Magnetic structure of Er$_5$Si$_4$

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As part of our ongoing study of giant magnetocaloric compounds, we have determined the magnetic structure of Er$_5$Si$_4$ by high-resolution neutron powder diffraction, ac-susceptibility, and $^{166}$Er Mössbauer spectroscopy. The crystal space group is orthorhombic $Pnma$ and the magnetic space group is $Pnm'a$. The magnetic ordering temperature is 32(3) K and the magnetic structure is characterized by ferromagnetic order of the three Er sites ($4c$, $8d_1$, and $8d_2$) along [010], together with antiferromagnetic order of the $8d$ sites in the perpendicular (010) plane. The Er-4$c$ magnetic mode is $F_2$ and the $8d$ magnetic mode is $C_4^x F_2^z G_2^z$. At 3.6 K, the Er magnetic moments are 7.4(1), 6.9(2), and 7.6(2) $\mu_B$ at the $4c$, $8d_1$, and $8d_2$ sites, respectively, and the corresponding $^{166}$Er hyperfine magnetic fields, at 5 K, are 715(5), 627(2), and 736(3) T. The neutron diffraction data show tentative evidence of a reorientation of the magnetic structure, most likely involving the development of an antiferromagnetic component at the 4$c$ site, between 14 and 4 K. © 2004 American Institute of Physics. [DOI: 10.1063/1.1667810]

INTRODUCTION

The R$_5$Si$_4$ and R$_5$Ge$_4$ compounds (R = rare earth) were first studied by Smith et al. and Holtzberg et al. about 35 years ago and are enjoying renewed interest in the magnetism community due to the observation of a giant magnetocaloric effect in R$_5$(Si,Ge)$_4$ compounds, being particularly large for R = Gd. Recently, the magnetic structure of Nd$_5$Si$_4$ was determined by Cadogan et al. and magnetic ordering in the Tb$_5$(Si,Ge)$_4$ system was studied by Ritter et al. both studies using neutron diffraction.

In this paper, we present the determination of the magnetic structure of Er$_5$Si$_4$ using high-resolution neutron powder diffraction, complemented by ac-susceptibility and $^{166}$Er Mössbauer spectroscopy.

EXPERIMENTAL METHODS

The Er$_5$Si$_4$ sample was prepared in a tri-arc furnace with a base pressure of $6 \times 10^{-7}$ mbar by arc-melting stoichiometric amounts of Er (99.99%) and Si (99.99%) under Ti-gettered argon, allowing a 2 wt % excess of Er to compensate for the inevitable boil-off during melting. The arc-melted ingot was turned and remelted several times. Initial sample characterization employed x-ray powder diffraction with Cu K$_\alpha$ radiation on an automated Nicolet-Stoe diffractometer. Ac susceptibility measurements were made on a Quantum Design physical property measurement system using a driving field of 398 A/m (rms) and a frequency of 137 Hz.

Neutron powder diffraction experiments were carried out on the DUALSPEC C2 high-resolution diffractometer at the NRU reactor, Chalk River Laboratories, operated by Atomic Energy Canada Ltd. The neutron wavelength was 2.3685(1) Å. Diffraction patterns were obtained at 3.6, 14, and 295 K, and all patterns were analyzed using the Rietveld method and the FULLPROF and GSAS programs.

The source for the $^{166}$Er Mössbauer spectroscopy was made by neutron irradiating HHo$_3$Y$_{0.6}$H$_2$ at the SLOWPOKE Reactor Laboratory, Ecole Polytechnique Montréal, to produce ~1 GBq initial activity of the 27 h $^{166}$Ho parent isotope. The $^{166}$Er spectrum was obtained at 5 K in a helium-flow cryostat. The source was heated to ~5 K to avoid line broadening and the 80.6 keV $^{166}$Er gamma rays were detected using a high-purity germanium detector. The spectrometer was calibrated using the 819.4 T magnetic splitting in ErFe$_2$ at 1.4 K (for a discussion, see Ref. 8). The source linewidth on the ErFe$_2$ calibration was 2.49(4) mm/s and the spectrum was fitted to the full nuclear hyperfine Hamiltonian using a nonlinear least squares routine.

RESULTS AND DISCUSSION

Despite several attempts, it proved impossible to prepare single-phase Er$_5$Si$_4$. The sample of Er$_5$Si$_4$ contained ~5 wt % each of ErSi and Er$_5$Si$_3$. The impurity levels were determined from the refinements of the neutron diffraction patterns. Er$_5$Si$_4$ is orthorhombic, with the Sm$_5$Ge$_4$ prototype structure ($oP36$ in the Pearson classification). The space group is $Pnma$ (#62), the Er ions occupy three sites ($4c$, $8d_1$, and $8d_2$), and Si occupies three sites ($4c_1$, $4c_2$, and $8d_3$). The lattice parameters of Er$_5$Si$_4$, determined by neu-
tron diffraction at 14 K, are \( a = 7.2968(4) \), \( b = 14.3890(9) \), and \( c = 7.6051(4) \) Å. The refined atomic position parameters are given in Table I.

In Fig. 1, we show the in-phase component of the ac-susceptibility of Er\(_5\)Si\(_4\). The peak in \( \chi_{ac}(T) \), which marks the magnetic ordering of the Er sublattice, occurs at 32(3) K.

In Fig. 2, we show the neutron diffraction pattern of Er\(_5\)Si\(_4\) obtained at 3.6 K. In the fitting procedure we included the contributions from the magnetic order of the Er\(_3\)Si\(_3\) and ErSi impurities. Briefly, Er\(_3\)Si\(_3\) is a commensurate antiferromagnet below 11.5 K, which changes to a commensurate, cell-doubled antiferromagnet below 5.75 K.\(^{10}\)

The magnetic ordering of the Er sublattices in Er\(_5\)Si\(_4\) is most clearly illustrated by the appearance of a strong, purely magnetic, (010) peak at \( 2\theta \approx 10^\circ \), which completely dominates the entire diffraction pattern.

To determine the magnetic structures of the Er sublattices in Er\(_5\)Si\(_4\) we carried out a group theory analysis of the magnetic space groups and magnetic ordering modes derived from the \( Pnma \) space group. There are eight magnetic space groups associated with the \( Pnma \) crystal space group, and we have presented a detailed analysis of the magnetic space groups derived from \( Pnma \) in our study of Nd\(_4\)Ge\(_4\), which has the same crystal structure as Er\(_5\)Si\(_4\). The reader is referred to our paper\(^4\) on Nd\(_4\)Si\(_4\) and Nd\(_4\)Ge\(_4\) for further details on the analysis and the notation employed here.

The point group of the Er 4c site is \( m_y \) and the admissible magnetic point groups of the Er 4c sites are therefore

- \( m_y \) with the Er magnetic moment perpendicular to the mirror (010) plane; that is, along the \( b \)-axis (from the \( \Gamma_1^- \), \( \Gamma_2^+ \), \( \Gamma_3^- \) or \( \Gamma_4^+ \) representations)
- \( m_y' \) with the Er magnetic moment lying in the mirror (010) plane (from the \( \Gamma_1^+ \), \( \Gamma_4^- \), \( \Gamma_1^- \) or \( \Gamma_2^+ \) representations).

The point group of the Er 8d sites is \( I \), which leads to a completely arbitrary magnetic moment direction; that is, no symmetry restrictions.

The \( \Gamma_2^+ \) representation, corresponding to the magnetic space group \( Pn'\)ma', provides the best fit to the 3.6 K neutron diffraction pattern of Er\(_5\)Si\(_4\). The refinement \( R \)-factors (%) are \( R(\text{Bragg}) = 5.7 \) and \( R(F) = 4.8 \). Thus, the magnetic structure of Er\(_5\)Si\(_4\) comprises Er ferromagnetic (FM) order along [010] and Er antiferromagnetic (AM) order in the perpendicular (010) plane. Using standard notation, this order corresponds to magnetic modes of \( F_2 \) and \( C_4^+F_1^+G_2^- \) at the Er 4c and 8d sites, respectively. The \( \Gamma_1^+ \) magnetic moments derived from our neutron diffraction data at 3.6 K are shown in Table I.

The magnetization of Er\(_5\)Si\(_4\) was measured at 4.2 K by Holtzberg et al.\(^2\) Their value of 180 J/T/kg in a field of 2.5 T yields a FM component (per formula unit \( f.u. \)) of the Er magnetization of 6.1(5) \( \mu_B/\text{f.u.} \), ignoring any contribution from field-induced canting of the Er 8d AF order. This FM component compares well with our refined value of 5.7(5) \( \mu_B/\text{f.u.} \).

In our 3.6 K neutron diffraction pattern, we observe a very weak peak at \( 2\theta \approx 18^\circ \), which is not fitted by the magnetic space group \( Pn'\)ma' and is absent in the 14 K pattern. This peak indexes as the (001) peak of the Er\(_5\)Si\(_4\) structure which suggests that the magnetic structure of Er\(_5\)Si\(_4\) might
undergo a slight change at low temperature. Ritter et al.5 observed a change in the magnetic structure of Tb5Si4 at low temperature which they ascribed to the development of a FM coupling along the c-axis, and they described this low-temperature structure as a mixing of the magnetic space groups Pnm’a’ and Pn’m’a. In Er5Si4, the appearance of the very weak (001) magnetic peak cannot be due to FM order, and one possible explanation is a slight canting of the Er4c magnetic order, resulting in dominant ferromagnetism along the b-axis [010] with a small AF component in the a–c plane (010). The two possible AF modes are A4cCZ or G4FZ, arising from the magnetic space groups Pn’m’a’ and Pn’m’a, respectively. Further investigations of this change in magnetic structure are planned.

We have used 166Er Mössbauer spectroscopy as an independent, and, more importantly, a local determination of the Er magnetic moments, as in our recent study of ErFe6Sn6.8 In Fig. 3, we show the 166Er Mössbauer spectrum of Er5Si4, obtained at 5 K. The excited and ground state nuclear spins are 2 and 0, respectively, and the spectrum comprises three overlapping magnetically split pentets. Here, we will concentrate on the hyperfine magnetic fields since these provide the local measurement of the Er3+ magnetic moments.

The hyperfine magnetic fields at the 166Er nuclei at the three Er sites in Er5Si4 at 5 K are 715(5) T (Er4c), 627(2) T (Er8d), and 736(3) T (Er8d). These fields may be converted into the corresponding Er3+ moment using the conversion factor 87.2±1.2 T/μB, which we have shown works well in Er5Ge4.11 Thus, the Er3+ moments at 5 K in Er5Si4 are 8.1(1) μB (Er4c), 7.2(1) μB (Er8c) and 8.5(1) μB (Er8d). These moments are slightly larger than the values deduced from our neutron diffraction data. We refer the reader to our paper8 on ErFe6Sn6 for a discussion of this common observation.

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