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NEUTRON DIFFRACTION STUDY OF $RECo_2Si_2$ INTERMETALLICS

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A neutron diffraction study of polycrystalline $RECo_2Si_2$ intermetallics (RE = Pr, Nd, Tb, Ho, Er) carried out at liquid helium temperature shows the presence of a collinear antiferromagnetic ordering of + − + − type. Magnetic moment is localized on RE ions only and amounts to the RE^{3+} free ion value. In $ErCo_2Si_2$ the magnetic moment is normal to the tetragonal unique axis, whereas in the remaining compounds the magnetic moment is aligned along it. Néel points were determined from the temperature dependence of magnetic peak heights.

1. INTRODUCTION

INTERMETALLIC COMPOUNDS of general formula REM_2X_2 (where RE is a rare earth metal, M is a transition metal, and X stands for silicon or germanium), became in recent years a subject of intensive studies.

They were synthesized for the first time by Rieger and Parthé [1] and Rossi *et al.* [2].

According to X-ray diffraction data, REM_2X_2 compounds crystallize in the body centered tetragonal structure (space group $I4/mmm$), with RE, M and X atoms occupying the 2(a), 4(d) and 4(e) positions, respectively. The structure consists of atomic layers perpendicular to the c-axis, stacked with the sequence RE–X–M–X–RE.

The magnetic properties of $RECo_2Si_2$ compounds have been reported by Yakinthos *et al.* [3] and Kolenda *et al.* [4]. The majority of them are antiferromagnets with Néel temperature below 80 K. Compounds with RE = La, Ce, Yb, Lu are temperature-independent paramagnets. ^{155}Gd Mössbauer effects measurements indicate that the magnetic moment vector in $GdCo_2Si_2$ lies in the basal plane [5].

We report here the results of X-ray and neutron diffraction study on powder samples of $RECo_2Si_2$, (RE = Pr, Nd, Tb, Ho, Er) undertaken in order to determine their crystal and magnetic structures.

2. EXPERIMENT AND RESULTS

The samples were prepared by melting rare-earth metal (4N), cobalt (4N) and silicon (5N purity) in an induction furnace. The samples were then annealed in a quartz tube at 800°C for 100 hr and cooled to room temperature.

The single-phase nature of the compounds was established by X-ray 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 obtained previously [1, 2] (see Table 1).

Neutron diffraction data ($\lambda = 1.324 \times 10^{-1}$ nm) were obtained on DN-500 diffractometer at the EWA reactor in Świerk. Neutron diffraction patterns were taken at room (RT) and liquid helium temperatures (LHT). Additionally, the temperature dependence of the magnetic peak intensity was measured in the temperature range 4.2–80 K. Refinement of the nuclear and magnetic data was performed using line profile analysis of Rietveld [6]. The nuclear scattering lengths were taken after [7] and the magnetic form factor of RE^{3+} ions after [8–12].

All the reflections on neutron diffraction patterns at 300 K are indexable on a tetragonal unit cell. The observed intensities were compared with those calculated for the $ThCr_2Si_2$ type model yielding the values of the free parameter z. The refined values of z and corresponding minimum R factors are listed in Table 1. A test for mixing of Co and Si ions among 4(d) and 4(e) sites gave a negative result.

Magnetic structures were determined from neutron diffraction patterns taken at 4.2 K. For all samples investigated extra peaks of magnetic origin are observed. They are indexable on a tetragonal unit cell with the same dimensions as the chemical one and obey the (see

Table 1. Crystal structure parameters for $RECo_2Si_2$ *compounds*

RE	Pr		Nd		Tb		Ho		Er	
T (K)	300	4.2	300	4.2	300	4.2	300	4.2	300	4.2
a (Å)	3.969(1)	3.972(5)	4.007(2)	3.982(4)	3.901(2)	3.857(4)	3.884(1)	3.902(5)	3.883(1)	3.892(1)
c (Å)	9.925(4)	9.949(9)	10.002(5)	9.968(9)	9.781(6)	9.665(9)	9.748(5)	9.827(2)	9.761(3)	9.779(6)
c/a	2.500	2.505	2.496	2.504	2.507	2.506	2.510	2.518	2.513	2.512
V (Å^3)	156.35(14)	156.96(54)	160.59(24)	157.98(46)	148.84(25)	143.78(43)	147.05(15)	149.62(40)	147.17(12)	148.13(13)
z	0.3719(4)	0.3759(11)	0.3742(7)	0.3805(10)	0.3715(6)	0.3844(3)	0.3736(7)	0.3733(4)	0.3750(5)	0.3896(3)
R_N (%)	9.9	5.8	6.9	9.9	6.3	10.8	2.2	3.6	5.8	5.3

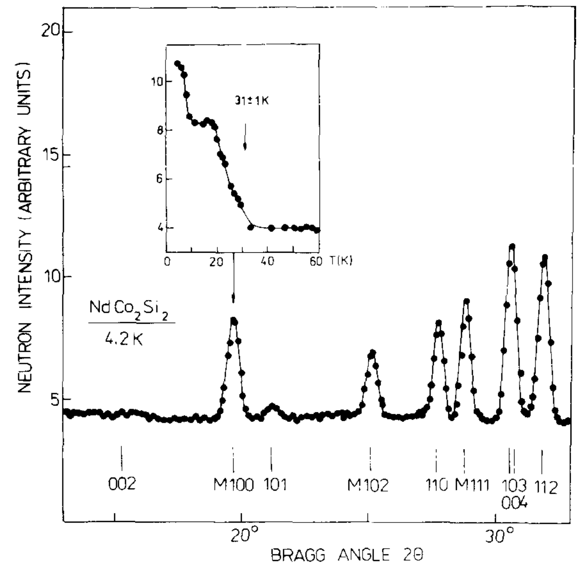

Fig. 1. A part of LHT neutron diffraction pattern of $NdCo_2Si_2$. Temperature dependence of M100 magnetic peak height is indicated.

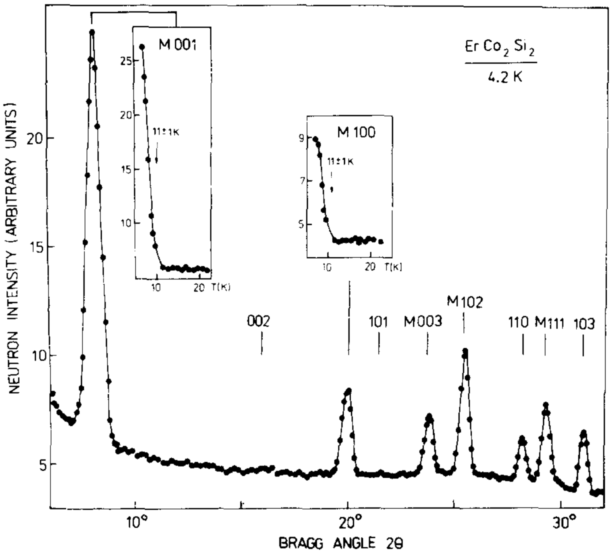

Fig. 2. A part of LHT neutron diffraction pattern of $ErCo_2Si_2$. Peak height vs temperature curves are shown for M001 and M100 magnetic reflections.

Fig. 1) $h + k + l = 2n + 1$ rule, with 0 0 1 reflections absent for RE = Pr, Nd, Ho and Tb. This indicates that the magnetic moments are localized on RE ions situated at 0 0 0 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ sites and are pointing along the tetragonal c-axis. This type of magnetic ordering can be visualized as a $+ - + -$ sequence of ferromagnetic sheets piled up along the c-axis.

A different magnetic structure is observed at 4.2 K in $ErCo_2Si_2$. The presence of magnetic reflections M001 and M003 (see Fig. 2) indicates that the magnetic moment on Er forms an angle ϕ with the tetragonal axis. From the analysis of peak intensities it follows that ϕ amounts to 90°. $ErCo_2Si_2$ is thus an antiferromagnet with Er magnetic moments in the basal plane. The coupling within this plane is ferromagnetic, but antiferromagnetic between the adjacent planes.

Table 2. Magnetic parameters of $RECo_2Si_2$ *compounds*

RE	T_N (K) ND	M	μ (μ_B) at 4.2 K	gJ
Pr	49(19)	30	3.19(6)	3.2
Nd	26(2)		3.39(5)	3.27
Tb	45(1)	45	8.9(2)	9.0
Ho	10(1)	11.2	10.4(8)	10.0
Er	11(1)	6	8.7(2)	9.0

A test for a model in which magnetic moments are localized on RE and Co ions shows that the magnetic moments are on RE ions only. Their magnitudes were derived using RE free ion form factors. All of them are found to be close to the free ion value $\mu = gJ$ (see Table 2).

Additionally, the temperature dependence of the intensity of reflection of magnetic origin has been measured. $NdCo_2Si_2$ was the only compound that revealed an anomaly in such dependence, suggesting the existence of a magnetic phase transition at about 10 K (see Fig. 1). The remaining samples show these dependences to be characteristic for an antiferomagnetic–paramagnetic transition.

The determined values of the Néel temperatures are in good agreement with those obtained from magnetic susceptibility vs temperature curves.

3. CONCLUSIONS

All $RECo_2Si_2$ intermetallics belong to the $ThCr_2Si_2$ type of crystal structure. A comparison of lattice constants determined at the liquid helium and room temperatures indicates the presence of strong magnetostriction effect at low temperatures.

All $RECo_2Si_2$ investigated exhibit at 4.2 K collinear antiferromagnetic ordering of $+ - + -$ type. Except $ErCo_2Si_2$, in the remaining compounds magnetic moments are aligned along the tetragonal unique c-axis. In $ErCo_2Si_2$ they are normal to it.

Orientation of the magnetic moments in the unit cell is connected with signs of B_2^0 coefficients. The CF Hamiltonian for a rare earth ion with tetragonal site symmetry is

$$H_{GF} = B_2^0O_2^0 + B_4^0O_4^0 + B_4^4O_4^4 + B_6^0O_6^0 + B_6^4O_6^4$$

where the c-axis of the tetragonal cell has been chosen as quantization axis. The operators O_n^m and the coefficients B_n^m are as defined by Hutchings [13]. For the first approximation, the last two terms can be omitted [13].

According to Greedan and Rao [14] the positive value of the B_2^0 coefficient indicates that the magnetic moment lies in basal plane or makes ϕ angle with the c-axis.

The following values of the B_2^0 coefficient can be found in original papers: $-3.0(1.0)$ K for $CeCu_2Si_2$ from inelastic neutron scattering [15], -1.0 K for $DyCo_2Si_2$ and -1.8 K for $DyFe_2Si_2$ [16] and $+0.12(2)$ K for $TmCu_2Si_2$ [17] from the Mössbauer effect measurements. This suggests that increasing number of the f-electrons leads to a change of sign in B_2^0 value. It follows from our data that for the $RECo_2Si_2$ compounds this change occurs for RE = Er.

It was found that magnetic moments are localized on RE ions only and amount to the free ion values, similarly as it was observed by magnetometric measurements in the paramagnetic region. No localized moment is observed with the experimental accuracy on Co ion.

This behaviour could be caused by the following two effects:

(1) the filling of the $3d$ band of cobalt by electrons donated from silicon. In all compounds of $ThCr_2Si_2$ type crystal structure a Co metal atom is surrounded by four Si atoms (the distance is about 2.3 Å) arranged in a flat tetrahedron. The Co–Si distance is less than the sum of atomic radii, indicating an overlap of the electronic shells. Consequently, the spin transfer from the $3p$ shell of Si to the $3d$ shell of Co seems very likely, resulting in a decrease of magnetic moment on Co atoms.

(2) $3d$ electrons of Co atoms in these compounds form bands coinciding with the valence band. Similar results concerning the valence band were obtained by Buschow *et al.* [18] for $EuCu_2Si_2$ and YCu_2Si_2 by means of XPS spectrum. The $3d$ band of Cu lies within the distance 0.4 eV from the Fermi level, and it is therefore completely filled. Whenever the number of electrons within this band decreases, the whole band moves up towards the Fermi level, as it has been shown for the MS_2 compounds [19]. Within the group of compounds under consideration, only those with M = Mn show a localized magnetic moment.

Néel points determined from magnetic peak intensity against temperature dependence are consistent with those obtained from magnetometric data. In $NdCo_2Si_2$ a rapid change in the magnitude of magnetic moment at about 10 K is observed suggesting the presence of a magnetic phase transition possibly of the same kind as discovered many years ago in uranium monophosphide [20].

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