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The incommensurate magnetic structure of $Er_3Cu_4Ge_4$ below 1 K

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Abstract. The magnetic structure of $Er_3Cu_4Ge_4$ was previously studied down to 1.5 K by Wawrzyńska *et al.* who found that the Er(2d) sublattice orders at 8 K in a commensurate, doubled structure ($\mathbf{k_d} = [0\ \frac{1}{2}\ 0]$) with an Er moment close to the free-ion value of 9 μ_B. By contrast, the Er(4e) sublattice ordered at 3.5 K in an incommensurate structure ($\mathbf{k_e} = [0\ 0.883(2)\ 0]$) with a greatly reduced moment (about one-third of the free-ion value). We have extended this study by high-resolution neutron powder diffraction down to 0.34 K in an effort to establish if the Er(4e) sublattice eventually locks-in and attains its free-ion moment (in keeping with our ^{166}Er Mössbauer work). We observed a change in the Er(4e) order, beginning at 1.4 K, leading to a magnetic structure at 0.34 K which has almost locked-in but with ($\mathbf{k_e} = [0.1\ \frac{2}{3}\ 0]$) and a still-reduced Er moment.

1. Introduction

The orthorhombic $R_3Cu_4X_4$ (X = Si, Ge, Sn) compounds exhibit a rich variety of magnetic ordering behaviour which depends on both the rare-earth (R) and metalloid (X) present. The R atoms occupy two crystallographic sites in the 3:4:4 structure (2d and 4e), and the magnetic moments observed at the two R sites are generally quite different from each other. In some cases, the refined R moment is greatly reduced from the corresponding R^{3+} free-ion value. Furthermore, the magnetic ordering temperatures and directions at the two R sites are often different.

Wawrzyńska *et al.* [1] carried out neutron powder diffraction on $Er_3Cu_4Ge_4$ down to 1.5 K and reported that the Er(2d) site orders at 8 K whilst the Er(4e) site orders at 3.5 K. At 1.5 K, the refined Er(2d) moment was 8.9(2) μ_B, ordered along the crystal c-axis, with a propagation vector $[0\ \sim\frac{1}{2}\ 0]$. This is the free-ion Er^{3+} moment of 9 μ_B. The Er(4e) order was reported to be incommensurate, with the Er^{3+} moments ordered along the a-axis, described by a propagation vector [0 0.883(2) 0]. Curiously, the refined Er(4e) at 1.5 K was only 3.2(2) μ_B, about one-third of the free-ion value.

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] in which we presented the results of our ^{166}Er Mössbauer spectroscopy work. ^{166}Er Mössbauer spectroscopy showed that at 2 K the Er(2d) moment in $Er_3Cu_4Ge_4$ is 8.5(1) μ_B and the Er(4e) moment is 7.1(1) μ_B, more than twice the value deduced

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from neutron diffraction data. However, our own neutron diffraction experiments confirmed the findings of Wawrzyńska *et al.* [1] that the refined Er(4e) moment at 1.5 K is only about one-third of the free-ion value. The apparent dichotomy in the measured magnetic moments at the Er(4e) site is a consequence of 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 extend our neutron powder diffraction measurements on $Er_3Cu_4Ge_4$ down to 0.34 K in order to follow the ordering behaviour and the temperature dependence of the magnetic 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 $Er_3Cu_4Ge_4$ sample was prepared in a tri-arc furnace with a base pressure of less than 6 $\times 10^{-7}$ mbar. Stoichiometric amounts of the pure elements (Er (99.9%), Cu (99.99%), Ge (99.999%) were melted several times under pure (less than 1 ppm impurity) argon to ensure homogeneity. The resulting ingot was annealed *in vacuo* 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 $Er_3Cu_4Ge_4$ phase, ($Gd_3Cu_4Ge_4$-type structure [3], with the *Immm* space group #71). The sample also contained about 3 wt.% ErCuGe (hexagonal $P6_3/mmc$) impurity. The $Er_3Cu_4Ge_4$ structure has two Er sites (2d and 4e), one Cu site (8n) and two Ge sites (4f and 4h). The refined lattice parameters of $Er_3Cu_4Ge_4$ at RT are a = 13.8356(4) Å, b = 6.6295(2) Å and c = 4.1650(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 $Er_3Cu_4Ge_4$ at 0.34 K, 1.8 K and 5.4 K. The only magnetic contribution to the 5.4 K pattern is from the order of the Er(2d) moments which is clearly shown by the appearance of the prominent $(0 \pm\frac{1}{2}\ 0)$ and $(1 \pm\frac{1}{2}\ 0)$ peaks, at $2\theta = 10.3°$ and 14.3°, respectively. The refined Er(2d) moment at 5.4 K is 7.9(1) μ_B.

The Er(4e) order sets in around 3.5 K but is superimposed on a broad background which we showed in our previous paper [2] reflects the short-range ordering. In figure 2 we show the temperature dependences of the integrated intensities of three of the Er(4e) magnetic peaks in the diffraction patterns of $Er_3Cu_4Ge_4$. The sudden change in magnetic order of the Er(4e) sublattice around 1.4 K is striking.

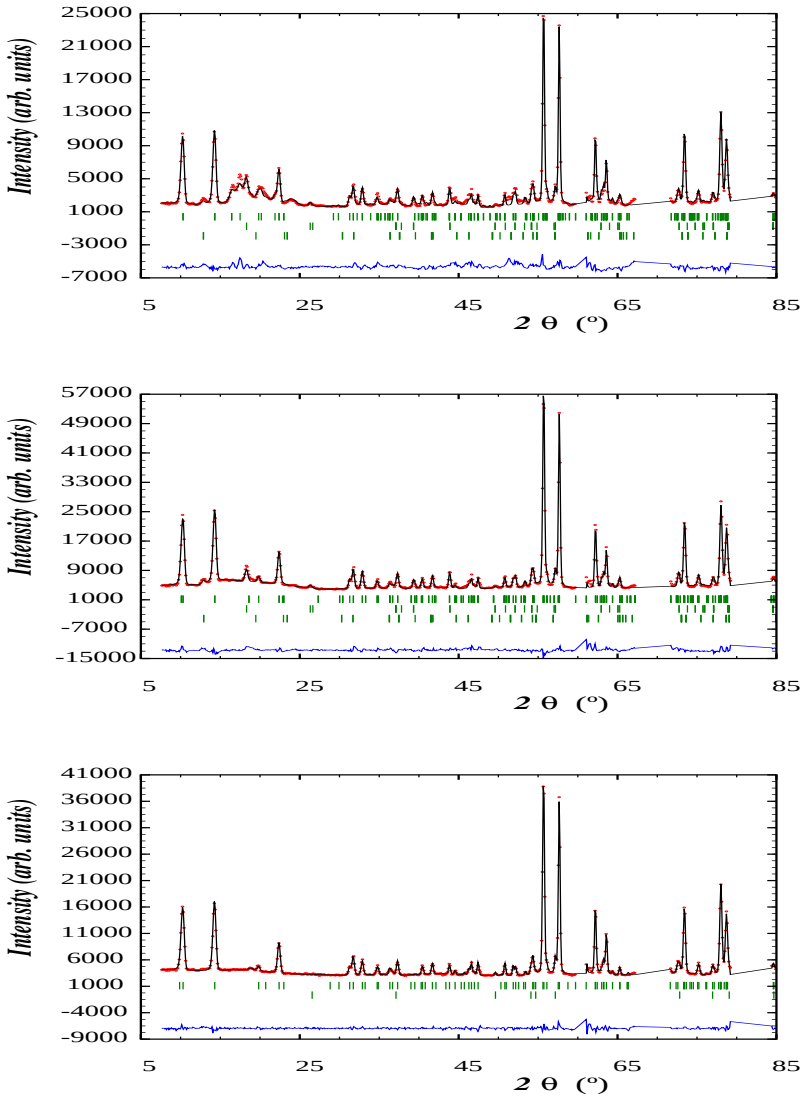


Figure 1. Comparison of the neutron powder diffraction patterns of $Er_3Cu_4Ge_4$ obtained at 0.34 K (top), 1.8 K (middle) and 5.4 K (bottom). Two sections ($2\theta \sim 69°$; $\sim 82°$) containing the strong peaks from the copper have been removed.

Our refinement of the 0.34 K pattern is shown in figure 1. The standard refinement factors are R(Bragg)=7.0 and R(F)=7.9. We find that the Er(2d) order remains unchanged from that found at higher temperatures. The Er(2d) propagation vector 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 almost locked-in, with a propagation vector $[0.1\ \frac{2}{3}\ 0]$ and a still-reduced Er moment of only 3.5(2) μ_B. This behaviour is different from that we have observed in the isostructural silicide $Er_3Cu_4Si_4$ where we recently found that the Er(4e) has locked-in by 0.34 K [7]. This difference in magnetic behaviour is most likely related to the increased Er-Er separation in the germanide and the ensuing reduction in the strength of the indirect exchange between Er^{3+} spins.

One remaining question 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). The effect

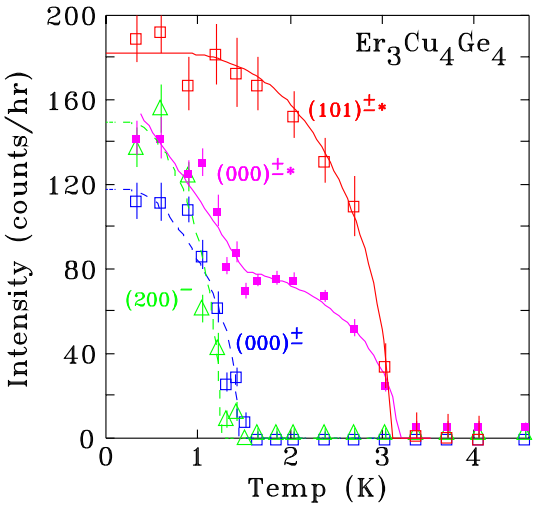


Figure 2. Temperature dependences of selected Er(4e) magnetic peaks in $Er_3Cu_4Ge_4$. The asterisk after some indices refers to the higher-T propagation vector [0 0.883(2) 0]

of the third-harmonic of the Er(4e) propagation vector is difficult to observe in these patterns but we have some evidence, albeit tentative, for its appearance. This would confirm our claim based on our ^{166}Er Mössbauer work that the (4e) order is square-wave.

In conclusion, the magnetic structure of the Er(2d) sublattice in $Er_3Cu_4Ge_4$ is commensurate and doubled along the crystal b-axis. The Er(2d) moments attain the free-ion value and are ordered along the crystal c-axis. By contrast, the magnetic structure of the Er(4e) sublattice is short-range and incommensurate down to 0.34 K, with the refined Er(4e) moments still significantly reduced from the free-ion value of 9 μ_B.

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