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Crystal and Magnetic Structures of $PrCo_2Ge_2$ and $HoCo_2Ge_2$

By

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The crystal and magnetic structures of $PrCo_2Ge_2$ and $HoCo_2Ge_2$ are determined by neutron diffraction using powder samples. The crystallochemical structures of these compounds are of the $ThCr_2Si_2$ type. At temperatures below 28 K $PrCo_2Ge_2$ is antiferromagnetic with a sinusoidal magnetic structure. The propagation vector $k = (0, 0, \tau)$, $\tau = 0.73$ is along the c-axis. The amplitude of magnetic moment is $(3.98 \pm 0.15)\,\mu_B$. $HoCo_2Ge_2$ is an antiferromagnet with a Néel temperature of 8 K. The magnetic structure of this compound consists of ferromagnetic layers perpendicular to the c-axis which are antiferromagnetically coupled to adjacent layers. The magnetic moment is $(8.64 \pm 0.08)\,\mu_B$. In both the compounds the magnetic moment is aligned along the c-axis.

Методом дифракции нейтронов были определены кристаллические и магнитные свойства порошковых образцов $PrCo_2Ge_2$ и $HoCo_2Ge_2$. Кристаллохимические структуры этих соединений оказались типа $ThCr_2Si_2$. При температурах ниже 28 K $PrCo_2Ge_2$ обладает антиферромагнитными свойствами с синусоидальной магнитной структурой. Вектор пропагации $k = (0, 0, \tau)$, $\tau = 0{,}73$ направлен по c-оси. Амплитуда магнитного момента — $(3{,}98 \pm 0{,}15)\,\mu_B$. $HoCo_2Ge_2$ является антиферромагнетиком с температурой Нееля 8 K. Магнитная структура этого соединения состоит из ферромагнитных слоев перпендикулярных c-оси; между ними имеет место антиферромагнитное сопряжение. Магнитный момент равен $(8{,}64 \pm 0{,}08)\,\mu_B$. Магнитный момент для обоих образцов направлен по c-оси.

1. Introduction

The crystal structure and magnetic properties of the RCo_2Ge_2 compounds where R is rare-earth element have been reported by McCall et al. [1]. They crystallize in the $ThCr_2Si_2$-type, body-centred tetragonal structure (space group I4/mmm). It was found that the compounds for which R = La, Ce, Sm, Er, Tm, Yb, and Y exhibit paramagnetic behaviour down to 4.2 K. $ErCo_2Ge_2$ and $TmCo_2Ge_2$ probably order at lower temperatures. For R = La, Tb, Lu, and Y the susceptibilities are independent of temperature. This suggests that the paramagnetism is caused by the conduction electrons and that the cobalt in these compounds does not order magnetically. The compounds for which R = Dy, Gd, Tb, and Ho order antiferromagnetically. $PrCo_2Ge_2$ and $NdCo_2Ge_2$ show an unusual magnetic behaviour. $PrCo_2Ge_2$ exhibits a susceptibility which decreases from 4.2 K, then rises to a peak at 27.5 K. $NdCo_2Ge_2$ has two peaks in the susceptibility versus temperature curve at 13.5 and 27.5 K. The Néel points for the heavy rare-earth compounds follow the Gennes function.

In the present paper we report the results of X-ray, neutron diffraction, and magnetometric measurements on powder samples of $PrCo_2Ge_2$ and $HoCo_2Ge_2$ undertaken in order to determine the crystal and magnetic structures.

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2. Experimental and Results

The samples were prepared by melting rare-earth metal (4N), cobalt (4N), and germanium (5N purity) in an induction furnace. The samples were then annealed in a quartz tube at 800 °C for 100 h and cooled to room temperature. The single-phase nature of the compounds was established by X-ray analysis using FeK_α radiation. All the lines observed could be indexed on a tetragonal $ThCr_2Si_2$-type structure.

Magnetometric measurements were carried out in the temperature range 4.3 to 300 K using a vibrating sample magnetometer. The thermal variation of the susceptibility exhibits a maximum (see Fig. 1) which is characteristic of an antiferromagnetic behaviour below a Néel temperature of 28 K for $PrCo_2Ge_2$ and 8 K for $HoCo_2Ge_2$. At high temperatures the reciprocal susceptibility obeys a Curie-Weiss law. The paramagnetic temperatures are negative giving evidence for predominant negative interactions. The paramagnetic moment is in good agreement with the theoretical values for a free ion. The magnetic data are listed in Table 1.

Table 1

The Néel temperatures, Weiss constants, effective moments, and theoretical effective moments

compounds	T_N (K)	θ (K)	μ_{eff} (μ_B)	gJ $(J + 1)^{1/2}$
$PrCo_2Ge_2$	28	− 9	2.9	3.58
$HoCo_2Ge_2$	8	−10	10.0	10.60

Neutron diffraction data ($\lambda = 1.324$ Å) were obtained on a diffractometer at the EWA reactor in Swierk. For $PrCo_2Ge_2$ neutron diffraction patterns were taken at room temperature (RT) and liquid helium temperature (see Fig. 2). For $HoCo_2Ge_2$ neutron diffraction patterns were taken at room temperature, 4.2, and 1.6 K (see Fig. 3). All the reflections observed in the RT patterns could be indexed on the basis of the tetragonal unit cell. Nuclear intensities were calculated for the structure shown Fig. 4 with

R atoms in the position 2a: $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$;
Co atoms in 4d: $0, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, 0, \frac{1}{4}; 0, \frac{1}{2}, \frac{3}{4}; \frac{1}{2}, 0, \frac{3}{4}$;
Ge atoms in 4e: $0, 0, z; 0, 0, \bar{z}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z$.

The parameter z and the Debye-Waller factor were determined from nuclear reflections by the profile refinement method [2] using scattering lengths of 0.44, 0.25, and 0.819×10^{-14} m for Pr, Co, and Ge, respectively [3]. The refined parameters and corresponding R-factors are given in Table 2. The mixing of Co and Ge atoms among 4d and 4e positions [4] was not confirmed by our experiment.

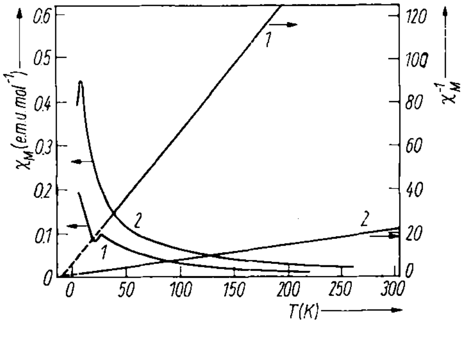

Fig. 1. Magnetic susceptibility vs. temperature curve for (1) $PrCo_2Ge_2$ and (2) $HoCo_2Ge_2$

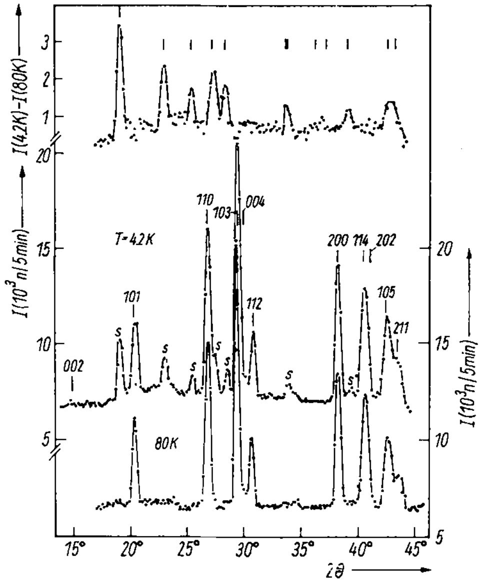

Fig. 2. Neutron diffraction patterns of $PrCo_2Ge_2$ taken at 4.2 and 80 K and a difference pattern revealing magnetic reflections only

In the second step the magnetic structure was determined. In the case of $PrCo_2Ge_2$ seven superlattice lines are observed on the LT pattern and indexed as satellites of the nuclear peaks. The propagation vector is $\boldsymbol{k} = (0, 0, \tau)$ with $\tau = 0.73$. From the analysis of magnetic peak intensities, the following model of a spiral magnetic structure was obtained:

1. The magnetic moment is localized only on Pr atoms, the refined value of the magnetic moment $\mu = (3.98 \pm 0.15)\,\mu_B$ is larger than the expected free-ion value of $3.2\mu_B$.
2. The magnetic structure is sinusoidal along the c-axis.

In the case of $HoCo_2Ge_2$ neutron diagrams taken at 4.2 and 1.6 K show a series of extra peaks of magnetic origin which could be indexed on the basis of the crystallochemical unit cell with the indices obeying the $h + k + l = 2n + 1$ condition. This corresponds to an antiparallel coupling of magnetic moments of holmium atoms in (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ positions. The magnitudes of magnetic moments were determined from magnetic reflection intensities using profile line analysis. The calculations were carried out for two models:

(i) Magnetic moments are localized only on holmium atoms.

(ii) Magnetic moments are localized on Ho atoms and Co atoms.

The results corresponding to minimum R-factor are given in Table 2. The best fit was obtained with magnetic moments localized only on Ho atoms. Its value $(8.64 \pm 0.08)\,\mu_B$ at temperature 1.6 K is smaller than that expected for the Ho^{3+} free-ion ($gJ = 10.0\mu_B$).

The absence of 001 reflections indicates that magnetic moments are parallel to the c-axis. The magnetic structure could be visualized as a piling of ferromagnetic sheets along the c-axis with the sequence + — + — etc.

Table 2

Structural and magnetic parameters in $PrCo_2Ge_2$ and $HoCo_2Ge_2$

$PrCo_2Ge_2$			$HoCo_2Ge_2$		
temperature	4.2	80	1.6	4.2	300
a_0 (Å)	4.053(7)	4.056(4)	3.966(1)	3.978(4)	3.988(4)
c_0 (Å)	10.230(10)	10.233(8)	10.034(3)	10.088(11)	10.099(12)
c_0/a_0	2.524	2.523	2.530	2.536	2.532
V (Å^3)	168.01(81)	168.34(46)	157.84(16)	159.62(51)	159.54(53)
z	0.374(1)	0.3724(6)	0.3730(6)	0.3759(18)	0.3706(11)
R_n (%)	9.8	6.1	2.5	9.5	3.9
μ (μ_B)	3.98(15)		8.64(8)	8.16(22)	
R_m (%)	16.0		3.34	9.74	

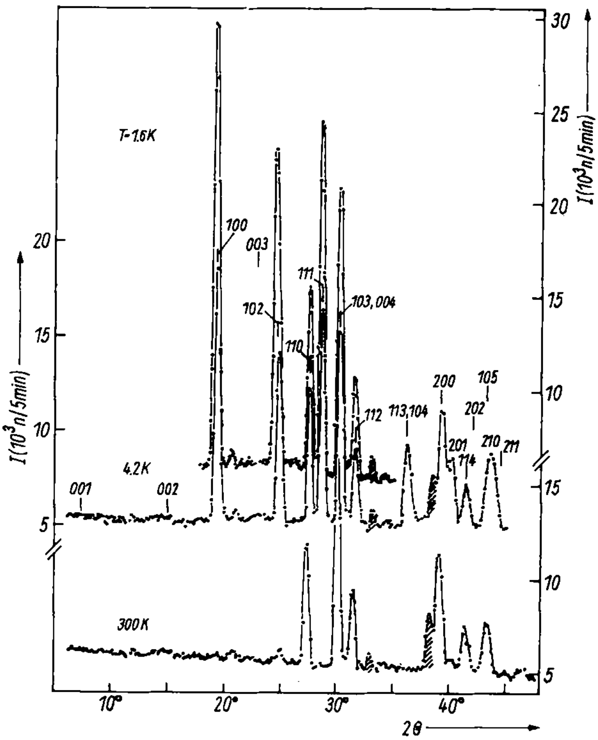

Fig. 3

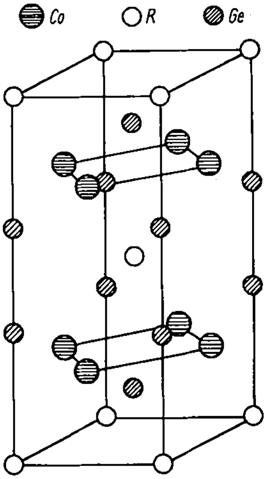

Fig. 4

Fig. 3. A part of neutron diffraction patterns of $HoCo_2Ge_2$ taken at 1.6, 4.2 K, and RT

Fig. 4. Crystallochemical unit cell of $HoCo_2Ge_2$ and $PrCo_2Ge_2$

The magnetic structure of $PrCo_2Ge_2$ as determined in our study agrees well with that reported recently by Pinto et. al. [7].

Our results demonstrate that cobalt in these compounds does not participate in magnetic ordering. This behaviour could be caused by filling the cobalt 3d band by electrons donated from germanium.

The similar compounds RFe_2Si_2 (R = Nd, Eu, Dy) and $GdMn_2Ge_2$ [5, 6] are all electrical conductors, so that the magnetic exchange interactions occur most probably via conduction electrons.

References

[1] W. M. McCall, K. S. V. L. Narasimhan, and R. A. Butera, J. appl. Phys. **44**, 4724 (1973).
[2] H. M. Rietveld, J. appl. Cryst. **2**, 65 (1969).
[3] G. E. Bacon, Acta cryst. **A28**, 357 (1972).
[4] H. Pinto and H. Shaked, Phys. Rev. B **7**, 3261 (1973).
[5] I. Felner and I. Mayer, Mater. Res. Bull. **8**, 1317 (1973).
[6] K. S. V. L. Narasimhan, V. U. S. Rao, R. L. Bergner, and W. E. Wallace, J. appl. Phys. **46**, 4957 (1975).
[7] H. Pinto, M. Melamud, and E. Gurewitz, Acta cryst. A **35**, 533 (1979).

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