interpretation of all the inelastic neutron scattering data available in this series [26].

REFERENCES