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The Locked-in magnetic structure of $Er_3Cu_4Si_4$ below 1 K

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Abstract. We have determined the magnetic structure of $Er_3Cu_4Si_4$ by high-resolution neutron powder diffraction down to 0.34 K. The magnetic ordering temperatures of the Er(2d) and Er(4e) sublattices are 14 K and 3.3 K, respectively. The Er(2d) order is commensurate down to 0.34 K, with a propagation vector [0 $\frac{1}{2}$ 0] and a moment of 8.7(2) μ_B at 0.34 K. The Er(4e) order is initially short-range and incommensurate, with a propagation vector [0 0.876(5) 0] and a refined moment of only 4.4(2) μ_B at 1.5 K. Below about 1.4 K, the Er(4e) order starts to lock-in to a commensurate cell described by the propagation vector [$\frac{1}{3}$ $\frac{1}{2}$ $\frac{1}{2}$] with the moments aligned in the crystal bc-plane, canted about 4° away from the b-axis. The lock-in is complete by 0.8 K and the Er(4e) moment is 8.8(2) μ_B at 0.34 K.

1. Introduction

The orthorhombic $R_3Cu_4X_4$ (X = Si, Ge, Sn) compounds show a complex variety of magnetic ordering behaviour. The R atoms occupy two crystallographically distinct sites in these compounds (2d and 4e), and the moments observed at the two R sites are generally quite different from each other. Often, the refined R moment is greatly reduced from the corresponding R^{3+} free-ion value. Furthermore, the ordering temperatures of the two R sites are usually different, as are the ordering directions.

Wawrzyńska *et al.* [1] carried out neutron powder diffraction on $Er_3Cu_4Si_4$ down to 1.5 K and they reported that the magnetic ordering temperatures for the Er(2d) and Er(4e) sites are 14 K and 3.3 K, respectively. At 10 K, the refined Er(2d) moment was 8.6(1) μ_B, ordered along the crystal c-axis, with a propagation vector [0 $\sim\frac{1}{2}$ 0]. At 1.5 K, the Er(2d) order is virtually unchanged, with a refined Er(2d) moment of 9.5(1) μ_B, which is actually larger than the free-ion Er^{3+} moment of 9 μ_B. Curiously, the refined magnetic moment at the Er(4e) site at 1.5 K was only 4.4(2) μ_B, about one half of the free-ion value, lying in the crystal ac-plane, with a propagation vector [0 0.903(2) 0].

At the same time as the Wawrzyńska *et al.* [1] study, we published a study of the $R_3Cu_4X_4$ (X = Si, Ge, Sn) compounds [2] where we presented the results of our ^{166}Er and ^{119}Sn Mössbauer spectroscopy work, along with neutron powder diffraction on the silicide. ^{166}Er Mössbauer spectroscopy showed that at 2 K, the Er(2d) moment in $Er_3Cu_4Si_4$ is 8.5(1) μ_B and the Er(4e) moment is 7.1(1) μ_B. However, our neutron diffraction confirmed the findings of Wawrzyńska *et* *al.* [1] that the refined Er(4e) moment at 1.5 K is less than half the free-ion value. The apparent conflict in the Er(4e) measured moments reflects the *local* versus *extended* natures of the two measurement techniques. We showed that at 2.4 K, the Er(4e) order is incomplete and quite short-range, and we estimated the correlation length to be about 10 Å from the width of the broad feature in the neutron diffraction patterns.

In this paper we report neutron powder diffraction measurements on $Er_3Cu_4Si_4$ at temperatures down to 0.34 K in order to follow the ordering behaviour and the temperature dependence of the ordered moments on the two Er sites in detail. In particular, our aim was to determine if the Er(4e) moment eventually forms an extended magnetic structure with a long enough correlation for neutron diffraction to yield a free-ion moment for the Er(4e) sublattice, consistent with our ^{166}Er Mössbauer work [2].

2. Experimental Methods

The $Er_3Cu_4Si_4$ sample was prepared in a tri-arc furnace with a base pressure of less than 6×10^{-7} mbar. Stoichiometric amounts of the pure elements (Er (99.9%), Cu (99.99%), Si (99.999%)) were melted several times under pure (less than 1 ppm impurity) argon to ensure homogeneity. The resulting ingot was annealed under vacuum at 800°C for two weeks and water-quenched. Powder x-ray diffraction measurements were made at room temperature using Cu Kα radiation. Analysis confirms that the sample was primarily composed of the orthorhombic $Er_3Cu_4Si_4$ phase, ($Gd_3Cu_4Ge_4$-type structure [3], with the *Immm* space group #71). The sample also contained about 3 wt.% ErCuSi (hexagonal $P6_3/mmc$) impurity. The $Er_3Cu_4Si_4$ structure has two Er sites (2d and 4e), one Cu site (8n) and two Si sites (4f and 4h). The refined lattice parameters of $Er_3Cu_4Si_4$ at RT are a = 13.5597(4) Å, b = 6.4977(2) Å and c = 4.0890(1) Å.

Neutron powder diffraction experiments were carried out on the DUALSPEC C2 high-resolution diffractometer at the NRU reactor, Chalk River Laboratories. The neutron wavelength was 2.37164(14) Å. Diffraction patterns were obtained over the temperature range 0.34–295 K and all patterns were analysed using the Rietveld method and the FULLPROF/WinPLOTR program [4] [5]. For the neutron diffraction experiments, the sample was mixed with an approximately equal volume of pure (99.99 %) copper powder and hydraulically pressed into an OFHC copper sample holder in order to ensure proper thermalisation of the powder sample at the very low temperatures used here [6]. From 295 K to 4 K, the neutron diffraction data were collected with the sample loaded into a vanadium sample can in a Janis closed cycle fridge using Helium exchange gas. The lower temperature data from 20 K to 0.34 K were collected using an Oxford Heliox insert working with a standard Helium cryostat and a copper can [6].

3. Results

In figure 1 we show a comparison of the neutron powder diffraction patterns obtained on $Er_3Cu_4Si_4$ at 0.34 K, 1.42 K, 2.37 K, 6.67 K and 19.5 K. In figure 1 we also show an expanded-range comparison. At 19.5 K, the scattering is purely nuclear and the only peaks seen in the range $7° \leq 2\theta \leq 44°$ are the (200) at $2\theta = 20.1°$ and the (011) at $2\theta = 40.1°$.

The ordering of the Er(2d) sublattice is clear from the prominent $(0 \pm\frac{1}{2}\ 0)$ and $(1 \pm\frac{1}{2}\ 0)$ peaks, at $2\theta = 10.5°$ and 14.5°, respectively, and marked 'd' in the figure. There is also a clear magnetic peak from the Er(2d) sublattice at $2\theta = 22.7°$ the $(2 \pm\frac{1}{2}\ 0)$, also marked 'd' in the figure. The Er(4e) order sets in around 3 K but is superimposed on a broad background, reflecting the short-range ordering of the Er(4e) sublattice [2]. As the temperature is lowered, the Er(4e) long-range order is established and the broad background gives way to a set of peaks, two of which are marked 'e' in figure 1.

In figure 2 we show the temperature dependences of the integrated intensities of four of the Er(4e) magnetic peaks in the diffraction patterns of $Er_3Cu_4Si_4$. At about 1.4 K the magnetic

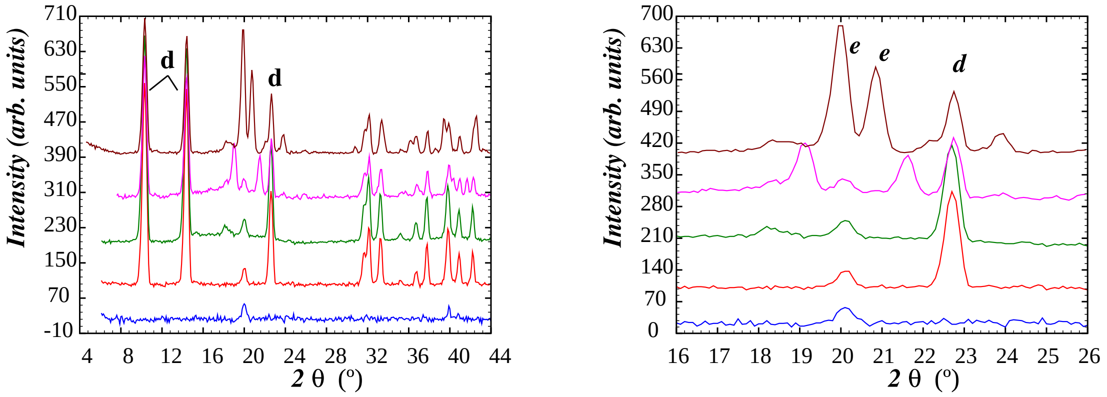

Figure 1. Comparison of the neutron powder diffraction patterns of $Er_3Cu_4Si_4$. From top to bottom, the temperatures are 0.34 K, 1.42 K, 2.37 K, 6.67 K and 19.5 K.

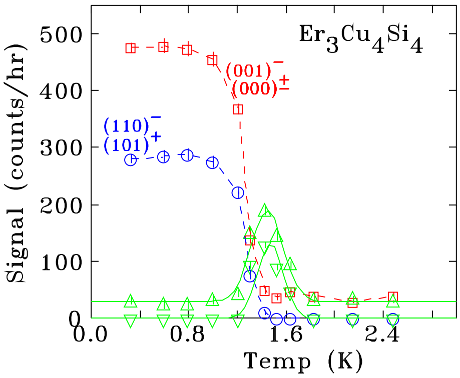

Figure 2. Temperature dependences of selected Er(4e) magnetic peaks in $Er_3Cu_4Si_4$.

order of the Er(4e) sublattice begins to change from the incommensurate, short-range phase towards a commensurate, long-range phase. The change is complete by 0.8 K.

Our refinement of the 0.34 K pattern is shown in figure 3. The standard refinement factors (%) are R(Bragg)=6.3, R(F)=3.9, R(mag-2d)=12.1 and R(mag-4e)=13.8. We find that that the Er(2d) order remains unchanged from that found at higher temperatures. The Er(2d) propagation vector ($\mathbf{q}_d$) is $[0\ \frac{1}{2}\ 0]$ with a refined Er(2d) moment of 8.7(1) μ_B. The Er(4e) order at 0.34 K has locked-in to a commensurate structure which is described by the propagation vector ($\mathbf{q}_e$) $[\frac{1}{3}\ \frac{1}{2}\ \frac{1}{2}]$ with the Er(4e) moments aligned in the crystal bc-plane, canted about 4° away from the b-axis. The Er(4e) moment at 0.34 K is 8.8(2) μ_B, i.e. the free-ion value.

The only question remaining now is whether the modulation of the Er(4e) order is square or sinusoidal. Our ^{166}Er Mössbauer work [2] strongly suggested that the Er(4e) order is a square-wave since we found no evidence of a distribution of ^{166}Er hyperfine field (and hence Er^{3+} moment). In figure 4 we show a small region of the fit to the 0.34 K diffraction pattern with the third-harmonic of the Er(4e) propagation vector included. For comparison, we show the same region without the third-harmonic. The effect of the Er(4e) third-harmonic is evident as a pronounced shoulder at $2\theta = 22.2°$ on the low-angle side of the (200)± q_d magnetic peak at $2\theta = 22.7°$. Thus, the Er(4e) order is square-wave which is fully consistent with our Mössbauer work.

In conclusion, the magnetic structures of the Er(2d) and Er(4e) sublattices in $Er_3Cu_4Si_4$ are

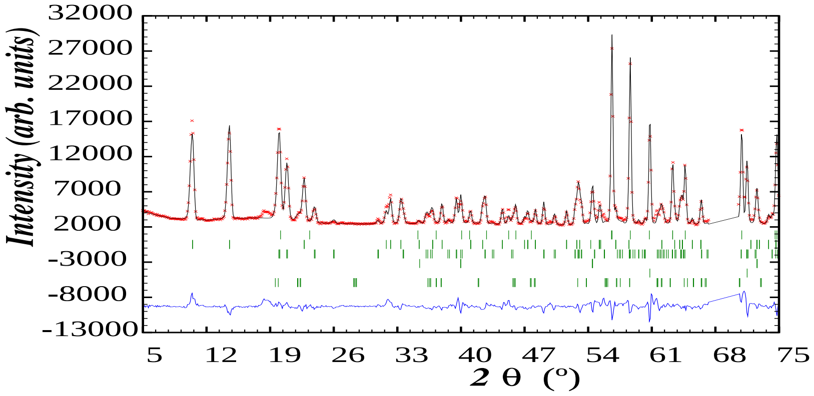

Figure 3. Neutron powder diffraction pattern at 0.34 K of $Er_3Cu_4Si_4$. A strong peak from the copper used in the sample mounting has been removed ($2\theta \sim 69°$).

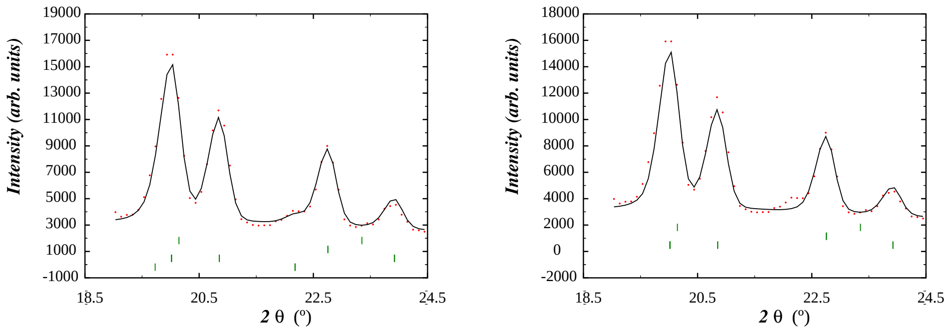

Figure 4. Section of the refined neutron powder diffraction pattern at 0.34 K of $Er_3Cu_4Si_4$ with and without the third-harmonic of the Er(4e) propagation vector included (Left and Right, respectively).

both commensurate (doubled and tripled, respectively) and long-range at 0.34 K, with both Er^{3+} magnetic moments attaining the free-ion value of 9 μ_B.

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