HTML ABSTRACT + LINKS

Magnetic structure of Er_5Si_4

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As part of our ongoing study of giant magnetocaloric compounds, we have determined the magnetic structure of Er_5Si_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 $Pn'ma'$. 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 $4c$ magnetic mode is F_Y and the $8d$ magnetic mode is $C_X^+F_Y^+G_Z^+$. At 3.6 K, the Er magnetic moments are 7.4(1), 6.9(2), and 7.6(2) μ_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 $4c$ site, between 14 and 4 K. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1667810]

INTRODUCTION

The R_5Si_4 and R_5Ge_4 compounds (R=rare earth) were first studied by Smith *et al.*[1] and Holtzberg *et al.*[2] 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.[3] Recently, the magnetic structure of Nd_5Si_4 was determined by Cadogan *et al.*[4] and magnetic ordering in the $Tb_5(Si,Ge)_4$ system was studied by Ritter *et al.*,[5] both studies using neutron diffraction.

In this paper, we present the determination of the magnetic structure of Er_5Si_4 using high-resolution neutron powder diffraction, complemented by ac-susceptibility and ^{166}Er Mössbauer spectroscopy.

EXPERIMENTAL METHODS

The Er_5Si_4 sample was prepared in a tri-arc furnace with a base pressure of 6×10^{-7} mbar by arc-melting stoichiometric amounts of Er (99.9%) 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_α 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.[6,7]

The source for the ^{166}Er Mössbauer spectroscopy was made by neutron irradiating $Ho_{0.4}Y_{0.6}H_2$ 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_5Si_4. The sample of Er_5Si_4 contained ~5 wt % each of ErSi and Er_5Si_3. The impurity levels were determined from the refinements of the neutron diffraction patterns. Er_5Si_4 is orthorhombic, with the Sm_5Ge_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_5Si_4, determined by neu-

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TABLE I. Atomic positions and Er magnetic moments in Er_5Si_4.

Atom	Site	x $\mu_x(\mu_B)$	y $\mu_y(\mu_B)$	z $\mu_z(\mu_B)$	$\mu_{net}(\mu_B)$
Er	4*c*	0.3473(5)	$\frac{1}{4}$	−0.0068(3)	
	moment→	0.	7.4(1)	0.	7.4(1)
Er	8*d*	0.1777(9)	0.1232(3)	0.3239(8)	
	moment→	2.8(1)	4.2(1)	4.7(1)	6.9(2)
Er	8*d*	0.0192(3)	0.0966(9)	0.8180(1)	
	moment→	3.1(1)	6.4(1)	2.6(1)	7.6(2)
Si	4*c*	0.9774(6)	$\frac{1}{4}$	0.1046(6)	
Si	4*c*	0.2252(6)	$\frac{1}{4}$	0.6339(6)	
Si	8*d*	0.1567(23)	0.9596(8)	0.5276(6)	

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_5Si_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_5Si_4 obtained at 3.6 K. In the fitting procedure we included the contributions from the magnetic order of the Er_5Si_3 and ErSi impurities. Briefly, Er_5Si_3 is a commensurate antiferromagnet below 18(2) K[9] and ErSi is a sine-modulated 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_5Si_4 is most clearly illustrated by the appearance of a strong, purely magnetic, (010) peak at $2\theta\sim10°$, which completely dominates the entire diffraction pattern.

To determine the magnetic structures of the Er sublattices in Er_5Si_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_4Ge_4, which

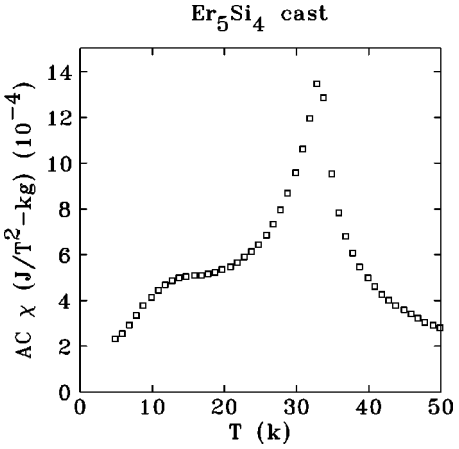

FIG. 1. In-phase component of the ac-susceptibility of Er_5Si_4, measured at 137 Hz and 398 A/m (rms).

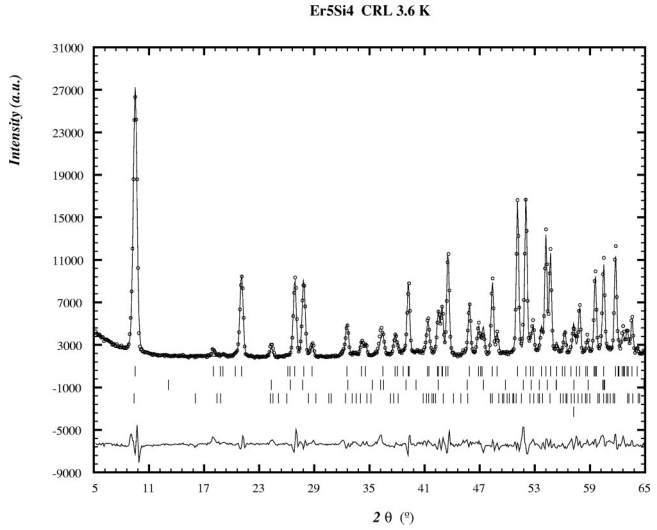

FIG. 2. Neutron powder diffraction pattern of Er_5Si_4, obtained 3.6 K. The Bragg markers represent (top to bottom) Er_5Si_4, ErSi, and Er_5Si_3.

has the same crystal structure as Er_5Si_4. The reader is referred to our paper[4] on Nd_5Si_4 and Nd_5Ge_4 for further details on the analysis and the notation employed here.

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

- m_y with the Er magnetic moment perpendicular to the mirror (010) plane; that is, along the *b*-axis (from the Γ_1^+, Γ_2^+, Γ_3^- or Γ_4^- representations) and
- m_y' with the Er magnetic moment lying in the mirror (010) plane (from the Γ_3^+, Γ_4^+, Γ_1^- or Γ_2^- representations).

The point group of the Er 8*d* sites is *1*, which leads to a completely arbitrary magnetic moment direction; that is, no symmetry restrictions.

The Γ_2^+ representation, corresponding to the magnetic space group $Pn'ma'$, provides the best fit to the 3.6 K neutron diffraction pattern of Er_5Si_4. The refinement *R*-factors (%) are $R(\text{Bragg})=5.7$ and $R(\text{F})=4.8$. Thus, the magnetic structure of Er_5Si_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_Y and $C_X^+F_Y^+G_Z^+$ at the Er 4*c* and 8*d* sites, respectively. The Er^{3+} magnetic moments derived from our neutron diffraction data at 3.6 K are shown in Table I.

The magnetization of Er_5Si_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) $\mu_B/f.u.$, ignoring any contribution from field-induced canting of the Er 8*d* AF order. This FM component compares well with our refined value of 5.7(5) $\mu_B/f.u.$

In our 3.6 K neutron diffraction pattern, we observe a very weak peak at $2\theta\sim18°$, 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_5Si_4 structure which suggests that the magnetic structure of Er_5Si_4 might

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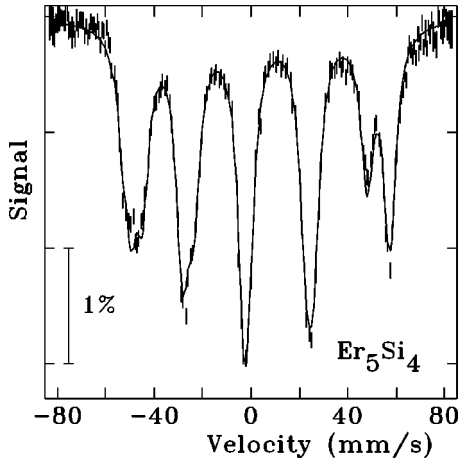

FIG. 3. ^{166}Er Mössbauer spectrum of Er_5Si_4, obtained at 5 K.

undergo a slight change at low temperature. Ritter *et al.*[5] observed a change in the magnetic structure of Tb_5Si_4 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 Er_5Si_4, 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 Er $4c$ 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 A_XC_Z or G_XF_Z, 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 ^{166}Er Mössbauer spectroscopy as an independent, and, more importantly, a local determination of the Er magnetic moments, as in our recent study of $ErFe_6Sn_6$.[8] In Fig. 3, we show the ^{166}Er Mössbauer spectrum of Er_5Si_4, 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 Er^{3+} magnetic moments.

The hyperfine magnetic fields at the ^{166}Er nuclei at the three Er sites in Er_5Si_4 at 5 K are 715(5) T (Er $4c$), 627(2) T (Er $8d$), and 736(3) T (Er $8d$). These fields may be converted into the corresponding Er^{3+} moment using the conversion factor 87.2 ± 1.2 T/μ_B, which we have shown works well in Er_3Ge_4.[11] Thus, the Er^{3+} moments at 5 K in Er_5Si_4 are 8.1(1) μ_B (Er $4c$), 7.2(1) μ_B (Er $8c$) and 8.5(1) μ_B (Er $8d$). These moments are slightly larger than the values deduced from our neutron diffraction data. We refer the reader to our paper[8] on $ErFe_6Sn_6$ for a discussion of this common observation.

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