JOURNAL OF SOLID STATE CHEMISTRY 3, 154–160 (1971)

Magnetic and Crystallographic Structures of Me_xNbS_2 and Me_xTaS_2

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Received September 2, 1970

The crystal structures of the compounds Me_xNbS_2 and Me_xTaS_2 with $x = 1/3$ and $1/4$ are described. The magnetic structures of those compounds which show magnetic ordering at 4.2°K were also determined by means of neutron powder diffraction. The compounds with $x = 1/4$ show an anomaly in the χ^{-1} versus T curve. This phenomenon is shown to be correlated with a discontinuity in the variation of the c/a ratio with temperature.

Introduction

The work described in this paper deals with compounds the crystal structures of which can be deduced from the 2*s*-NbS_2 structure (*1*) by introducing transition metal atoms into the octahedral holes between the sulphur layers. Only those phases in which the transition metal atoms are ordered were taken into consideration.

The crystal structure of the phase with one transition metal atom per three NbS_2 units has been reported by Van den Berg and Cossee (*2*) and by Anzenhofer, Van den Berg, Cossee, and Helle (*3*), who obtained their results from single crystal X-ray diffraction data. Their findings are essentially in accordance with the results from neutron diffraction powder data which are presented in this paper.

Recently (*4–6*), evidence has been obtained for the existence of a phase with one transition metal atom per four NbS_2 units. The structure of this phase was, in Ref. (*4*), deduced from neutron data and the structural parameters were determined.

The occurrence of magnetic ordering at 4.2°K has been studied by neutron diffraction. Of all compounds in which such ordering was detected the susceptibility as function of the temperature has been measured.

Experimental

Preparation of the Samples

The samples were prepared from the oxides of the constituent elements by mixing thoroughly and heating the mixture in platinum crucibles in air at 1000°C for one day. The resulting product was powdered, reduced in a H_2S atmosphere at 1150°C using carbon crucibles, annealed during four days at 800°C and subsequently slowly cooled down. The samples obtained by this method were completely free of oxides.

All samples were checked for other phases by taking X-ray diagrams with a Philips diffractometer (CuK_α radiation).

Single-phase products were obtained for the following compositions:

Me_xNbS_2: $x \approx 1/4$, Me = Mn, Cr;
$x \approx 1/3$, Me = Mn, Fe, Co, Ni, V;

Me_xTaS_2: $x \approx 1/4$, Me = Mn, Cr;
$x \approx 1/3$, Me = Fe, Co, Ni.

Neutron Diffraction

The neutron diffraction data have been collected on the powder diffractometer at the High Flux Reactor at Petten. The neutron wavelength was

TABLE I

ASYMPTOTIC CURIE TEMPERATURE θ, MOLAR CURIE CONSTANT C_{mol}, PARAMAGNETIC MOMENT $\mu_{eff} = \sqrt{8C_{mol}}$ AND EFFECTIVE NUMBER OF UNPAIRED ELECTRONS μ

(Standard deviations in units of the last decimal are given in parentheses).

	θ (K)	C_{mol}	μ_{eff}	μ
$Fe_{1/3}NbS_2$	−100(6)	3.04(3)	4.93(2)	4.03(2)
$Mn_{1/3}NbS_2$	+ 33(4)	3.87(3)	5.56(2)	4.65(2)
$Cr_{1/4}NbS_2$, high T	−243(24)	2.81(7)	4.74(6)	3.84(5)
low T	− 4(2)	2.09(1)	4.09(1)	3.21(1)
$Mn_{1/4}NbS_2$, high T	− 97(11)	4.63(6)	6.09(4)	5.17(4)
low T	+119(1)	3.68(1)	5.42(1)	4.51(1)
$Mn_{1/4}TaS_2$, high T	− 20(8)	3.92(4)	5.60(3)	4.69(3)
low T	+113(1)	3.51(1)	5.30(1)	4.39(1)

2.57 Å, obtained from the (111) planes of a copper crystal. As a second-order filter, a block of pyrolytic graphite with a thickness of 10 cm was employed (*7*). Between reactor and monochromator Soller slits with a horizontal angular divergence of 30′ were placed. The divergence of the slits in front of the BF_3 counter was 30′ in all cases except one in which slits of 10′ were used. The samples were contained in cylindrical vanadium sample holders with a diameter of 15 or 20 mm.

From all compounds, neutron diffraction diagrams were taken both at room temperature and at liquid helium temperature. From $Mn_{1/4}TaS_2$ a diagram was also taken at $T = 725$°K.

Magnetic Measurements

Susceptibility versus temperature measurements of the samples showing magnetic ordering at 4.2°K were carried out down to 80°K. It is assumed that the susceptibility can be described by

$$\chi_{mol} = A_{mol} + \frac{C_{mol}}{T - \theta},$$

where A_{mol} is a temperature independent contribution to the susceptibility, approximately equal to the diamagnetic correction. With A_{mol} being kept constant at these values, the parameters C_{mol} and θ were refined by a least-squares procedure. Their final values together with the resulting values for the paramagnetic moment $\mu_{eff} = \sqrt{8C_{mol}}$ and for μ, the number of unpaired electrons ($\mu_{eff} = \sqrt{\mu(\mu+2)}$), are given in Table I. Refinement of A_{mol} generally resulted in unacceptable values, due to the very strong correlation between A_{mol} and the other parameters.

Of the compounds with $x = 1/3$, the one with Me = Fe has a negative asymptotic Curie temperature θ while the one containing Mn has a positive θ (Fig. 1).

Although the θ values reported in Ref. (*2*) and (*3*) are somewhat different from ours they show the same behaviour.

Of the compounds with $x = 1/4$, those with Me = Mn show a definite transition point in their susceptibility curves (Fig. 2). For $Mn_{1/4}NbS_2$ and $Mn_{1/4}TaS_2$ these points are at 680 and 690°K respectively.

From the parts of the curves below and above

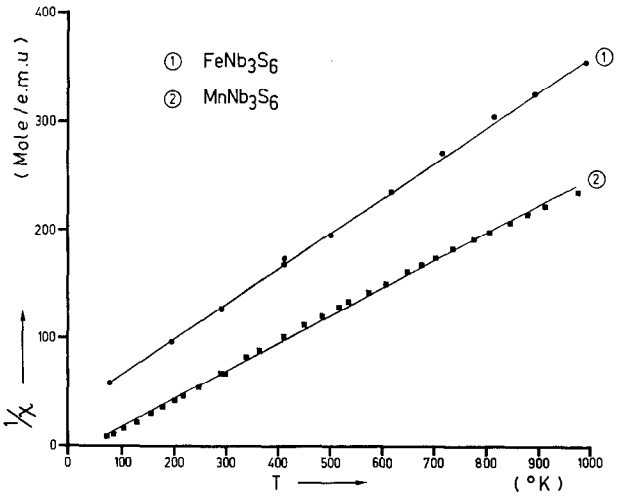

FIG. 1. Reciprocal susceptibility versus temperature of $Fe_{1/3}NbS_2$ and $Mn_{1/3}NbS_2$.

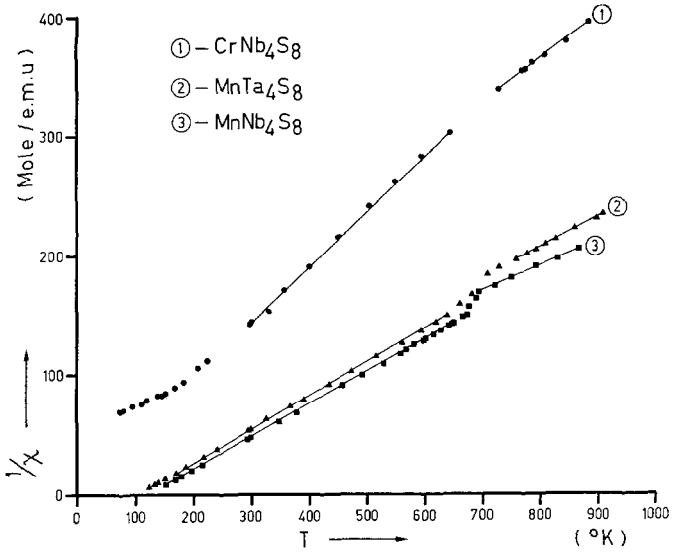

FIG. 2. Reciprocal susceptibility versus temperature of $Cr_{1/4}NbS_2$, $Mn_{1/4}TaS_2$, and $Mn_{1/4}NbS_2$.

the transition point, different values for θ and C_{mol} were obtained. It is noted that for both compounds negative values for θ were obtained from data above and positive values from data below the transition point. Also $Cr_{1/4}NbS_2$ shows a discontinuity in the susceptibility curve at 690°K but the effect is much less pronounced than in the two Mn compounds mentioned above.

Crystal Structures

$Me_{1/3}NbS_2$ and $Me_{1/3}TaS_2$

The cell constants of these hexagonal phases are related to the constants of the $2s$-NbS_2 type subcell, a' and c', by:

$$a \approx a'\sqrt{3} \quad \text{and} \quad c \approx c'.$$

The structure can be described as follows

Space group $P6_322(D_6^6)$;

2Nb(Ta) in (2a): 0, 0, 0;

4Nb(Ta) in (4f): $\frac{1}{3}, \frac{2}{3}, z$ with $z \approx 0$;

12S in (12*i*); x, y, z with $x \approx \frac{1}{3}$, $y \approx 0$, $z \approx \frac{1}{8}$;

2Me in (2c): $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$, and/or

(2a): 0, 0, 0, and/or

(2d): $\frac{2}{3}, \frac{1}{3}, \frac{1}{4}$.

The refinement of the structures from the neutron diffraction data has been performed by means of the profile refinement method (*8*). This method determines the estimates of the various parameters by finding a least-squares fit between the observed and calculated diagrams.

In addition to the positional parameters of the different atoms and the overall temperature factor, the occupation numbers of the transition metal atoms on the (2c), (2a), and the (2d) sites were also determined. These occupation numbers are defined as the fraction of a site which is occupied by metal atoms. In the case of the vanadium compound, this determination was not possible because of the negligibly small coherent scattering length of vanadium. The final least squares parameters are listed in Table II.

It can be seen that the deviations from the ideal structure are small. Furthermore it is clear that by far the larger part of the transition metal atoms are located at the (2c) site.

As an example the observed and calculated diffraction profile of $Fe_{1/3}NbS_2$ is shown in Fig. 3.

$Me_{1/4}NbS_2$ and $Me_{1/4}TaS_2$

The diagrams from these compounds were indexed on the basis of a hexagonal unit cell with $a = 2a'$ and $c = c'$, where a' and c' are again the cell constants of the $2s - NbS_2$ subcell.

The observed reflection condition (*hhl*: $l = 2n$) is compatible with the space group $P6_3/mmc$ (D_{6h}^4), which has been adopted throughout the investigation.

The assumption that in this compound the $2s - NbS_2$ (or $2s - TaS_2$) lattice remains more or

TABLE II

STRUCTURAL PARAMETERS AND MAGNETIC MOMENTS PER ATOM (μ_{at}) AND PER FORMULA UNIT (μ_{mol}), IN THE COMPOUNDS $Me_{1/3}NbS_2$ AND $Me_{1/3}TaS_2$

Me	$Me_{1/3}NbS_2$							$Me_{1/3}TaS_2$						
	Mn		Fe		Co	Ni	V	Fe		Co		Ni		
T (°K)	293	4.2	293	4.2	293	293	293	293		293		293		
a (Å)	5.7853(2)	5.7794(4)	5.7685(3)	5.7609(3)	5.7567(4)	5.7518(3)	5.7387(3)	5.7383(8)		5.7393(8)		5.7336(9)		
c (Å)	12.6377(8)	12.5993(13)	12.2056(6)	12.1786(8)	11.8667(11)	11.8796(8)	12.1126(10)	12.2392(16)		11.9329(19)		11.9353(20)		
N(2c)	0.94(3)	↓	0.922(6)	↓	0.87(5)	0.901(7)	1	0.779(6)		1.05(4)		0.824(5)		
N(2d)	0.05(2)	↓	0.026(5)	↓	0.11(4)	0.014(6)	—	0.004(6)		0.01(4)		0.022(5)		
N(2b)	0.01(3)	↓	0.019(5)	↓	0.06(5)	0.062(7)	—	0.066(7)		0.20(5)		0.065(6)		
x	0.335(7)	↓	0.323(3)	↓	0.31(1)	0.325(4)	$\frac{1}{3}$	0.283(5)		0.29(1)		0.304(5)		
z(4f)	0.9981(5)	0.9994(8)	0.9987(2)	0.9986(2)	0.9944(7)	0.9980(3)	0.9960(9)	0.9984(3)		0.9978(7)		0.9983(2)		
x(12i)	0.6727(38)	0.6746(45)	0.6717(17)	0.6711(15)	0.6615(46)	0.6667(21)	0.6733(56)	0.6700(24)		0.6659(42)		0.6688(18)		
y(12i)	0.0072(24)	0.0033(42)	0.0014(11)	0.0005(11)	−0.0122(25)	0.0030(15)	0.0011(55)	0.0016(13)		0.0024(33)		0.0017(11)		
z(12i)	0.1242(3)	0.1238(4)	0.1292(3)	0.1292(4)	0.1326(3)	0.1315(4)	0.1298(3)	0.1296(3)		0.1334(3)		0.1329(3)		
μ_{at} (μ_B)	—	4.0(1)	—	3.8(1)	—	—	—	—		—		—		
$3\mu_{mol}$ (μ_B)	—	3.8(1)	—	3.5(1)	—	—	—	—		—		—		

less unchanged, leads to the following positions for the atoms:

2Me in (2a): 0, 0, 0;
2Nb(Ta) in (2b): 0, 0, $\frac{1}{4}$;
6Nb(Ta) in (6h): x, $2x$, $\frac{1}{4}$ with $x \approx \frac{1}{2}$;
4S in (4f): $\frac{1}{3}$, $\frac{2}{3}$, z with $z \approx \frac{1}{8}$;
12S in (12k): x, $2x$, z with $x \approx \frac{5}{6}$, $z \approx \frac{1}{8}$.

This structure is identical to that given in the text of Ref. (5). It should be noted that in this reference an error has been made in the assignment of special positions to the metal atoms.

The structural parameters were also determined from neutron data by means of the profile refinement method. The resulting values for the different parameters are given in Table III. In this case the deviations from the ideal structure can also be seen to be very small.

In an attempt to relate the anomaly in the susceptibility versus temperature curve of the Mn-compounds to a structural change a neutron diagram of $Mn_{1/4}TaS_2$ was obtained at $T = 725$°K. The overall appearance of this diagram was almost identical with that of the diagram obtained at room temperature, and also the resulting parameters were almost equal (Table III). The only difference was in the c/a ratio which was 1.9039(2) at 725°K against 1.8893(2) and 1.8844(2) at room temperature and 4.2°K, respectively.

By means of high temperature Guinier X-ray photographs it was found that both compounds show a discontinuous change in the c axis at the transition points while the a axis remains practically constant.

Magnetic Ordering at 4.2°K

The neutron diagram at 4.2°K of $Co_{1/3}NbS_2$ showed a large number of very weak peaks, probably of magnetic origin, which could not be interpreted.

The diagrams of $Fe_{1/3}NbS_2$, $Mn_{1/3}NbS_2$, $Mn_{1/4}NbS_2$, and $Mn_{1/4}TaS_2$ showed clear magnetic peaks. The diagram of $Cr_{1/4}NbS_2$ showed a few, very weak, extra peaks while all other compounds failed to reveal any magnetic ordering at 4.2°K.

$Mn_{1/3}NbS_2$, $Mn_{1/4}NbS_2$, and $Mn_{1/4}TaS_2$

The magnetic scattering of these compounds occurred in the same directions as the nuclear scattering. This is what would be expected for ferromagnetic compounds.

Our neutron data were in accordance with a

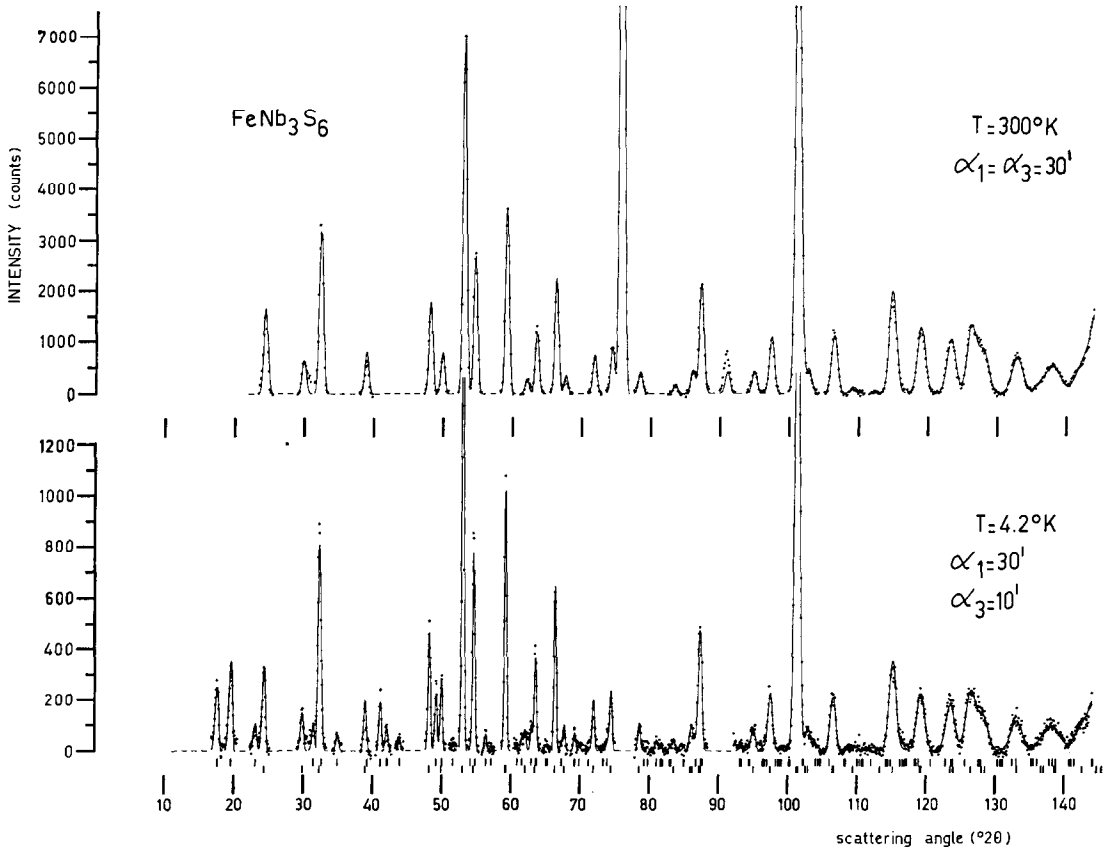

FIG. 3. Observed and calculated neutron diffraction profile of $Fe_{1/3}NbS_2$ at two different temperatures. The dots represent the observed profile, the full line the calculated profile.

model in which all moments are parallel to a certain direction in the hexagonal basal plane. From powder data this direction cannot be determined.

The structural and magnetic parameters, as determined with the line profile refinement method, are given in Tables II and III. In the refinement the spherical formfactor for Mn^{++} by Watson and Freeman (*9*) was used.

TABLE III

STRUCTURAL PARAMETERS AND MAGNETIC MOMENTS IN THE COMPOUNDS $Me_{1/4}NbS_2$ AND $Me_{1/4}TaS_2$

	$Me_{1/4}NbS_2$				$Me_{1/4}TaS_2$		
Me	Mn		Cr		Mn		
T (°K)	293	4.2	293	4.2	725	293	4.2
a (Å)	6.670(1)		6.634(1)	6.626(1)		6.645(1)	
c (Å)	12.491(2)		11.976(2)	11.952(2)		12.552(2)	
c/a	1.8726(2)	1.8676(2)	1.8054(1)	1.8038(1)	1.9039(2)	1.8893(2)	1.8844(2)
x(6h)	0.4947(9)	0.4942(11)	0.5049(6)	0.5023(14)	0.4949(4)	0.4910(4)	0.4921(8)
z(4f)	0.1244(18)	0.1154(27)	0.1169(11)	0.1156(14)	0.1182(31)	0.1213(11)	0.1221(23)
x(12k)	0.8322(10)	0.8361(18)	0.8319(7)	0.8307(8)	0.8342(27)	0.8315(7)	0.8319(14)
z(12k)	0.3759(7)	0.3713(11)	0.3822(5)	0.3812(5)	0.3731(10)	0.3742(4)	0.3753(9)
$\mu_{at}(\mu_B)$	—	3.4(1)	—	1.5(1)	—	—	4.2(1)

$Fe_{1/3}NbS_2$

All magnetic scattering from $Fe_{1/3}NbS_2$ occurred in directions other than the nuclear scattering. This indicates that no ferromagnetic component is present in the spinstructure.

The magnetic peaks could be indexed on an orthohexagonal cell with dimensions

$$a = 2a''$$
$$b = a''\sqrt{3}$$
$$c = c'',$$

where a'' and c'' are the sides of the crystallographic hexagonal cell. This orthohexagonal cell contains eight iron atoms.

Magnetic scattering was only apparent for those reflections which fulfilled both the conditions: $h = 2n + 1$ and $2k + 3l \neq 6m$, n and m being integers. This means that in this orthohexagonal cell each magnetic moment has antiparallel partners at $+(\frac{1}{2}, 0, 0)$ and at $+(0, \frac{1}{3}, \frac{1}{2})$. In terms of the nuclear hexagonal cell, this can be interpreted as follows: each moment has antiparallel partners at $+(1, 1, 0)$ and at $+(-\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$. All moments are parallel or antiparallel to the c axis. The ordering scheme of the moments is identical to that in the wurtzite form of β-MnS (*10*). In this scheme, usually referred to as an ordering of the third kind, the moment of each Fe atom is antiparallel to that of eight of the twelve nearest neighbours and parallel to the other four. Of the next-nearest neighbours two are antiparallel and four parallel.

The final structural and magnetic parameters, obtained with line profile refinement, are listed in Table II. In the refinement the spherical formfactor for Fe^{++} of Watson and Freeman (*9*) was used. The observed and calculated profile of $Fe_{1/3}NbS_2$ is shown in Fig. 3.

$Cr_{1/4}NbS_2$

The observed extra intensities from this compound at 4.2°K are few and very weak. Therefore it was not at all immediately clear that they could be considered to be of magnetic origin. It was found, however, that they could be indexed on the nuclear unit cell with the reflection condition $l = 2n + 1$. This suggests an arrangement of ferromagnetic planes perpendicular to the c axis with adjacent planes coupled antiferromagnetically. Inspection shows the moments to be aligned parallel and antiparallel to the c axis. The final parameters are listed in Table III. The low value of the observed Cr moment probably indicates that the magnetic ordering is not complete in the present sample.

Discussion

As indicated by Jellinek (*1*), trigonal prismatic MS_2 layers can be stacked in several ways. Introduction of transition metal atoms in the octahedral holes between two sulphur layers always gives rise to the occurrence of a 2*s*-NbS_2 structure type while introduction of copper in tetrahedral holes leads to a MoS_2 type of structure (*11*). In both cases the distances from the extra metal atoms to the nearest Nb-atoms, i.e. the distances along the c axis, are rather short. This suggests that some interaction between these atoms is present. This could explain that the number of unpaired electrons, deduced from the low temperature paramagnetic susceptibility data, is not an integer in most cases.

In the compounds with $x = \frac{1}{4}$ infinite rows –Me–Nb–Me–Nb– are present. The positions of the atoms on these strings are fixed by symmetry and the Me–Nb distance is exactly $c/4$. This causes a direct coupling of a variation of this distance to a variation in the length of the c axis in a fully cooperative process. This is in accordance with our observation, namely that in the compounds with $x = \frac{1}{4}$ an anomaly in the susceptibility versus temperature curve is correlated to a discontinuity in the length of the c axis. This transition is probably correlated to a change in the Me–Nb interaction.

In the susceptibility curve of $Mn_{1/3}NbS_2$ a deviation from the Curie–Weiss law is apparent (Fig. 1). The slope of the curve varies between values corresponding to $\mu_{eff} \approx 5.4\ \mu_B$, $\theta \approx 50$°K at low temperature and $\mu_{eff} \approx 5.8\ \mu_B$, $\theta \approx -40$°K at high temperature. Contrary to the case of $x = \frac{1}{4}$, no anomaly is found here; the variation takes place very gradually. This observation can also be described in the above developed formalism.

In the compounds with $x = \frac{1}{3}$, the Me atoms are not located in infinite rows but in more isolated Nb–Me–Nb groups. The z coordinates of the Nb atoms in these groups are not fixed by symmetry which means that a change in the Nb–Me interaction, and thus in the distance between these two atoms, will not necessarily manifest itself as a variation in the length of the c axis. The process will therefore be noncooperative and no anomaly will occur.

Acknowledgment

The authors wish to express their gratitude to Mr. K. Verhoeven and Dr. J. W. Roelofsen for performing the magnetic measurements. The assistance of Mr. J. F. Strang with the experimental diffraction work was very much appreciated.

References

1. F. JELLINEK, *Ark. Kemi* **20**, 447 (1963).
2. J. M. VAN DEN BERG AND P. COSSEE, *Inorg. Chim. Acta* **2**, 143 (1968).
3. K. ANZENHOFER, J. M. VAN DEN BERG, P. COSSEE, AND J. N. HELLE, *J. Phys. Chem. Solids* **31**, 1057 (1970).
4. B. VAN LAAR, H. M. RIETVELD, AND D. J. W. IJDO, III International Conference on Solid Compounds of Transition Elements, 1969, Oslo, Norway, Conference Abstracts page 79.
5. J. M. VOORHOEVE-NEE VAN DEN BERG AND M. ROBBINS, *J. Solid State Chem.* **1**, 134 (1970).
6. F. HULLIGER AND E. POBITSCHKA, *J. Solid State Chem.* **1**, 117 (1970).
7. B. O. LOOPSTRA, *Nucl. Instrum. Methods* **44**, 181 (1966).
8. H. M. RIETVELD, *J. Appl. Crystallogr.* **2**, 65 (1969).
9. R. F. WATSON AND A. J. FREEMAN, *Acta Crystallogr.* **14**, 27 (1961).
10. L. CORLISS, N. ELLIOTT, AND J. HASTINGS, *Phys. Rev.* **104**, 924 (1956).
11. K. KOERTS, *Acta Crystallogr.* **16**, 432 (1963).