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NEUTRON DIFFRACTION STUDY OF MAGNETIC ORDERING IN $ErMn_2Si_2$, $ErMn_2Ge_2$ AND $ErFe_2Si_2$

J. LECIEJEWICZ

Institute of Nuclear Research, Świerk Establishment, 05-400 Otwock, Poland

S. SIEK

Institute of Physics, Technical University of Cracow, 30-084 Cracow, Podchorążych 1, Poland

and A. SZYTUŁA

Institute of Physics, Jagiellonian University, 30-059 Cracow, Reymonta 4, Poland

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Neutron diffraction study of polycrystalline compounds $ErMn_2Si_2$, $ErMn_2Ge_2$ and $ErFe_2Si_2$ was performed in the temperature range between 1.8 and 293 K. All compounds have tetragonal, $ThCr_2Si_2$-type crystal structure. The antiferromagnetic collinear structure of $ErMn_2Si_2$ and $ErMn_2Ge_2$ at both RT and LNT, consists of a sequence $+-+-$ of ferromagnetic layers of Mn atoms. The magnetic moment of an Mn atom ($\approx 2\mu_B$) is parallel to the c-axis. At low temperatures (LHT and lower), the ferromagnetic ordering within the Er sublattice is observed. The magnetic moment ($\mu_{Er} \approx 9\mu_B$) is perpendicular to the *c*-axis. From the temperature dependence of the intensities of the magnetic peaks, the following values for the Curie temperatures were obtained: (10 ± 5) K for $ErMn_2Si_2$ and (8.5 ± 3) K for $ErMn_2Ge_2$. For $ErFe_2Si_2$ a collinear antiferromagnetic structure of the $+--+$ type was found, the magnetic unit cell consisting of the chemical one, doubled along the *c*-axis.

1. Introduction

Magnetic properties of the RET_2X_2 compounds, where RE is a rare-earth metal, T a transition metal and X is silicon or germanium, have been extensively studied [1–5]. These compounds crystallize in the tetragonal $ThCr_2Si_2$ type structure belonging to the space group I4/mmm [15]. In the unit cell the rare-earth, transition metal and silicon or germanium atoms occupy the 2(a), 4(d) and 4(e) sites, respectively. According to magnetometric measurements on polycrystalline samples, $ErMn_2Si$ and $ErMn_2Ge_2$ exhibit ferromagnetic properties at low temperatures and anti-ferromag-

Table 1
Magnetic parameters of $ErMn_2Si_2$, $ErMn_2Ge_2$ and $ErFe_2Si_2$

Compound	$T_{C,N}$(K)		Magnetic moment		g_J
	M	ND	μ_B/FU	$\mu_{Er}(\mu_B)$	
$ErMn_2Si_2$	34 [3]	10 ±5	4.2 [a] [3]	8.9±0.2 [c]	9.0
$ErMn_2Ge_2$	38 [2]	8.5±3	6.0 [b] [2]	7.7±0.3 [d]	
$ErFe_2Si_2$	2.6			7.4±0.3 [c]	

[a] Measured at 50 kOe and $T = 4.2$ K.
[b] Measured at 120 kOe and $T = 4.2$ K.
[c] Determined at 1.8 K.
[d] Determined at 4.2 K.

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netic at high temperatures [1–3]. The magnetometric data are collected in table 1.

On the other hand $ErFe_2Si_2$ orders antiferromagnetically with the Néel temperature at 2.6 K [4], but $ErFe_2Ge_2$ remains paramagnetic at 4.2 K [5].

We report here the results of neutron diffraction study on powdered samples of $ErMn_2Si_2$, $ErMn_2Ge_2$ and $ErFe_2Si_2$ undertaken in order to determine their crystal and magnetic structures.

2. Experiment

The samples were prepared by melting Er metal (4N), Mn (4N) or Fe (4N) and silicon (5N) or germanium (5N purity) in an induction furnace. The samples were then annealed in quartz tubes at 800°C for 100 h and cooled to room temperature.

The single phase nature of the compounds was checked by X-ray diffraction using FeK_α radiation. All the lines observed could be indexed assuming the tetragonal, $ThCr_2Si_2$ type structure. The resultant lattice parameters were found to be in good agreement with those reported previously [1–4] (see table 2).

Neutron diffraction data ($\lambda = 1.326 \times 10^{-1}$ nm) were collected by means of the DN-500 diffractometer at the EWA reactor in Świerk. Neutron diffraction patterns were taken at 293, 78, 4.2 and 1.8 K. Additionally, the temperature dependence of magnetic peak intensities was measured for the temperature range 4.2–80 K. The observed neutron intensities were corrected for absorption and treated with the line profile analysis method [6]. Nuclear scattering lengths $b_{Er} = 0.79$, $b_{Mn} = -0.39$, $b_{Fe} = 0.95$, $b_{Si} = 0.42$ and $b_{Ge} = 0.819 \times 10^{-14}$ m [7] were used. The magnetic form factor Er^{3+} was taken from ref. [8].

Table 2
Structural and magnetic parameters of the $ErMn_2Si_2$, $ErMn_2Ge_2$ and $ErFe_2Si_2$

Compound	$ErMn_2Si_2$			
T(K)	293	78	4.2	1.8
a(Å)	3.905(2)	3.920(3)	3.911(4)	3.913(4)
c(Å)	10.420(8)	10.455(9)	10.437(7)	10.437(7)
c/a	2.668	2.667	2.669	2.667
V(Å^3)	158.89(21)	160.66(31)	159.68(35)	159.81(35)
z	0.3763(4)	0.3748(14)	0.3735(22)	0.3735(22)
$\mu_{Mn}(\mu_B)$	2.17(9)	2.24(8)	2.30(13)	2.30(13)
$\mu_{Er}(\mu_B)$			7.3(2)	8.9(2)
R_n(%)	5.7	4.7	6.4	6.5
R_m(%)	6.4	4.9	8.6	7.6

$ErMn_2Ge_2$			$ErFe_2Si_2$	
293	78	4.2	293	1.8
3.948(2)	3.948(4)	3.881(8)	3.882(2)	3.806(3)
10.791(5)	10.828(7)	10.627(12)	9.876(7)	9.585(9)
2.733	2.743	2.738	2.544	2.518
168.20(24)	168.77(35)	160.06(85)	148.81(27)	138.84(35)
0.3827(6)	0.3816(21)	0.3885(30)	0.3753(16)	0.3744(32)
1.7(2)	2.2(2)	2.3(2)		
		7.7(4)		7.4(3)
4.7	8.7	7.8	8.7	8.9
5.4	7.9	8.9		9.7

3. Results

3.1. $ErMn_2Si_2$ and $ErMn_2Ge_2$

Neutron diffraction patterns of $ErMn_2Si_2$ and $ErMn_2Ge_2$ taken at 1.8 and 293 K do not differ much, including peaks of magnetic origin, therefore only that one for $ErMn_2Si_2$ is shown in fig. 1.

Room temperature diffractograms of the above two compounds consist of strong reflection, satisfying the condition $h + k + l = 2n$, plus two superlattice lines, indexed as (111) and (113). The latter are preserved down to 4.2 K. The observed nuclear intensities for the reflections with $h + k + l = 2n$ were compared with those calculated for the $ThCr_2Si_2$ type model, to yield the values of the free parameter z. The refined values of z and corresponding minimum R factor are listed in table 2. A test for mixing of Mn or Fe and Si or Ge atoms among 4(e) sites gave negative results.

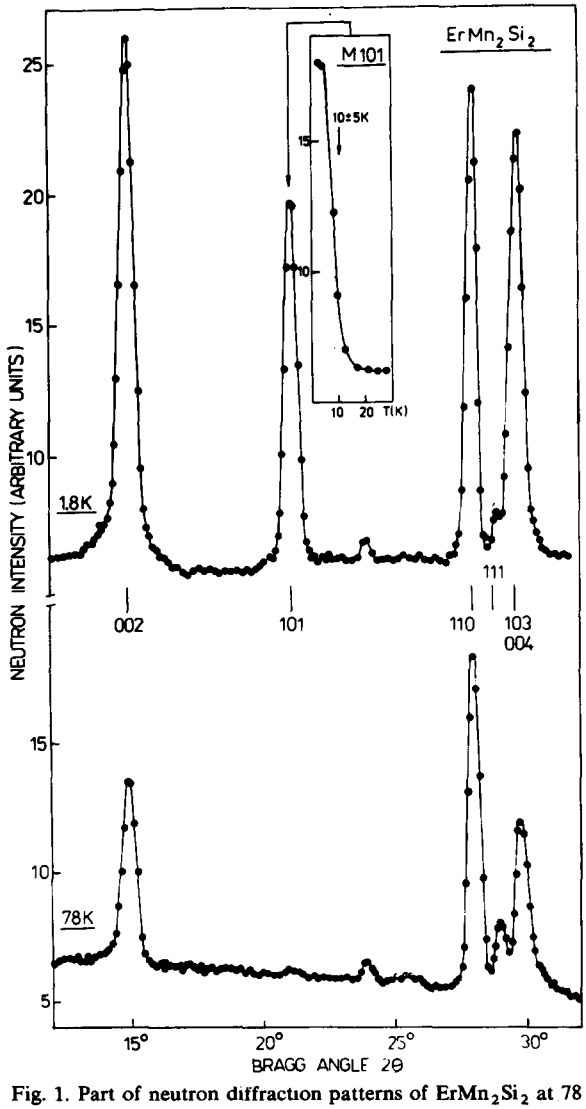

Fig. 1. Part of neutron diffraction patterns of $ErMn_2Si_2$ at 78 and 1.8 K. Temperature dependence of the M101 peak height is indicated.

The observed (111) and (113) lines are of magnetic origin. Their analysis was performed on the assumption that a collinear magnetic ordering, similar to this one, encountered in the magnetic structures of $REMn_2Si_2$ (RE = Ce, Pr, Nd) [9,10], is present. This structure consists of ferromagnetic layers composed on Mn atoms piled up along the c axis. Each layer is antiferromagnetically coupled with the neighbouring one (see fig. 3).

On the neutron diffraction pattern obtained at 4.2 K, an increase of intensity of all reflection with $h + k + l = 2n$ is observed (see fig. 1). This indicates the presence of a ferromagnetic ordering. The analysis of the intensities proved that the magnetic moments are localized on Er atoms and

Table 3
A comparison of neutron intensities observed at 4.2 K with calculated values for the proposed model of magnetic structure of $ErFe_2Si_2$

hkl	2θ	I_{obs}	I_{calc}
$00\frac{3}{2}$	11.4	38306	33828
$00\frac{5}{2}$	19.4	12960	52609
$10\frac{1}{2}$	19.9	47895	
$10\frac{3}{2}$	22.9	35962	31412
$00\frac{7}{2}$	27.5	6067	
$10\frac{5}{2}$	27.9	23221	43755
$11\frac{1}{2}$	28.3	11339	
$11\frac{3}{2}$	30.5	10826	10753
$10\frac{7}{2}$	34.2	14430	24114
$11\frac{5}{2}$	34.5	9291	
R(%)			9.7

are perpendicular to the c-axis. The obtained value of magnetic moment localized on Er atom at 1.8 K is equal to $(8.9 \pm 0.2)\mu_B$.

The temperature dependence of the magnetic peaks gave the Curie temperature at (10 ± 5) K for $ErMn_2Si$ and at (8.5 ± 3) K for $ErMn_2Ge_2$.

3.2. $ErFe_2Si$

The reflections observed at room temperature on the neutron diffractogram of $ErFe_2Si_2$ were indexed according to the rule $h + k + l = 2n$. Nuclear intensities were calculated for the Er atoms in position 2(a), Fe in 4(d) and Si in 4(e). The best fit was achieved for the parameters given in table 2.

On the pattern obtained at 1.8 K (see fig. 2) seven superlattice lines are visible. These lines are indexable on the magnetic unit cell with the lattice constants of $a = (3.802 \pm 2) \times 10^{-1}$ nm and $c = (19.171 \pm 15) \times 10^{-1}$ nm (that is, roughly $a, a, 2c$)

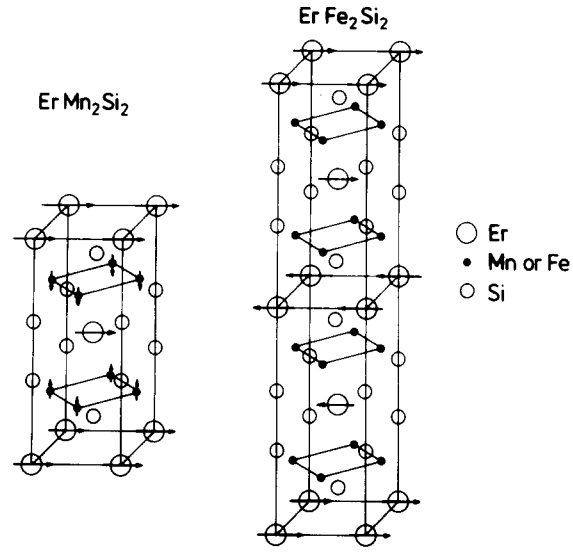

Fig. 3. Magnetic structures of $ErMn_2Si_2$ and $ErFe_2Si_2$.

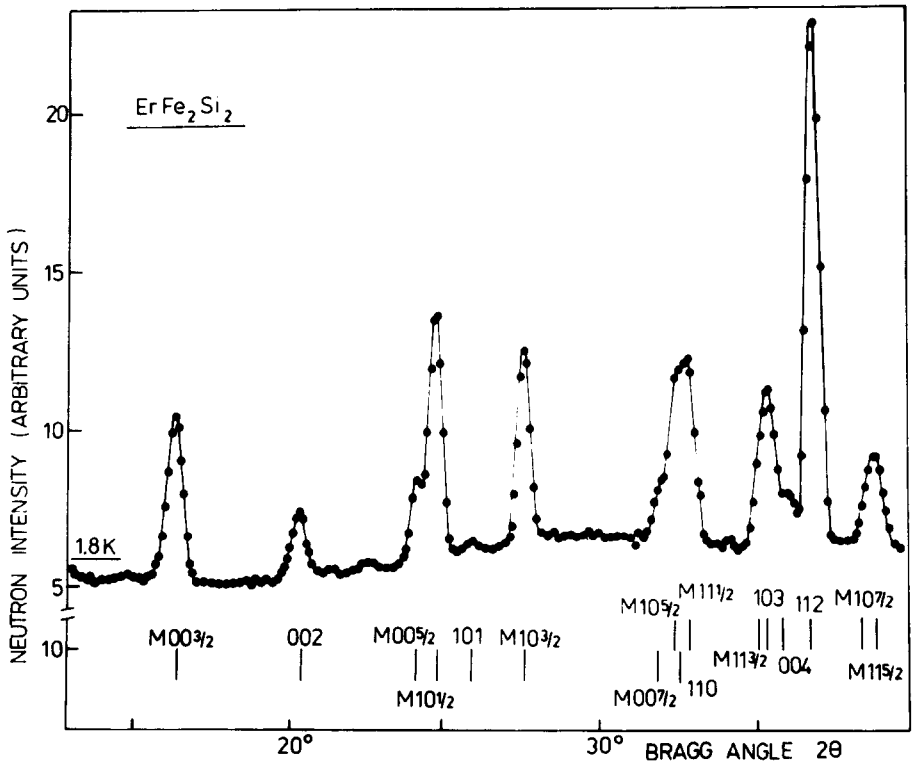

Fig. 2. Part of the LHT neutron diffraction pattern of $ErFe_2Si_2$.

as (003), (005) and (101), (103), (007), (105), (111), (113), (107), (115). From the Mössbauer effect data it follows that the occurrence of a magnetic moment on Fe atoms is improbable. Consequently, the observed superlattice neutron reflections originate from Er magnetic moments only, and indicate that they order anti-ferromagnetically. The proposed magnetic structure, consistent with experimental data, is collinear, composed of ferromagnetic layers, perpendicular to the *c*-axis and is arranged according to the pattern + − − + (see fig. 3). The presence of the (003), (005) and (007) lines implies that the magnetic moment forms an angle ϕ with the tetragonal axis. The best least squares fit gave $\phi = 90°$, magnetic moments of Er amount to $(7.4 \pm 0.3)\mu_B$ and are distributed in the basal plane.

4. Discussion

In the determined magnetic structures of $ErMn_2Si_2$, $ErMn_2Ge_2$ and $ErFe_2Si_2$ magnetic moment localized on Er atom lies in the basal plane. The same has been previously observed in other ER intermetallics of $ThCr_2Si_2$ type [11,12]. The compounds under consideration differ with respect to their magnetic structures: those with Mn ($3d^5$) are collinear ferromagnets, while those with Fe ($3d^6$) are collinear antiferromagnets of AF II type (+ − − + sequence). $ErCo_2X_2$–Co ($3d^7$) exhibit also anti-ferromagnetic ordering, but of AF I type (+ − + − sequence). The above results indicate strong influence of 3d elements upon magnetic ordering of the RE sublattice in RET_2X_2 intermetallics.

Generally speaking, in all those magnetic structures, the RE magnetic moments within (001) planes are coupled ferromagnetically, while the neighbouring planes are coupled either ferromagnetically or anti-ferromagnetically. They are neighbouring but not adjacent, since they are separated by three atomic layers, composed of Si or Ge and transition metal atoms.

An increase in the number of 3d electrons leads to a decrease in the *c* constant, while the *a* constant remains almost unchanged. Comparing the values of Néel or Curie temperatures in the ErT_2Si_2 series one notices than oscillatory character, i.e. in the 3d-series T = Mn: 10 K, Fe: 2.6 K, Co: 11 K, Cu: 2.0 K [11,13]. Similar dependence of the Néel temperature is observed for isostructural EuT_2Ge_2 and GdT_2Ge_2 compounds [14]. This implies that the RE–RE interactions are most probably of indirect character and could be described by a conduction electron spin polarization mechanism: however, no quantitative analysis has been made up to now. The strength of the coupling depends on the total number n_0 of free conduction electrons per RET_2X_2 formula unit and on interatomic distance.

The calculated value of the magnetic moment localized on Er is close to that one of a free ion. The absence of a localized magnetic moment on Fe atoms is in agreement with Mössbauer effect data [4] and suggests that Fe atoms have a spin-paired $3d^6$ configuration.

The magnitude of magnetic moment localized on Mn atom results from of an overlap of electronic shells of Mn and Si or Ge atoms, leading to spin transfer from the p shell of Si or Ge to the 3d shell of Mn.

5. Conclusions

In the course of the present study the magnetic structure of $ErMn_2Si_2$, $ErMn_2Ge_2$ and $ErFe_2Si_2$ was determined. Two former compounds exhibit ferromagnetic ordering of Er magnetic moments and anti-ferromagnetic order of Mn magnetic moments. The magnetic moments of Er atoms lie in basal plane, while those of Mn atoms are parallel to the *c*-axis.

$ErFe_2Si_2$ is a collinear antiferromagnet with the magnetic moment localized on the Er atom lying in the basal plane. The magnetic structure is composed of ferromagnetic planes (001) with the sequence + − − + in the direction of the *c*-axis. The magnetic unit cell is doubled with respect to the chemical one in the *c*-axis direction. The Fe atom has no localized magnetic moment.

References

[1] K.S.V.L. Narasimhan, V.U.S. Rao, W.E. Wallace and I. Pop, AIP Conf. Proc. 29 (1975) 594.
[2] K.S.V.L. Narasimhan, V.U.S. Rao, R.L. Bergner and W.E. Wallace, J. Appl. Phys. 46 (1976) 4957.
[3] A. Szytuła and I. Szott, Solid State Commun. 40 (1981) 199.
[4] A.M. Umarji, D.R. Noakes, P.J. Viccaro, G.K. Shenoy, A.T. Aldred and D. Niarchos, J. Magn. Magn. Mat. 36 (1983) 61.
[5] S.K. Malik, S.G. Sankar, V.U.S. Rao and R. Obermyer, A.I.P. Conf. Proc. 34 (1976) 87.
[6] H.M. Rietveld, J. Appl. Cryst. 2 (1969) 65.
[7] G.E. Bacon, Acta Cryst. A28 (1972) 357.
[8] A.J. Freeman and J.J. Desclaux, J. Magn. Magn. Mat. 12 (1979) 11.
E.R. Watson and A.J. Freeman, Acta Cryst. 14 (1961) 231.
[9] S. Siek, A. Szytuła and J. Leciejewicz, Phys. Stat. Sol. (a) 46 (1978) K101.
[10] S. Siek, A. Szytuła and J. Leciejewicz, Solid State Commun. 39 (1981) 863.
[11] J. Leciejewicz, M. Kolenda and A. Szytuła, Solid State Commun. 45 (1983) 145.
[12] J. Leciejewicz, A. Szytuła and A. Zygmunt, Solid State Commun. 45 (1983) 149.
[13] W. Schlabitz, J. Baumann, G. Neumann, D. Plümacher and K. Reggentin, Proc. Intern. Conf. on Crystalline Electric Field and Structural Effects in F-electron System, Wrocław, 1981, eds. R.P. Guertin, W. Suski and Z. Żołnierek (Plenum, New York, 1982) p. 289.
[14] I. Felner and I. Nowik, J. Phys. Chem. Solids 39 (1978) 763.
[15] Z. Ban and M. Sikirica, Acta Cryst. 18 (1965) 594.