Solid State Communications, Vol. 45, No. 2, pp. 209–213, 1983.
Printed in Great Britain

0038–1098/83/020209–05$03.00/0
Pergamon Press Ltd.

NEUTRON DIFFRACTION STUDIES OF THE MAGNETIC ORDERING IN THE RARE EARTH COMPOUNDS $TbNi_2Si_2$, $HoCo_2Si_2$ AND $TbCo_2Si_2$

V.N. Nguyen, F. Tcheou and J. Rossat-Mignod

Centre d'Etudes Nucleaires de Grenoble, Laboratoire de Diffraction Neutronique,
Departement de Recherche Fondamentale 85X, 38041 Genoble Cédex, France

and

R. Ballestracci

Faculté des Sciences de Toulon, 83130 La Garde, France

(*Received* 30 *July* 1982 *by E.F. Bertant*)

Neutron diffraction studies and magnetic measurements on the compounds $TbNi_2Si_2$ (1), $HoCo_2Si_2$ (2) and $TbCo_2Si_2$ (3) revealed a collinear antiferromagnetic order below $T_N = 10 \pm 1$ K (1), $T_N = 13 \pm 1$ K (2) and $T_N = 30 \pm 2$ K (3) with the rare earths moments oriented along the c-axis [$m_0 = 8.8 \pm 0.2\,\mu_B$ (1), $m_0 = 8.1 \pm 0.2\,\mu_B$ (2), $m_0 = 8.8 \pm 0.2\,\mu_B$ (3)] and the corresponding wavevector are $\mathbf{k} = [\frac{1}{2}\frac{1}{2}0]$ (1) and $\mathbf{k} = [0\,0\,1]$ (2) (3). The magnetic structure of the compounds $HoCo_2Si_2$ and $TbCo_2Si_2$ consists of ferromagnetic layers perpendicular to the c-axis coupled antiferromagnetically (+ − + −) while for $TbNi_2Si_2$ the ordering within (0 0 1) plane is antiferromagnetic and the planes (0 0 1) are indeed decoupled.

1. INTRODUCTION

THE CRYSTAL STRUCTURE and magnetic properties of the compounds RCo_2Si_2 and RNi_2Si_2 where R is a rare earth element have been reported by Rieger *et al.* [1], Yakinthos *et al.* [2, 3]. They crystallize in the $ThCr_2Si_2$ type, body centred tetragonal structure (space group $I(4/m).m.m$). For RNi_2Si_2 [2], it was found that the compounds with R = Gd, Tb and Dy order antiferromagnetically below respectively $T = 15.5$ K, $T = 14.0$ K, $T = 7.0$ K whereas the compounds with R = Ho, Er and Tm do not show any ordering down to 4.2 K. The temperature dependence of the reciprocal susceptibility was found to be curvilinear for $ErNi_2Si_2$ at high temperatures, while for the other compounds it follows a Curie–Weiss law.

For RCo_2Si_2 [3] it was found that the compounds for which R = Gd, Dy and Er are antiferromagnetic with Néel temperatures respectively 44, 21 and 6 K; their paramagnetic temperatures are negative whereas the compounds with R = Tb and Ho seem to be ferromagnetic with Curie temperatures of 8 and 15 K respectively. YCo_2Si_2 does not exhibit any magnetic moment, then in these compounds cobalt or nickel atoms are not magnetic.

In the present paper, we report the results of neutron diffraction and magnetic measurements on polycrystalline samples of $TbNi_2Si_2$, $HoCo_2Si_2$ and $TbCo_2Si_2$ undertaken in order to determine the magnetic structures.

2. EXPERIMENTAL

The samples were prepared by melting the rare earth metal (4 N), cobalt (4 N) and the silicium (4 N purity) in an induction furnace. The samples were then annealed in a quartz tube at 900°C for 100 hr and cooled down to room temperature. The single phase nature of the compounds was established by X-ray analysis using $FeK\alpha$ radiation. All the lines observed have been indexed in a tetragonal $ThCr_2Si_2$ type structure. Magnetic measurements were carried out in a magnetic field of 1 kOe with a translation balance installed at the Laboratoire de Louis Néel C.R.N.S. Grenoble. Neutron diffraction data ($\lambda = 1.41$ Å) were performed with the spectrometer DN_5 of the Siloe reactor of the Centre d'Etudes Nucléaires de Grenoble.

For $TbNi_2Si_2$, $HoCo_2Si_2$ and $TbCo_2Si_2$, neutron diffraction patterns were taken at room temperature and liquid helium temperatures (see Figs. 1 and 2). For $HoCo_2Si_2$ and $TbCo_2Si_2$, we have the same neutron diffraction pattern with the same magnetic peaks. Only the diffraction pattern of $HoCo_2Si_2$ is represented in Fig. 2.

3. RESULTS

3.1. *Magnetic measurements*

The thermal variation of the reciprocal susceptibility, in the temperature range 4.4 to 300 K, is shown in Fig. 3.

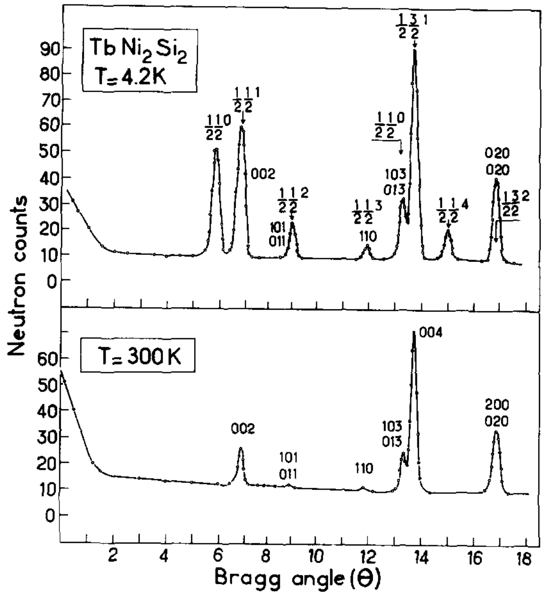

Fig. 1. Neutron diffraction patterns of $TbNi_2Si_2$ in the paramagnetic and in the ordered phases. Magnetic reflections are associated to a wavevector $\mathbf{k} = [\frac{1}{2}\frac{1}{2}0]$.

At low temperatures, $TbNi_2Si_2$, $HoCo_2Si_2$ and $TbCo_2Si_2$ exhibit antiferromagnetic properties with Néel temperatues $T_N = 10$, 13 and 30 K respectively. At high temperatures, the reciprocal susceptibility obeys a Curie–Weiss law, the paramagnetic Curie temperatures θ_p and the effective magnetic moments are given in Table 1. The paramagnetic temperatures are positive for $TbCo_2Si_2$ and $HoCo_2Si_2$ but slightly negative for $TbNi_2Si_2$ giving evidence for predominant positive interactions in $TbCo_2Si_2$, $HoCo_2Si_2$ and for negative interactions in $TbNi_2Si_2$.

3.2. *Crystal structure*

For $TbNi_2Si_2$, $HoCo_2Si_2$ and $TbCo_2Si_2$, the observed reflections in the neutron diffraction patterns in the paramagnetic region i.e. at room temperature were indexed in the quadratic system respecting the extinction condition of the space-group $I(4/m)m.m$. Nuclear intensities were calculated for the following atomic positions:

R atoms in the position $2a$: $(0, 0, 0)$

Co or Ni atoms in $4d$: $(0, \frac{1}{2}, \frac{1}{4})$; $(\frac{1}{2}, 0, \frac{1}{4})$

Si atoms in $4e$: $(0, 0, z)$; $(0, 0, \bar{z})$

The crystal structure can be described as a stacking of plans perpendicular to the c-axis with the sequence R–Si–Co–Si–R (with R = Tb, Ho) located respectively at the values $z = 0$, $\frac{1}{2} - z(\text{Si}) = 0.130$, $z(\text{Si}) = 0.370$, and 0.50 (Fig. 4).

The lattice parameters a and c of the tetragonal cell and the parameter of the silicon position $z(\text{Si})$ were refined by least squares routines leading to satisfactory agreement between observed and calculated values of the peaks positions and the integrated intensites using the following scattering lengths: $b_{\text{Tb}} = 0.76$, $b_{\text{Ho}} = 0.85$, $b_{\text{Co}} = 0.25$, $b_{\text{Ni}} = 1.03$ and $b_{\text{Si}} = 0.4 \times 10^{-14}$ m. The refined parameters and corresponding R_N factor are given in Table 1. The mixing of cobalt and silicon atoms $4d$ and $4e$ positions was not confirmed by our experiments.

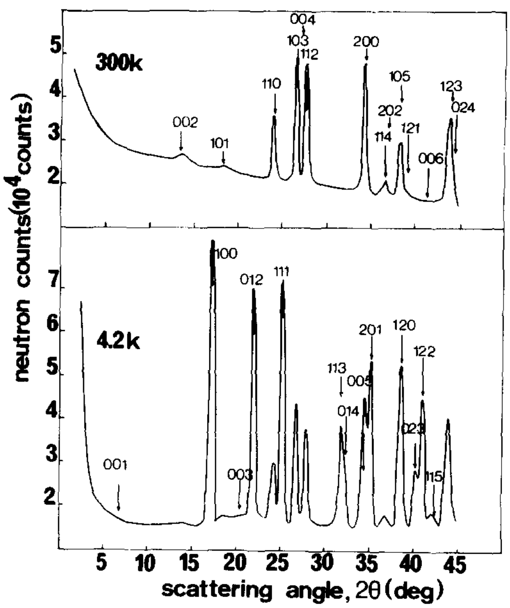

Fig. 2. Neutron diffraction patterns of $HoCo_2Si_2$ in the paramagnetic and in the ordered phases. Magnetic reflections are associated to a wavevector $\mathbf{k} = [0\,0\,1]$.

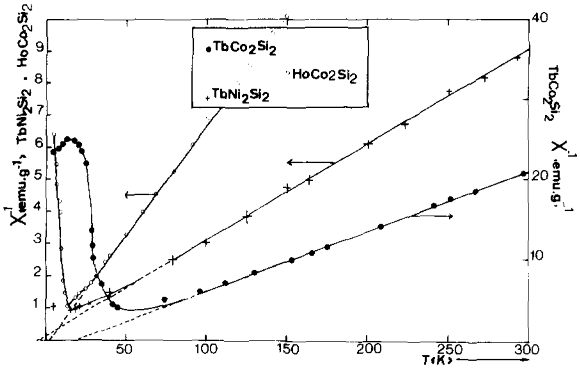

Fig. 3. Variation of the reciprocal susceptibility with temperature for $TbNi_2Si_2$, $HoCo_2Si_2$ and $TbCo_2Si_2$.

3.3. *Magnetic structures*

For $TbNi_2Si_2$, when cooling down to 4.2 K the sample, seven additional reflections have been observed in the neutron diffraction pattern (Fig. 1). No shift of the nuclear peaks was detected. The new reflections were easily indexed on the basis of the crystallographic

Table 1. Magnetic and structural parameters of the compounds $TbCo_2Si_2$, $HoCo_2Si_2$ *and* $TbNi_2Si_2$

	$TbNi_2Si_2$	$HoCo_2Si_2$	$TbCo_2Si_2$
a(Å)	3.952 ± 0.003	3.887 ± 0.003	3.885 ± 0.003
c(Å)	9.542 ± 0.002	9.688 ± 0.002	9.743 ± 0.002
z(Si)	0.372	0.371	0.370
R_n(%)	7	8	7.5
$\mu(\mu_B)$	8.8 ± 0.2	8.1 ± 0.1	8.8 ± 0.2
R_m(%)	8	5	5
$T_N(k)$	10 ± 1	13 ± 1	30 ± 2
$\theta_p(k)$	− 5	+ 4	20 ± 2
$\mu_{\text{eff}}(\mu_B)$	10.1	10.6	10.2

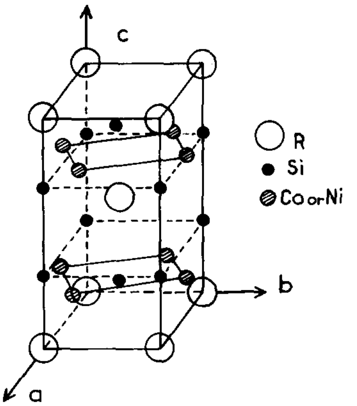

Fig. 4. Crystallographic unit cell of $TbNi_2Si_2$, $TbCo_2Si_2$ and $HoCo_2Si_2$.

unit cell with the Miller index (h_m, k_m, l_m) with $h_m = (h/2)$, $k_m = (k/2)$ and $l_m = l$, h and k taking odd numbers which conduct to the wavevector $k = [\frac{1}{2}\frac{1}{2}o]$. This vector is indeed a symmetry point of the first Brillouin zone, then it describes a simple antiferromagnetic ordering.

For $HoCo_2Si_2$ or $TbCo_2Si_2$, the neutron diffraction pattern at 4.2 K (Fig. 2) shows many superlattice peaks of magnetic origin which can be indexed on the basis of the crystallographic unit cell with the magnetic indices obeying the $\mathbf{H}_m = \mathbf{H}_N + [0\,0\,1]$ condition where $\mathbf{H}_m$ is the scattering magnetic vector, $\mathbf{H}_N$ is the nuclear lattice vector and $\mathbf{k} = [0\,0\,1]$ is the wavevector associated with the magnetic structure. This vector $\mathbf{k} = [0\,0\,1]$ is also a symmetry point of the first Brillouin zone corresponding to the space group $I(4/m)m.m$ in the case $c > a$.

In the structure of $ThCr_2Si_2$-type, the rare earth atoms can be generated only by one Bravais lattice located in (0 0 0). Then the arrays of the magnetic moments can be deduced from the knowledge of the wavevector by using the relation:

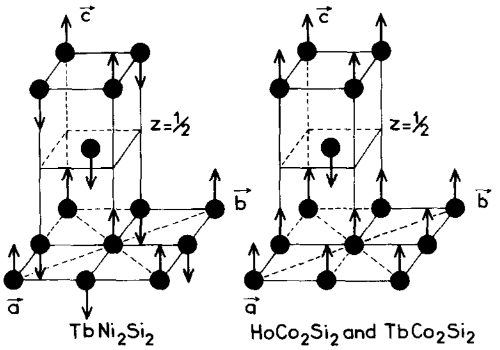

Fig. 5. Magnetic structures of $TbNi_2Si_2$ $[\mathbf{k} = (\frac{1}{2}\frac{1}{2}0)$, $\mathbf{m}_0 \parallel c]$ and $HoCo_2Si_2$ or $TbCo_2Si_2$ $[\mathbf{k} = (0\,0\,1)$, $\mathbf{m}_0 \parallel c]$.

$$\mathbf{m}(\mathbf{R}_n) = \mathbf{m}_0 \cdot e^{2\pi i(\mathbf{k}\cdot\mathbf{R}_n)} \tag{1}$$

For both cases $\mathbf{k} = [\frac{1}{2}\frac{1}{2}0]$ ($TbNi_2Si_2$) and $\mathbf{k} = |0\,0\,1|$ ($HoCo_2Si_2$ or $TbCo_2Si_2$), there are an antiparallel coupling of magnetic moments of rare earth atoms located in neighbouring (0 0 1) planes; the corresponding magnetic structure are represented in Fig. 5. The problem now is to determine the directions of the magnetic moments for the compounds $TbNi_2Si_2$, $HoCo_2Si_2$ and $TbCo_2Si_2$ which can be obtained from the intensities of the magnetic reflections.

The intensity associated with the magnetic scattering vector $\mathbf{h}_m$ is given by:

$$I(\mathbf{h}_n = \mathbf{H}_N + \mathbf{k}) = (0.27)^* f^2(h_m) \times \mathbf{F}(\mathbf{h}_m)^* \mathbf{F}^*(\mathbf{h}_m) - \frac{(\mathbf{F}(\mathbf{h}_m)^* h_m)(F(\mathbf{h}_m)\mathbf{h}_m)}{\mathbf{h}_m^2} \tag{2}$$

where $f_m(\mathbf{h}_m)$ is the form factor of rare earth ions R^{+3}, $\mathbf{h}_m = \mathbf{H}_N + \mathbf{k}$ ($\mathbf{H}_N$ is the nuclear vector and $\mathbf{k}$ is the wavevector associated with the magnetic structure).

$\mathbf{F}(\mathbf{h}_m)$ is the magnetic structure factor:

$$\mathbf{F}(\mathbf{h}_m = \mathbf{H}_N + \mathbf{k}) = \sum_{\substack{\text{Bravais}\\ \text{lattice}}} \mathbf{m}^{(i)}_{-k} \exp\left[2\pi i(\mathbf{H}_N + \mathbf{k})\cdot\mathbf{r}_i\right] \tag{3}$$

Table 2. Observed and calculated magnetic intensities (in barn/atom) for the compound $TbNi_2Si_2$

h_m, k_m, l_m	I_{ob}|barn/atom|	I_{cal}|barn/atom|
$\frac{1}{2}\frac{1}{2}0$	12.3	11.1
$\frac{1}{2}\frac{1}{2}1$	15.8	14.8
$\frac{1}{2}\frac{1}{2}2$	7.2	7.7
$\frac{1}{2}\frac{1}{2}3$	3.7	3.9
$\frac{1}{2}\frac{3}{2}0$	46.1	44.5
$\frac{1}{2}\frac{3}{2}1$		
$\frac{1}{2}\frac{3}{2}2$	19.3	22.3
$\frac{1}{2}\frac{1}{2}4$		
$\frac{1}{2}\frac{3}{2}3$	14.8	15.0

where the sum is performed over the Bravias lattices located at the positions $\mathbf{r}_i$. For $TbNi_2Si_2$ and $HoCo_2Si_2$ or $TbCo_2Si_2$, the fact that we have only one Bravais lattice and that the wavevectors $\mathbf{k} = [\frac{1}{2}\frac{1}{2}0]$ and $\mathbf{k} = [0\,0\,1]$ represent two symmetry points of the first Brillouin zone conduct to the very simple relations:

$$\mathbf{m}_{-k} = m_0 \cdot \mathbf{u} \quad \text{and} \quad \mathbf{F}(\mathbf{h}_m) = m_0 \cdot \mathbf{u} \tag{4}$$

where m_0 is the moment value and $\mathbf{u}$ is a unit vector defining the moment direction. Consequently, the magnetic intensity associated with the vector $\mathbf{h}_m$ and corresponding to one Bravais lattice is given by:

$$I(\mathbf{h}_m) = (0.27)^2 \cdot f_m^2(\mathbf{h}_m) m_0^2 \;\; 1 - \frac{(\mathbf{u} \cdot \mathbf{h}_m)^2}{\mathbf{h}_m^2} \cdot \tag{5}$$

Of course in a powder pattern, we must sum over the equivalent scattering vectors. The magnetic intensites have been normalized in comparison with the intensities calculated per one formula unit of $TbNi_2Si_2$.

The calculation of the magnetic intensities were carried out for two models:

(1) Only rare earth atoms carry a magnetic moment.

(2) Magnetic moments are located on rare earth atoms and cobalt or nickel atoms.

For $TbNi_2Si_2$, the fitting of the calculated magnetic intensities to the experimental data leads to a reliability factor $R = 8\%$ (Table 2) with the terbium moments oriented along the c-axis. The terbium moment value has been found to be $m_0 = 8.8 \pm 0.2\,\mu_B$ assuming that nickel has no magnetic moment. For $TbNi_2Si_2$, the magnetic structure is represented in Fig. 5(a). The magnetic structure of this compound consist of ferromagnetic planes which are no correlation between them leading to a two-dimensional magnetic behavior as it was shown in the known compound K_2NiF_4 [4].

For $HoCo_2Si_2$, the fact that the magnetic reflections (0 0 1) and (0 0 3) of the powder pattern were not observed at 4.2 K indicates that the rare earth magnetic moments are parallel to the c-axis.

Table 3. Calculated and observed magnetic intensities (in barn/atom) for the compound $HoCo_2Si_2$

$h_m\,k_m\,l_m$	$(I_m)_{calc}$	$(I_m)_{obs}$
0 0 1	0	0
0 1 0	17.5	20.0
1 0 0		
0 0 3	0	0
0 1 2	18.8	18.75
1 0 2		
1 1 1	26.8	26.0
1 1 3	17.6	17.1
0 1 4		
1 0 4		

Table 4 Calculated and observed magnetic intensities (in barn/atom) for the compound $TbCo_2Si_2$

h_m, k_m, l_m	$(I_m)_{calc}$	$(I_m)_{obs}$
0 0 1	0	0
0 1 0	17.6	17.5
1 0 0		
0 0 3	0	0
0 1 2	19.5	17.3
1 0 2		
1 1 1	26.6	25.5
1 1 3	17.0	16.8
0 1 4		
1 0 4		
0 0 5	0	0
2 0 1	20.0	21.0
0 2 1		
0 2 3	38.8	38.1
2 0 3		
1 2 2		
2 1 2		
1 1 5	5.0	4.3
1 0 6	7.5	7.6
0 1 6		

The fitting of the calculated magnetic intensities to the experimental data gives rise to a minimum R_m reliability factor of 5% (Table 3): the holmium moment value has been found to be $m_{Ho} = 8.1 \pm 0.1\,\mu_B$ at $T = 4.2$ K. This value is smaller than that expected for the Ho^{+3} free ion (e.g. $J = 10.0\,\mu_B$). The magnetic structure of the compound $HoCo_2Si_2$ is shown in Fig. 5(b). This magnetic structure corresponds to a stacking of ferromagnetic sheets along the c-axis with a (+ − + −) sequence. On the other hand, in the compound $HoCo_2Si_2$, our results demonstrate that cobalt atoms do not participate in the magnetic ordering. This result can be understood by the filling of the cobalt 3*d* band with electrons from silicon atoms.

For $TbCo_2Si_2$, the magnetic structure is similar to that of $HoCo_2Si_2$. The calculated and observed magnetic intensities are given in Table 4. The Terbium moments are also parallel to the c-axis and have the value $m_{Tb} = 8{,}8 \pm 0.2\,\mu_B$.

CONCLUSIONS

The magnetic structures of $HoCo_2Si_2$ and $TbCo_2Si_2$ at determined in our study, agrees well with that reported recently by Szytula *et al.* for the compound $HoCo_2Ge_2$ (4) and $TbCo_2Si_2$ (5): magnetic moment within a (0 0 1) plane are coupled ferromagnetically, indeed in the plane the distance between two neighbour ions is fairly small i.e. it is the lattice constant a. Adjacent planes are coupled antiferromagnetically so that their sequence in the direction of the c-axis is (+ — + —). Two adjacent planes are however separated by three atomic layers composed of non-magnetic Si, Co or Ni as the experiment shows, do not carry magnetic moments. Therefore, the magnetic interactions between two rate earth atoms belonging to adjacent planes must be much smaller than their plane interactions. Therefore the magnetic structure explains quite well the positive Curie temperature determined by susceptibility measurements which indicate that the interactions have mainly a ferromagnetic character.

In the compounds $TbNi_2Si_2$, the magnetic structure could be visualized as a piling up of antiferromagnetic planes along the c-axis: the (0 0 1) plane at $z = \frac{1}{2}$ is not correlated with those at $z = 0$ and $z = 1$. However for $TbNi_2Si_2$ and $HoCo_2Si_2$, our measurements are in contradiction with those of reference [3] which indicated a ferromagnetic behavior.

We also studied the compounds $HoNi_2Si_2$ and $DyNi_2Si_2$ that belong to the same series. For $DyNi_2Si_2$, a large bump appeared at 1.4 K which results from a short range ordering of the magnetic moments of dyposium ions. It is necessary to go down lower than 1.4 K to get a long range magnetic ordering.

For $HoNi_2Si_2$ a long range ordering associated with two wavevectors $\mathbf{k} = [0\,0\,1]$ and $\mathbf{k} = [0.517, 0, 0]$ was observer at $T = 1.4$ K, then the magnetic structure is different and much more complicated. More experimental data is needed to solve the magnetic structure.

Acknowledgements – The authors are grateful to Mr G. Quezel and M. Maeder of the Laboratoire Louis Néel C.N.R.S. Grenoble for their technical assistance and valuable discussions.

REFERENCES

1. W. Rieger & E. Parthe, *Monatsh Chem.* **100**, 444 (1969).
2. J.K. Yakinthos & P.F. Ikonomou, *Solid State Commun.* **34**, 777 (1981).
3. J.K. Yakinthos & P.F. Ikomonou. *J. Less-Common Met.* **72**, 205 (1980).
4. A.R. De Jough, & Ado Miedema, *Physic* **23**, 1 (1974).
5. A. Szytula, J. Leciejewicz & H. Binczycka, *Phys. Status Solidi* (*a*) **58**, 67 (1980).
6. A. Szytula, S. Siek & J. Leciejewicz, *IV International Conference on Crystal Electric Field and Structural effects in f electron-systems,* Wrockaw, 22–25 September 1981.
7. I. Felner & I. Mayer, *Mater. Res. Bull.* **8**, 1317 (1973).