Identifying Further Inelastic Neutron Crystal Field Transitions in $ErNiAl_4$

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Interim results are presented for a thermal INS project seeking to identify further crystal field transitions for the J = 15/2 ground state of Er^{3+} in $ErNiAl_4$. Previously reported transitions at 3, 7.4 and 11.3 meV are confirmed and a possible two further transitions have been located at 14.4 and 18.2 meV.

1. Introduction

The orthorhombic, intermetallic series $RNiAl_4$ (R = rare earth) exhibits interesting magnetic behaviour [1-2], including the potential for low temperature, inverse, magnetic cooling [3]. Given that the $RNiAl_4$ magnetism is associated solely with the R sub-lattice and is influenced strongly by the local crystal field (CF) interaction at the R-site, it is important that the CF interaction is characterised. Thermal neutrons are used here to extend a previous cold neutron inelastic neutron scattering (INS) investigation [4] of the crystal field (CF) transitions at the single Er^{3+} site in $ErNiAl_4$.

2. Experimental details

Substantial amounts of $ErNiAl_4$ (34.8 g) and $YNiAl_4$ (26 g) were prepared as a set of smaller 1-2 g lots via repeated argon arc melting followed by vacuum annealing for 5-6 d at 1050 °C. X-ray powder diffraction was used to identify the acceptable single-phase lots. All neutron scattering measurements were performed on the C5 polarised triple-axis spectrometer at CNBC in Chalk River, Canada. The INS spectra were accumulated with a final scattering energy of $E_f = 14$ meV.

3. Results

Neutron scattering measurements were performed using both the elastic and inelastic modes of operation for the C5 spectrometer.

3.1 Elastic neutron scattering

Neutron diffraction patterns ($\lambda = 2.37051$ Å) were recorded for $ErNiAl_4$ at 290 K and 3.9 K (Fig. 1). Rietveld analysis of the 3.9 K pattern (well below $T_N = 5.8$ K) using *FullProf* software [5] yielded an incommensurate sinusoidal structure with a propagation vector of [0.191 1.0 0.038] and a local moment amplitude of $\mu(Er^{3+}) = 7.0\ \mu_B$ aligned with the c-axis (Fig. 2). The propagation vector is similar to that reported earlier [6] although the moment is about 16% smaller (cf 8.3 μ_B). Recent ^{166}Er-Mössbauer results [7] rule out a spread in the local Er moment so that a square wave modulation is more appropriate. However, in subsequent reconsideration of the Rietveld analysis, it has proved difficult to identify the weak higher harmonics.

In order to confirm the magnetic origin of the reflection at $Q = 2.3134$ Å^{-1} ($2\theta \approx 51.75°$) its intensity was monitored as a function of temperature using polarised neutrons ($\underline{p}$ // $\underline{Q}$) with both spin flip (SF) and non spin flip (NSF) detection. From Fig. 3, it is evident that the net

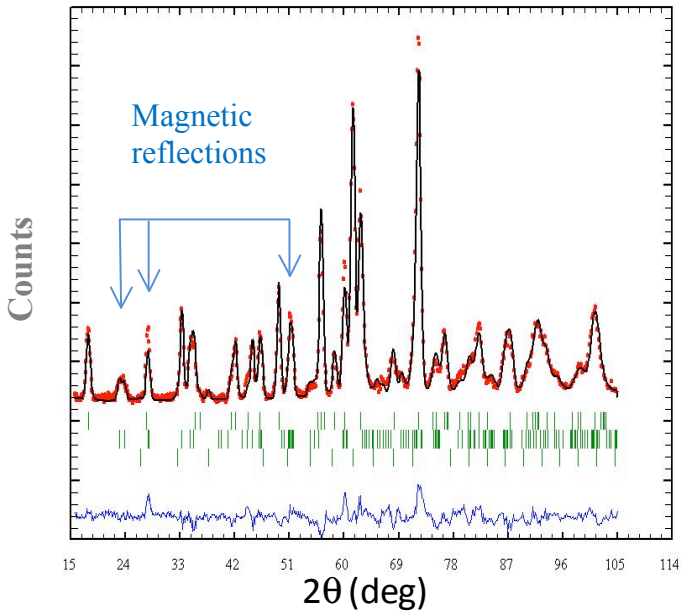

Fig. 1. Neutron diffraction pattern of $ErNiAl_4$ recorded at 3.9 K (λ = 2.37051 Å). The three rows of Bragg position markers are (top) nuclear, (middle) incommensurate magnetic, and (bottom) small component of Er_2O_3 impurity.

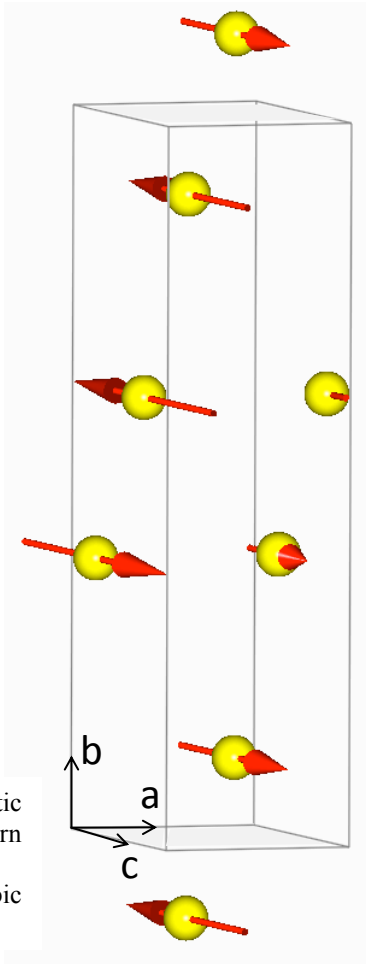

Fig. 2. Incommensurate sinusoidal magnetic structure fitted to the neutron diffraction pattern for $ErNiAl_4$ at 3.9 K. For simplicity, the Ni and Al atoms are ignored and just one orthorhombic crystallographic cell is shown.

magnetic intensity (SF - normalised NSF) drops to zero above the ordering temperature. The maximum of the differentiated net signal (upper inset in Fig. 3) yields an ordering temperature of 6.5 K, in close agreement with the bulk specific heat value of T_N = 5.8 K [6].

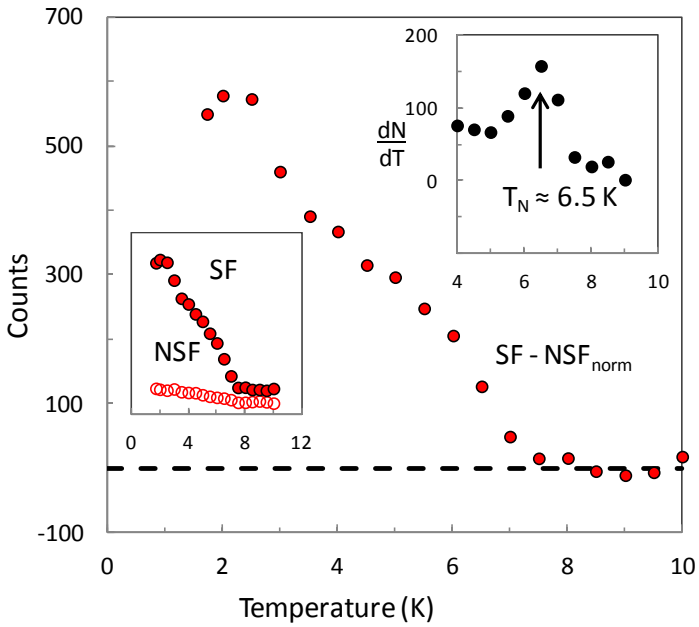

Fig. 3. Temperature dependent intensity of the $ErNiAl_4$ magnetic reflection at 2θ = 51.75° (λ = 2.37051 Å):
SF = spin flip, NSF = non spin flip, and NSF_{norm} indicates $\overline{NSF}$ normalised to $\overline{SF}$ in the temperature range 7.5 < T < 10 K.

3.1 Inelastic neutron scattering

Unpolarised INS spectra were recorded for $ErNiAl_4$ at 10 K with four different scattering vectors, Q, over the energy ranges of 0 - 25 meV (Q = 1.2 $Å^{-1}$), 0 - 41 meV (Q = 2.7 $Å^{-1}$), 0 - 50 meV (Q = 3.0 $Å^{-1}$), and 20 - 50 meV (Q = 5.2 $Å^{-1}$). As shown in Fig. 4, strong transitions were observed at 3.08(2), 7.53(2) and 11.6(1) meV. These energies are in excellent agreement with those observed previously using cold neutrons [4] and the evident Q-independence confirms that they are associated with "magnetic" CF transitions.

However, the objective of these new measurements was to identify additional CF transitions at higher energies. From Fig. 5 the INS spectra in the range of 15 - 50 meV are seen to be of relatively low intensity with broader features that are believed to be associated with phonon transitions. Because of this, additional INS spectra were recorded for non-magnetic $YNiAl_4$ whose Y^{3+} ion's ground S-state is not subjected to a CF interaction.

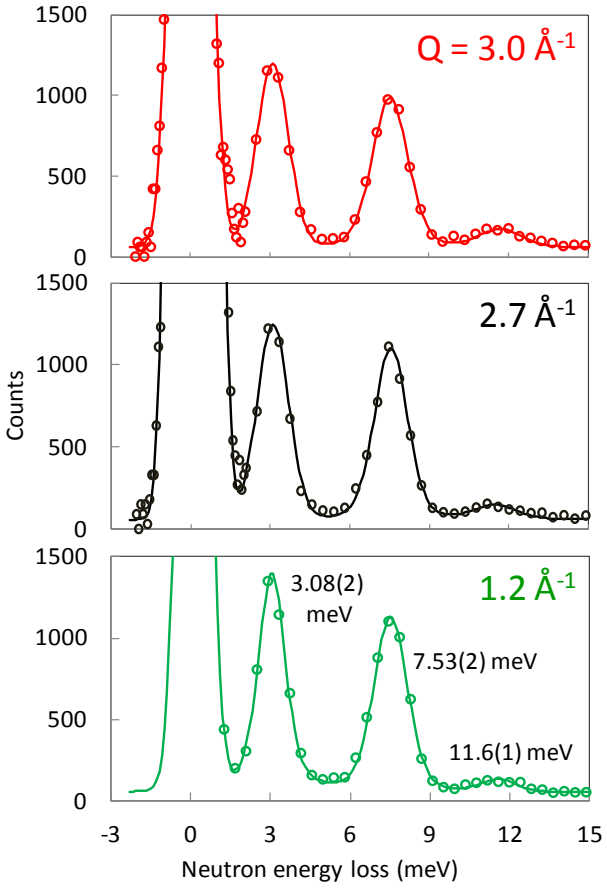

Fig. 4. The 0 < E < 15 meV region of the INS spectra recorded for $ErNiAl_4$ at 10 K with scattering vectors of Q = 1.2, 2.7 and 3.0 $Å^{-1}$. The solid lines are fitted Pseudo-Lorentzian peaks superimposed on a linear background.

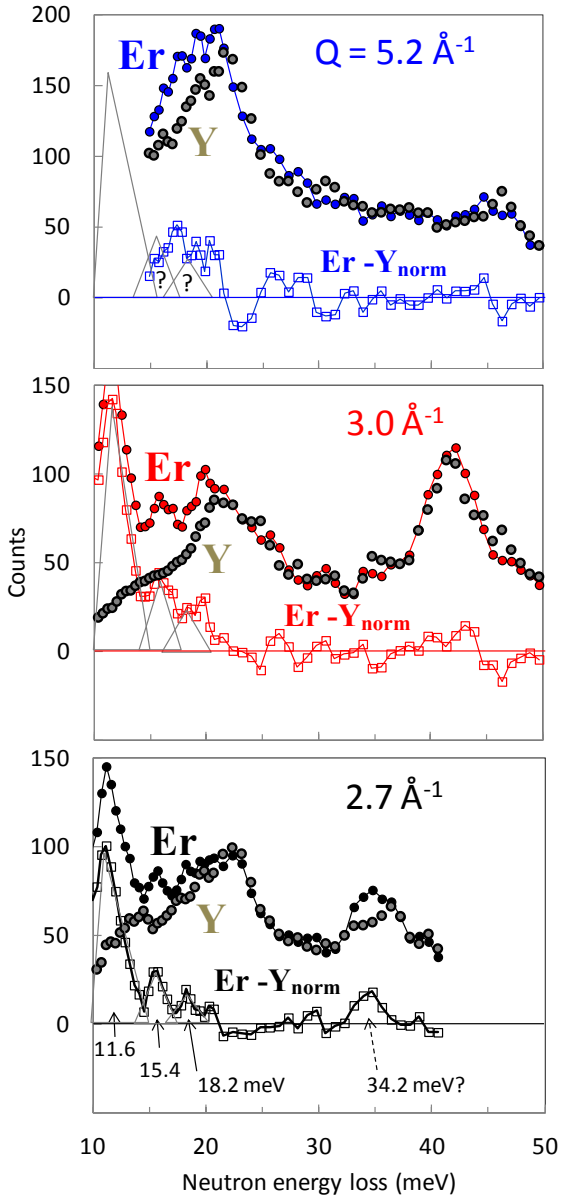

Fig. 5. The 10 < E < 50 meV region of INS spectra recorded at 10 K with scattering vectors of Q = 2.7, 3.0 and 5.2 $Å^{-1}$. The data for $ErNiAl_4$, the scaled up data for $YNiAl_4$, and their subtraction are indicated by the labels "Er", "Y" and "Er - Y", respectively. The scaling of the $YNiAl_4$ spectra employed a multiplying factor of the form A + B*E (where E is the neutron energy loss) and the spectra were smoothed prior to their subtraction.

The approach taken was to scale up the intensities of the$YNiAl_4$ spectra so that their broad features matched as closely as possible those of their $ErNiAl_4$ counterparts. To this end, it was found useful to employ a scaling factor that increased linearly across the spectra. The scaled $YNiAl_4$ spectra were then subtracted from the $ErNiAl_4$ spectra in an effort to identify the true CF transitions for $ErNiAl_4$. Based on this approach, possible additional CF transitions are located at 14.4 and 18.2 meV as indicated by the superimposed triangular peaks in Fig. 5. A further candidate is observed at 34.2 meV with Q = 2.7 $Å^{-1}$ but it is no longer evident for Q = 3.0 and 5.2 $Å^{-1}$.

Conclusions and on-going work

Valuable information has been gained regarding the incommensurate magnetic phase of $ErNiAl_4$ below T_N = 5.8 K and likely additional CF transitions have been located at 14.4 and 18.2 meV. It is hoped that further polarised neutron beam INS measurements currently being conducted on the C5 spectrometer at Chalk River will ultimately separate the remaining weak CF transitions out from the broad phonon signals via the comparison of SF and NSF spectra.

Acknowledgments

The CNBC is gratefully acknowledged for time allocated on the C5 spectrometer and Vernon Edge is thanked for his valuable assistance with the specimen preparation.

References

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