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DOI

[10.1016/0038-1098\(94\)00912-0](https://doi.org/10.1016/0038-1098(94)00912-0)

Publication date

1995

Published in

Solid State Communications

[Link to publication](#)

Citation for published version (APA):

Paci, B., Caciuffo, R., Amoretti, G., Moze, O., Buschow, K. H. J., & Murani, A. P. (1995). Neutron scattering determination of the crystal field parameters in ErCu₄Al₈ and ErFe₄Al₈ intermetallics. *Solid State Communications*, 94, 489-493. [https://doi.org/10.1016/0038-1098\(94\)00912-0](https://doi.org/10.1016/0038-1098(94)00912-0)

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0038-1098(94)00912-0

NEUTRON SCATTERING DETERMINATION OF THE CRYSTAL FIELD PARAMETERS IN
ErCu₄Al₈ AND ErFe₄Al₈ INTERMETALLICS

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(Received 25 October 1994 by P. Burlet)

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 ErCu₄Al₈ and ErFe₄Al₈ 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_2^0 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 ThMn₁₂ 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 3d 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 RE₄Al₈ 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 RETi_4Al_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 REMn_4Al_8 ($E = \text{Tb, Ho, Er}$) have been published earlier [15, 16]. The present article reports an INS determination of the CF parameters in ErCu_4Al_8 and ErFe_4Al_8 .

The crystallographic structure is body centred tetragonal with space group $I4/mmm$ [17] and two formula units per unit cell ($a = 8.712(3)\text{\AA}$ and $c = 5.130(3)\text{\AA}$ for $T = \text{Cu}$; $a = 8.700(4)\text{\AA}$ and $c = 5.028(3)\text{\AA}$ for $T = \text{Fe}$) [10]. The Er atoms occupy the 2(a) sites of point symmetry $4/mmm$, at the corners and the centres of tetragonal prisms. They are surrounded by four Al atoms at $3.0\text{\AA}$ (8(i) sites), eight Al at $3.2\text{\AA}$ (8(j) sites) and by eight transition metal atoms located at the 8(f) sites at $3.4\text{\AA}$. Neutron diffraction experiments on RETi_4Al_8 revealed only small deviations from the ideal site occupations [18].

In ErCu_4Al_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 ErFe_4Al_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 ErCu_4Al_8 and ErFe_4Al_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 ThMn_{12} structure. About 40 g of each compound

Fig. 1. Inelastic magnetic scattering spectra obtained at different temperatures for ErCu_4Al_8 . The phonon contributions have been subtracted by scaling similar measurements on the isostructural non-magnetic YMn_4Al_8 compound. The full lines are the fits to the model Hamiltonian, as described in the text. The single excitations contributing to the spectra are shown by dashed lines. At $T = 5\text{ K}$ the compound is magnetically ordered.

were mounted in an aluminium can onto a liquid He cryostat for the INS experiments. A sample of YMn_4Al_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 ϕ between 10 and 74 degrees at $T = 5, 50, 100$ and 150 K . The scattering functions obtained for ErCu_4Al_8 at

Fig. 2. Inelastic magnetic neutron scattering function obtained at 150 K for ErFe_4Al_8 . The phonon contributions have been subtracted by scaling similar measurements on the isostructural non-magnetic YMn_4Al_8 compound. The full line is the fit to the model Hamiltonian. The single excitations contributing to the spectrum are shown by dashed lines.

$T = 5, 50$ 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_4Al_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_4Al_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 $S(\mathbf{Q}, \hbar\omega)$ for unpolarized neutrons and small values of the momentum transfer $\mathbf{Q}$ is given, in the case of a system of N non-interacting ions, by [19]:

$$S(\mathbf{Q}, \hbar\omega) = \frac{N}{4} (g_N r_e)^2 f^2(Q) g_f^2 \sum_{i,f} p_i \times |\langle f | J_\perp | i \rangle|^2 P(\hbar\omega - \Delta_{fi}, \Gamma_{fi}), \quad (1)$$

where $(g_N r_e)^2/4 = 0.0724$ barn str^{-1} , $\Delta_{fi} = E_f - E_i$, $\hbar\omega$ is the neutron energy transfer, $|i\rangle$ are the $4f$ -electron eigenstates with energies E_i and thermal occupation probabilities $p_i = \exp(-\beta E_i) / \sum_i \exp(-\beta E_i)$ ($\beta = 1/k_B T$), $J_\perp$ is the total angular momentum component perpendicular to $\mathbf{Q}$ and $f(Q)$ is the single

ion magnetic form factor. $P(\hbar\omega - \Delta_{fi}, \Gamma_{fi})$ is the line-shape function for a peak of full width at half maximum Γ_{fi} and energy transfer centred at Δ_{fi} . 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 $\mathbf{Q}$.

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

$$H_{CF} = \sum_{n>0}^{\min(2l, 2J)} \sum_{m=0}^n B_n^m \hat{O}_n^m \quad (2)$$

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

$$H_{CF} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^4 \hat{O}_4^4 + B_6^0 \hat{O}_6^0 + B_6^4 \hat{O}_6^4. \quad (3)$$

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 $B_2^0 = \alpha_J \langle r^2 \rangle A_2^0$, where α_J is the second-order Stevens constant, $\langle r^2 \rangle$ is the second moment of the $4f$ radial wavefunction and A_2^0 is a CF parameter which is independent of the RE. For Er^{3+} ions, $\alpha_J \langle r^2 \rangle = 5.06 \times 10^{-4} \text{ \AA}^2$. Experimental information on A_2^0 can be obtained from ^{155}Gd Mössbauer spectroscopy data for GdT_4Al_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]

$$A_2^0 = -2021 \frac{e^2 q Q}{Q(1 - \gamma_\infty)} \quad (\text{meV } a_0^{-2}). \quad (4)$$

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 γ_∞ is the Sternheimer anti-shielding factor. For ^{155}Gd it is $Q(1 - \gamma_\infty) = 121$ barn [21]; moreover, the values $e^2 q Q = -1.182 \text{ mm s}^{-1}$ and $e^2 q Q = -3.425 \text{ mm s}^{-1}$ have been reported for the GdCu_4Al_8 and the GdFe_4Al_8 compounds, respectively [10].

Table 1. Crystal field parameters for ErCu_4Al_8 and ErFe_4Al_8 as obtained from the present experiment. The B_n^m parameters are in meV units, the A_n^m in $\text{meV } a_0^{-n}$ ($n = 2, 4, 6$), a_0 being the Bohr radius

	$10 B_2^0$	$10^4 B_4^0$	$10^5 B_6^0$	$10^3 B_4^4$	$10^4 B_6^4$
ErCu_4Al_8	0.20(4)	0.2(1)	-0.69(2)	-0.3(2)	-0.44(5)
ErFe_4Al_8	0.40(4)	2.1(2)	-0.27(3)	0.2(1)	-0.06(2)
	A_2^0	A_4^0	A_6^0	A_4^4	A_6^4
ErCu_4Al_8	11(6)	4(2)	-0.69(2)	-5(3)	-4.4(5)
ErFe_4Al_8	22(2)	37(6)	-0.27(3)	4(2)	-0.6(2)

Table 2. Largest components of the ground state CF wave functions in (a) ErCu_4Al_8 and (b) ErFe_4Al_8

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

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 $\text{RE}d_{2-x}\text{Al}_x$ 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 $A_2^0 = -6.8 e^2qQ$, 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 $5s^2 5p^2$ 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

Fig. 3. Crystal field energy levels calculated for the Er^{3+} ions in ErCu_4Al_8 and ErFe_4Al_8 .

fact that at $T = 5\text{ K}$ the system is magnetically ordered. Even though the molecular field is expected to be small ($T_N = 6\text{ K}$), 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_4Al_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_4Al_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_2^0 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_4Al_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_4^0/B_4^A and B_6^0/B_6^A 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_4Al_8 ($\text{RE} = \text{Tb, Ho, Er}$). 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].

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