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Magnetic Structure of $PrCo_2Ge_2$, a Neutron Diffraction Study

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Abstract

The crystallographic structure of the compound $PrCo_2Ge_2$ is of the $BaAl_4$ type. The space group is $I4/mmm$ and the lattice constants are $a = 4{\cdot}048$ and $c = 10{\cdot}178$ Å. A neutron diffraction study revealed a transition to a magnetically ordered state at $T_N \sim 27$ K and six superlattice lines below T_N. It is possible to index these lines according to a sinusoidal magnetic structure with a period $\tau^{-1} = 13{\cdot}94$ Å along **c**. Observed intensities are consistent with ordering of the Pr sublattice with the magnetic axis along **c**.

I. Introduction

The compound $PrCo_2Ge_2$ belongs (McCall, Narasimhan & Butera, 1973*a*) to the series of compounds AB_2X_2 (A = U, Th, rare-earth; B = Mn, Fe, Co; X = Si, Ge). These compounds crystallize with the $BaAl_4$-type structure, which belongs to the tetragonal space group $I4/mmm$ (D_{4h}^{17}). The lattice constants of $PrCo_2Ge_2$ as determined by X-rays (McCall *et al.*, 1973*a*) are $a = 4{\cdot}048$ and $c = 10{\cdot}178$ Å. Magnetic-susceptibility measurements (McCall, Narasimhan & Butera, 1973*b*) exhibit a peak at 28 K with the susceptibility rising with decreasing temperature down to 4·2 K. It was suggested that this behaviour is due to the antiferromagnetic ordering of the Pr ion. In the present paper we report the results of a neutron diffraction study of a powder sample of $PrCo_2Ge_2$, undertaken in order to determine the magnetic structure of this compound.

II. Experimental

The powder sample was synthesized by arc melting under an atmosphere of argon gas. Neutron diffraction patterns were taken at room temperature (RT) and liquid-helium temperature (LT). The RT and LT patterns are shown in Fig. 1. All the reflections observed in the RT pattern are in agreement with the reported lattice constants (McCall *et al.*, 1973*a*). Six superlattice lines are observed in the LT pattern. The remaining lines can be indexed according to the unit cell with lattice constants $a = b = 4{\cdot}037$ and $c = 10{\cdot}173$ Å.

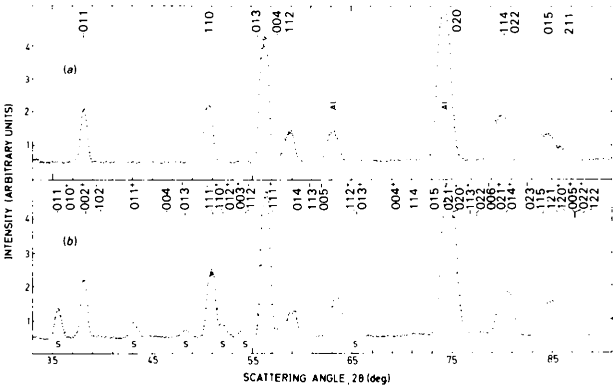

Fig. 1. Neutron ($\lambda = 2{\cdot}45$ Å) diffraction patterns of $PrCo_2Ge_2$ at (*a*) RT and (*b*) LT. No reflection was observed in the range $5° < 2\theta < 33°$ (not shown). The subscripts S in the LT pattern are for superlattice lines. The RT and the LT patterns were indexed according to $a = 4{\cdot}048$, $c = 10{\cdot}178$ Å and $a' = 4{\cdot}037$, $c' = 10{\cdot}173$ Å and $\tau^{-1} = 13{\cdot}94$ Å respectively.

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The *d* values of the six superlattice lines are noncommensurate with this lattice or its integral multiples (up to 4). The peak intensity *vs* temperature curves of two of these lines are shown in Fig. 2. The transition temperature at 27 ± 1 K is in agreement with the results of susceptibility measurements (McCall *et al.*, 1973*b*).

III. Crystallographic structure

Nuclear intensities were calculated for the structure shown in Fig. 3. The ionic positions are given in Table 1. The parameter z and the Debye–Waller constant B were found to give a best fit (least squares) of the calculated to the observed integrated intensities. The calculated intensities together with the observed integrated intensities are given in Table 2. The weighted R factor* is 6·8%. Ban & Sikirica (1965) suspected a statistical distribution of the atoms in positions 4(*d*) and 4(*e*). Such a distribution in our case leads to a considerable increase in intensity of the reflection {002} However, the observed intensity for this reflection is zero. Therefore, this possibility was rejected.

IV. Magnetic structure

The intensity *vs* temperature curves of the superlattice lines indicate a transition at 27 ± 1 K. The fact that this temperature corresponds to the susceptibility measurements suggests that these lines are of magnetic origin. These lines do not lead to an integral multiple of the crystallographic unit cell. However, they can be indexed as satellites of the nuclear lines with a propagation vector $\boldsymbol{\tau}$ along $\mathbf{c}$ and $\tau = 0{\cdot}07172$ Å^{-1}. The absence of the satellite 000^+ suggests that the moment direction is parallel to the propagation vector. Therefore the expected modulation is sinusoidal and not a spiral. If this is so, a possible model would be one in which moments lie parallel to $\mathbf{c}$ and are sinusoidally modulated with a period τ^{-1}. The next problem was to determine whether the Pr or the Co *or both types* of atoms carry moments.

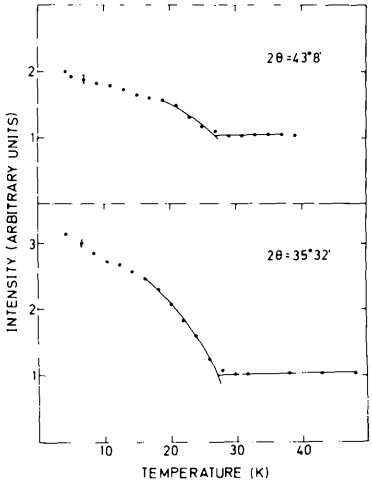

Fig. 2. Peak intensity *vs* temperature curves of the superlattice lines at $2\theta = 35°\,32'$ and $2\theta = 43°\,8'$.

Table 1. *Ionic positions in* $PrCo_2Ge_2$ (*space group* $I4/mmm$)

Position	Coordinates $+(000, \frac{1}{2}\frac{1}{2}\frac{1}{2})$	Ions
2(*a*)	000	Pr
4(*d*)	$0\frac{1}{2}\frac{1}{4}, \frac{1}{2}04$	Co
4(*e*)	$00z, 00\bar{z}$*	Ge

* $z \sim 0{\cdot}375$ (Ban & Sikirica, 1965).

Table 2. *Comparison of calculated and observed integrated intensities in the RT pattern of* $PrCo_2Ge_2$

The calculated intensities were obtained from the refined-parameter values of Table 4.

Number	*hkl*	$I_{obs} \pm \sigma$	I_{calc}
1	002	0 ± 500	530
2	011	18 500 ± 600	18 302
3	110	26 000 ± 600	29 317
4	013	59 450 ± 750	57 705
5	004	3 100 ± 650	2 214
6	112	15 260 ± 650	12 540
7	114, 022	31 200 ± 800	32 881
8	015, 211	31 600 ± 1300	30 261

According to Halpern & Johnson (1939) the magnetic elastic scattering cross section for unpolarized neutrons is proportional to $|\mathbf{P}(\mathbf{e})|^2 - |\mathbf{P}(\mathbf{e}).\hat{\mathbf{e}}|^2$, where $\mathbf{e}$ is the neutron scattering vector. In the sinusoidal case (Forsyth, Pickart & Brown, 1966), $\mathbf{e}$ equals $\mathbf{K} + \boldsymbol{\tau}$ or $\mathbf{K} - \boldsymbol{\tau}$ and

$$\mathbf{P}(\mathbf{K} \pm \boldsymbol{\tau}) \propto \sum_{\nu} f_{\nu}(\mathbf{K} \pm \boldsymbol{\tau})\,\tfrac{1}{2}\mathbf{c}^* \exp[2\pi i(\mathbf{K}.\mathbf{r}_{\nu} \mp \gamma_{\nu})], \quad (1)$$

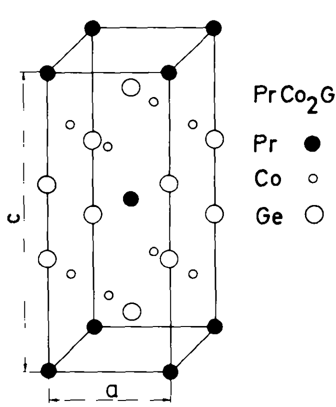

Fig. 3. Crystallographic structure of $PrCo_2Ge_2$. One crystallographic cell is shown.

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* The weighted R factor is given by $R = \{\sum[(I_{obs} - I_{calc})/\sigma]^2/\sum(I_{obs}/\sigma)^2\}^{1/2}$, where the σ's are the estimated errors in I_{obs}.

where $\mathbf{K}$ is a reciprocal-lattice vector, f_ν is the magnetic form factor for the νth magnetic atom, $\mathbf{r}_\nu$ is the vector from the origin to the νth atom in the unit cell, and γ_ν is the relative phase; the summation is over one unit cell. There are two Pr ions per unit cell. For an ordered Pr sublattice we therefore obtain:

$$I(\mathbf{K}\pm\boldsymbol{\tau}) \sim f^2(\mathbf{K}\pm\boldsymbol{\tau})\sin^2\alpha\,[1+(-1)^{h+k+l}\cos\varphi], \quad (2)$$

where I is the intensity, α is the angle between the scattering $(\mathbf{K}\pm\boldsymbol{\tau})$ and magnetization vectors $[\mathbf{P}(\mathbf{K}\pm\boldsymbol{\tau})]$, φ is the relative phase angle taking $\gamma_1 = 0$ and $\gamma_2 = \varphi$. In this case we have three parameters: the magnetic form factor, the magnitude of the magnetic moment and the phase angle. These three parameters together with the z parameter of the Ge ion were refined to give a best fit (least squares) of the calculated to the observed integrated intensities. The calculated intensities together with the observed integrated intensities are given in Table 3. The parameter values are given in Table 4. The weighted R factor is 7·3%. We have no explanation for the fact that the refined values of the magnetic moment ($\mu = 3{\cdot}7 \pm 0{\cdot}3\mu_B$) and the magnetic form factor are larger than the expected values: $gJ = 3{\cdot}2\mu_B$ for the magnetic moment and the approximated values (Blume, Freeman & Watson, 1962) for the magnetic form factor.

The ordering of the Co ion leads to more ambiguous results. There are four magnetic ions and therefore three relative phase angles. The highest symmetry case, relative phase angles equal to zero, leads to zero intensity for the satellites with l odd, in contradiction to the observed data. There is also the possibility of three arbitrary phase angles; in view of the limited amount of data (six lines) and the satisfactory agreement given by the ordering of the Pr ions, this possibility was not explored. We conclude that it is the Pr sublattice which orders magnetically in $PrCo_2Ge_2$. The magnetic structure is shown in Fig. 4.

Table 3. *Comparison of calculated and observed integrated intensities in the LT pattern of* $PrCo_2Ge_2$

The calculated magnetic intensities were obtained from the refined-parameter values of Table 4.

Number	$\{hkl\}$	$I_{obs} \pm \sigma$	I_{calc}
1	002^-	0 ± 500	0
2	001^+	0 ± 500	0
3	002	0 ± 500	807
4	003^-	0 ± 500	0
5	011^-	10 900 ± 570	11 330
6	$010^\pm$	0 ± 500	0
7	011, 002^+	21 500 ± 650	18 943
8	012^-	0 ± 500	0
9	011^+	6 700 ± 570	5 355
10	004^-	0 ± 500	0
11	013^-	4 200 ± 620	3 534
12	110, 111^-, $110^\pm$	34 700 ± 850	37 587
13	012^+, 003^+, 112^-	4 800 ± 500	4 574
14	013, 111^+, 004	70 900 ± 800	68 992
15	112, 014^-	14 100 ± 500	12 898
16	113^-	0 ± 500	0
17	005^-	0 ± 500	0
18	112^+, 013^+	4 150 ± 600	3 480
19	004^+	0 ± 500	0
20	114^-	2 200 ± 680	1 740
21	113^+	0 ± 500	0
22	006^-, 021^+, 114, 014^+, 022	34 000 ± 900	38 437
23	023^-, 121^-, 115^-, 015, $120^\pm$, 121, 005^+, 022^+, 122^-	38 600 ± 1300	39 949

Table 4. *Ionic parameters of* $PrCo_2Ge_2$ *at RT and LT*

	RT	LT
μ(Pr) (μ_B)	–	3·7 ± 0·3
g(Pr)*	–	1·7 ± 3·4
φ	–	0
z(Ge)	0·370 ± 0·001	0·368 ± 0·001
B (Å^2)	0·9 ± 0·9	0
R (%)	6·8	7·3

* $f(\mathbf{K}\pm\boldsymbol{\tau}) = e^{g(\mathrm{Pr})(\sin\theta/\lambda)^2}$.

V. Discussion and conclusion

Magnetic ordering of the A rather than the B sublattice was reported previously (Pinto & Shaked, 1973) in the isostructural compound $NdFe_2Si_2$. Ordering of the R sublattice where R = Pr, Gd, Tb in the series RFe_2Ge_2 has also been reported (Malik, Sankar, Rao & Obermyer, 1976). Susceptibility measurements on RCo_2Ge_2 [R = La, Yb, Lu and Y (McCall *et al.*, 1973*b*)] show that the susceptibilities are independent of temperature. From this they conclude that the Co in these compounds does not order magnetically. Our data are insufficient to test exhaustively models in which the Co atoms carry the moment *or* in which both

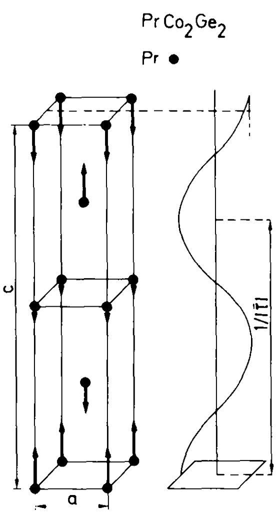

Fig. 4. Magnetic structure of $PrCo_2Ge_2$. Two crystallographic cells are shown.

Co and Pr atoms are magnetically ordered. Therefore the conclusion that it is the Pr atoms which give rise to the magnetic scattering, in spite of their apparently high moment, rests rather heavily on what has been found in structurally related materials. Neutron diffraction patterns of YCo_2Ge_2 at RT and LT measured in the course of this work are essentially the same. We also studied the compound $NdCo_2Ge_2$ that belongs to the same series. The neutron diffraction patterns indicate the existence of magnetic ordering at 28 ± 1 K, but the magnetic structure seems different and much more complicated; in view of the poorness of the data, we are not able, for the moment, to solve it.

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Refinement of Metal *d*-Orbital Occupancies from X-ray Diffraction Data*

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Abstract

Expressions are derived relating the occupancies of transition-metal *d* orbitals in a trigonal distortion of an octahedral field to the populations of multipole density functions refined from X-ray diffraction data. The expressions are used to obtain the iron *d*-orbital configuration in cubic FeS_2 by least-squares refinement of very high resolution single-crystal X-ray intensity measurements. The refined populations correspond to a large distortion of the iron electron density from spherical symmetry towards a low-spin configuration.

Introduction

Compounds containing transition-metal atoms have been the subject of a number of recent experimental electron-density determinations using accurate X-ray (and neutron) diffraction measurements (for example Iwata, 1977; Iwata & Saito, 1973; Marumo, Isobe, Saito, Yagi & Akimoto, 1974; Rees & Mitschler, 1976; Vicat, Tranqui & Aleonard, 1977; Wang & Coppens, 1976). Deviations from a spherical density distribution are generally found about the metal atom which can often be interpreted qualitatively in terms of partial occupancy of the *d* orbitals.

A more quantitative description of the electronic structure of the metal atom may be obtained by fitting the charge distribution with a small number of analytical density functions. Several models are currently in use for describing the electron density distribution in crystals with a series of atom-centered multipole functions (Hansen & Coppens, 1978; Harel & Hirshfeld, 1975; Stewart, 1976). Within the limits of the crystal field theory which neglects covalent interactions between the metal atom and ligands, simple relationships between populations of spherical harmonic functions on metal atoms and *d*-orbital occupancies can be derived. As an example, the relationships for a metal atom on a $\bar{3}m$ site are derived here and applied to the analysis of single-crystal diffraction data from iron pyrite (Stevens, DeLucia & Coppens, 1979).

Orbital products

For a trigonal distortion from octahedral symmetry (Ballhausen, 1962), it is convenient to express the

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* Electron Population Analysis of Accurate Diffraction Data. VIII. Part VII: Coppens, Guru Row, Leung, Stevens, Becker & Yang (1979).

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