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The magnetic ordering of the novel compound $ErGe_3$

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Abstract

The crystal structure and magnetic ordering of the novel orthorhombic compound $ErGe_3$ of RGe_3-type structure (*Cmcm*) was studied by neutron powder diffraction and magnetic measurements. $ErGe_3$ orders antiferromagnetically below $T_N = 7$ K with a collinear antiferromagnetic moment arrangement with the magnetic space group $C112_1/m'$ ($P2_1/m'$) (Sh_{11}^{53}). The Er magnetic moments are confined to the (*a,b*) plane making an angle of 15° with the *a* axis. The ordered magnetic moment value at 1.5 K is 8.6 μ_B per Er atom. Field-dependent magnetic measurements at 4.2 K show that $ErGe_3$ is metamagnetic, and transforms to a ferromagnetic state with the same ordered magnetic moment value in fields larger than about 2 T.

Keywords: Rare-earth germanium compounds; Neutron diffraction; Magnetic properties

1. Introduction

The phase diagram of the erbium–germanium system [1] exhibits several compounds on the germanium-rich side (65%–75% germanium content) with unknown structures. The compound $ErGe_{3-x}$, which is the richest in germanium content, has been reported to be isomorphic with the orthorhombic ($C222_1$) modification of $YGe_{3.5}$ [2] and has lattice constants of $a = 0.2077$ nm, $b = 0.399$ nm and $c = 0.388$ nm. However, its crystal structure has not been solved. For the unknown compound $ErGe_2$, two phase transitions have been reported at 907 and 932°C; in addition, the structure of a compound with the composition Er_3Ge_4 has been reported recently [3]. The present investigation deals with the crystal structure and magnetic properties of the compound $ErGe_3$. It is shown that $ErGe_3$ is isomorphic with other RGe_3 (R ≡ Dy, Tb, Ho) compounds reported in Refs. [4] and [5], having structures belonging to the space group *Cmcm* (No. 63). All of these compounds display complex magnetic ordering types (antiphase domain) associated with the presence of several wave vectors. It is shown that the magnetic ordering in $ErGe_3$ is very different from that found for the other isomorphic compounds.

2. Neutron diffraction and magnetic measurements

The polycrystalline sample of composition $ErGe_3$ used for neutron diffraction and magnetic measurements was prepared by the methods given in Refs. [4] and [5]. Magnetic measurements made at high temperatures (50–300 K) show that Curie–Weiss behaviour is followed (see Fig. 1) with $\mu_{eff} = 10.4$ μ_B per Er atom and a Curie–Weiss intercept of $\Theta_P = -3$ K. The

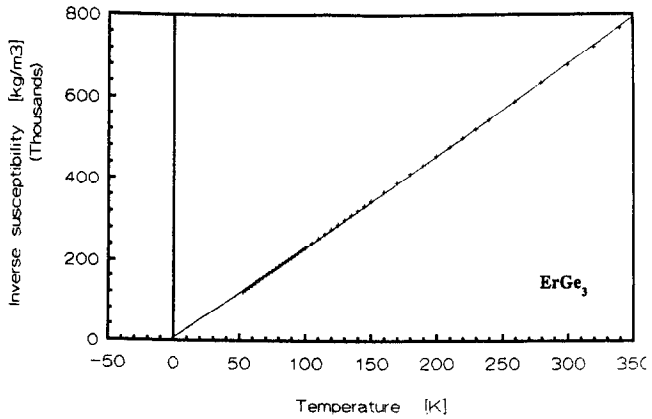

Fig. 1. Reciprocal susceptibility vs. temperature measured in a field of 2 T.

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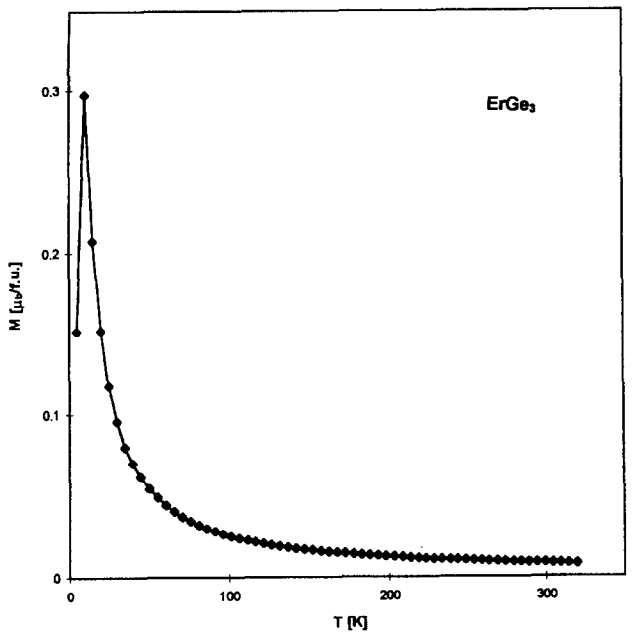

Fig. 2. Temperature dependence of the magnetic moment of $ErGe_3$ in a field of 0.1 T.

temperature dependence of the magnetization, measured in a field of 0.1 T (see Fig. 2), shows that $ErGe_3$ orders antiferromagnetically at $T_N = 7$ K. However, the antiferromagnetic state is not very stable. As can be seen from Fig. 3, the antiferromagnetic state is easily transformed into the ferromagnetic state by a metamagnetic transition. The saturation moment in the ferromagnetic state is 8.4 μ_B per Er atom, which is close to the free ion value of Er^{3+} ($gJ\mu_B = 9\ \mu_B$).

Neutron diffraction experiments were carried out at the facilities of the Orphée reactor (LLB-Saclay). The data between 1.5 and 20 K were collected on the G4.1 diffractometer (800 cell multidetector), $\lambda = 0.2427$ nm. The step increment in 2θ was 0.1°. The data were evaluated by the FULLPROF program [6]. The magnetic form factor for Er^{3+} was obtained from Ref. [7]. All refinements led to reliability factors R_n (nuclear) and R_m (magnetic) with values around 3% and 5% and R_{wp} (profile) of 12%–18%. Due to the presence of impurity phases, the χ^2 values were high in some cases. The 7.5 K neutron pattern shown in Fig. 4 (bottom part) could be indexed with the lattice constants given in Table 1. The low values of the reliability factors confirm the composition and structure proposed previously [4,5]. Next to the nuclear reflections of $ErGe_3$, the pattern comprises one non- overlapping foreign line at $2\theta = 43.6°$ identified as the Ge(111) reflection. Two additional overlapping lines visible in the differ-

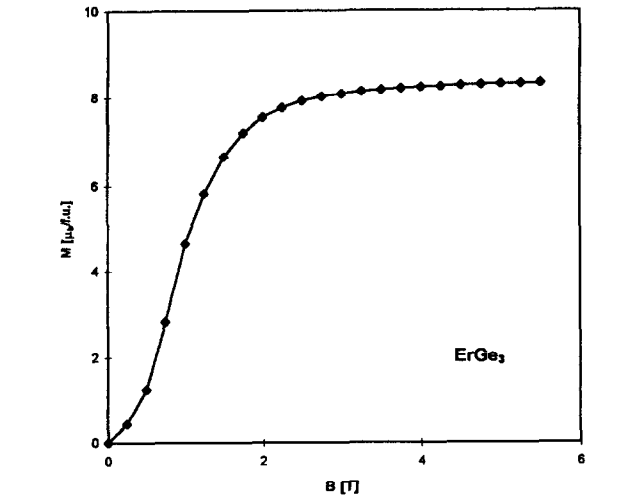

Fig. 3. Field dependence of the magnetic moment of $ErGe_3$ at 4.2 K.

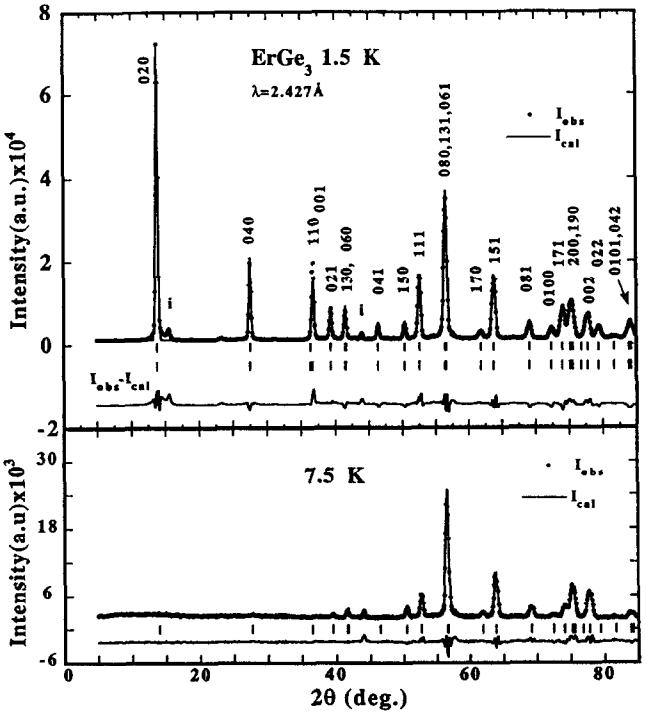

Fig. 4. Observed, calculated and difference neutron diagrams of $ErGe_3$ measured at 1.5 K (top part) and 7.5 K (bottom part).

Table 1
Refined parameters from neutron data at 7.5 K (paramagnetic state) and 1.5 K (magnetically ordered state) of $ErGe_3$. Space group *Cmcm* (No. 63), all atoms at site 4(c)

Atom parameter	7.5 K	1.5 K
y_{Er}: (0, y, 1/4)	0.4154(5)	0.4183(4)
y_{Ge1}: (0, y, 1/4)	0.0411(5)	0.0424(9)
y_{Ge2}: (1/2, y, 1/4)	0.1922(4)	0.1922(8)
y_{Ge3}: (1.2, y, 1/4)	0.3128(5)	0.3126(8)
μ_{xEr} (μ_B), μ_{yEr} (μ_B)	—	8.3(1), 2.3(2)
μ_{TEr} (μ_B), ϕ_a (°)	—	8.6(1), 15(1)
a (nm)	0.39963(11)	0.39968(7)
b (nm)	2.0650(8)	2.0659(4)
c (nm), B_{of} (nm^2)	0.38841(10), 0.002	0.38843(6), 0.002
R_n (%), R_m (%)	6.8, —	3.76, 5.88
R_{wp} (%), R_{exp} (%), χ^2	18.4, 12.34, 2.2	16.0, 1.9, 68

ence diagram in Fig. 4 at $2\theta = 75°$ and 77° could possibly be attributed to the (200) and (002) reflections of the adjacent $ErGe_2$ (high temperature) phase (a = 0.3882 nm, b = 0.353414 nm, c = 0.39837 nm, C lattice) [8] with unknown structure.

The patterns collected in the magnetically ordered state, 1.5 K < T < 7 K, were indexed with the same C cell of the crystal structure ($\boldsymbol{q} = 0$). There are eight magnetic space groups associated with the magnetic C lattice and the wave vector ($\boldsymbol{q} = 0$) [9,10]. Three of these allow ferromagnetic modes. Because of the low symmetry of the 4(c) Wyckoff site, the magnetic moment directions of the Er atoms situated at the intersection of the 2_y axis (at $z = 1/4$) and the mirror planes m_x (at $x = 0$), m_z (at $z = 1/4$) are restricted to uniaxial moment arrangements of the F(++++) or G(+−+−) [11] type unless further symmetry reduction is observed. A uniaxial arrangement along y is invariant under the antimirror operations m'_x, m'_z (see Table 2). The corresponding magnetic space groups are $C2'/m'2/c2'_1/m'$ (Sh_{63}^{464} and $C2/m'2/c2_1/m'$ (Sh_{63}^{465}. From the strong intensity of the (020) magnetic reflection, it is obvious that the orientation of the magnetic moments deviates strongly from the y direction.

The refinement of the magnetic intensities has shown that the Er magnetic moments are oriented 15° off the a axis within the plane (001) as shown in Fig. 5.

Table 2
The magnetic space groups of *Cmcm* associated with the magnetic C lattice ($\boldsymbol{q} = 0$). The magnetic modes F(++++) and G(+−+−) of the 4(c) site. The signs refer to the atoms : (1), (0, y, 1/4); (2), (0, $-y$, 3/4); (3), (1/2, 1/2 + y, 1/4); (4), (1/2, 1/2 − y, 3/4)

Magnetic space group	x	y	z
$Cm'cm$ (Sh_{63}^{459})	—	—	G_z
$Cmc'm$ (Sh_{63}^{460})	—	—	—
$Cmcm'$ (Sh_{63}^{461})	G_x		
*$Cm'c'm$ (Sh_{63}^{462})			F_z
*$Cmc'm'$ (Sh_{63}^{463})	F_x		
*$Cm'cm'$ (Sh_{63}^{464})		F_y	
$Cm'c'm'$ (Sh_{63}^{465})		G_y	
$Cmcm$ (Sh_{63}^{458})	—	—	—

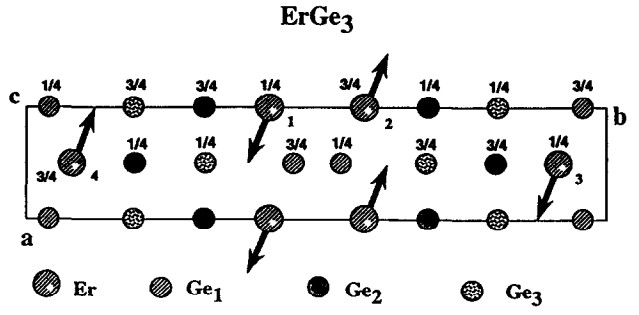

Fig. 5. Schematic representation of the collinear antiferromagnetic ordering of $ErGe_3$.

The Er atoms 1, 3 and 2, 4, related by the C-centring operation, have their magnetic moments parallel, while the atoms 1, 2 and 3, 4, related by the inversion operation, have their moments antiparallel (anti-inversion). This arrangement implies a symmetry reduction to the monoclinic $C112_1/m'$ ($P2_1/m'$) space group. The resulting ordered moment value of 8.6(1) μ_B per Er atom at 1.5 K is in good agreement with the moment value associated with the ferromagnetic configuration (8.4(1) μ_B per Er atom, see Fig. 3). The temperature dependence of the magnetic intensities and of the Er ordered magnetic moment value, shown in Fig. 6, confirms the ordering temperature T_N = 7 K of the magnetic measurements. The refined Er moment values indicate that the planar antiferromagnetic arrangement remains unchanged over the whole magnetically ordered region.

A weak line visible in the 1.5 K pattern close to the (020) reflection probably arises from the magnetic ordering of an impurity phase, e.g. the high temperature phase $ErGe_2$ with unknown structure. As can be seen in Fig. 6 (bottom part), this peak disappears at slightly lower temperatures than the other magnetic

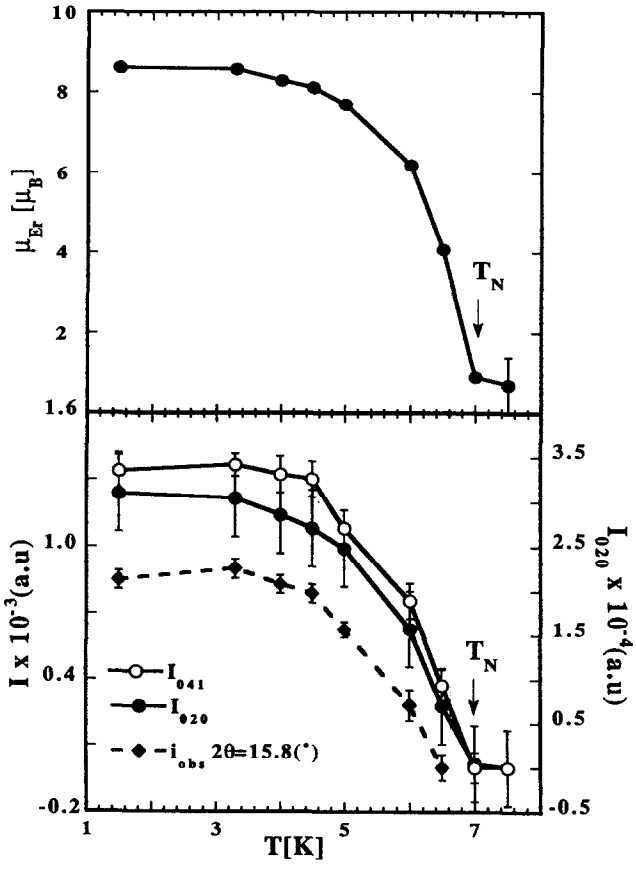

Fig. 6. Temperature dependence of the magnetic intensities (bottom part) of the (020) and (041) reflections of $ErGe_3$ and of the unidentified magnetic reflection i_{obs} at $2\theta = 15.8°$. Also shown is the temperature dependence of the Er magnetic moment (top part).

reflections. Several trials to incorporate this peak into the refinements by considering more complex ordering types with a small modulation of the main structure did not converge.

As usually observed in rare earth intermetallics, $ErGe_3$ is found to have the lowest ordering temperature within the series of isomorphic germanides of the type RGe_3 (R ≡ Tb, Dy, Ho), which order antiferromagnetically at 40 K, 24 K and 10 K respectively. In contrast with the other members, which display complex ordering types including incommensurate phases with several wave vectors, the magnetic ordering of the $ErGe_3$ compound is simple. The easy plane of antiferromagnetism of the Er compound (001), with the moments close to the *a* axis, is also different from Dy and Tb, which have an almost uniaxial arrangement parallel to the *c* axis [5,12].

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