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Structural Aspects and Magnetic Behaviour of NbS_2 and TaS_2 Containing Extra Metal Atoms of the First Transition Series

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A systematic investigation of the systems M–Nb–S and M–Ta–S (M=Mn, Fe, Co, Ni) revealed the presence of the compounds MNb_3S_6 and MTa_3S_6. Their structures were determined from powder diagrams. They proved to have a superstructure, derived from the 2s-NbS_2 type and resulting from an ordered distribution of the metal atoms M over the octahedral holes between the prismatic NbS_2 layers. The magnetic susceptibilities were measured; all the compounds showed a temperature-dependent paramagnetism with a spontaneous localized moment.

Introduction

An investigation of ternary transition-metal sulfides Cu_xNbS_2 and Cu_xTaS_2 ($x \sim 0.4$-0.67) showed that the additional copper atoms are statistically distributed over the tetrahedral holes between the prismatic sulfur layers, which are characteristic of NbS_2 and TaS_2.[1,2,3] This finding prompted us to investigate the behaviour of the elements Mn, Fe, Co, and Ni in the layer structures NbS_2 and TaS_2; it appeared that well-defined compounds MNb_3S_6 and MTa_3S_6 are formed, in which M is the first-row transition element. Their structural and magnetic properties were studied.

Experimental Section

Preparation. All the samples were prepared by heating weighed quantities of the elements in evacuated quartz tubes for one day; after crushing, the samples were reannealed at the same temperature for three days and cooled slowly.

Identification. From the change of cell dimensions of NbS_2 and TaS_2 observed on Guinier photographs it was concluded that the extra metal atoms M could be inserted in the empty octahedral interstices in the NbS_2 and TaS_2 lattice to give new compositions M_xNbS_2 and M_xTaS_2, with x ranging from 0 to $\sim 1/3$. In the range $x=0.30$-0.33 a single phase was detected with extra reflections pointing to a superstructure. The composition $x=1/3$ was chosen for further detailed work, because at this degree of filling one of the three possible crystallographic positions available for the extra metal atoms can be fully occupied, thus giving well-defined compounds MNb_3S_6 and MTa_3S_6.

Crystal Data. The compounds MNb_3S_6 and MTa_3S_6 could be indexed on a hexagonal lattice. The unit cell proved to be a supercell of the 2s-NbS_2 modification with an axis $a\sqrt{3}$ and about the same c-axis as that of NbS_2 and TaS_2. The cell parameters were determined from Guinier photographs calibrated with KCl, using a least-squares calculation. They are listed in Table I. The unit cell contained the formula unit $M_2(\text{Nb or Ta})_6S_{12}$ and the space group was found to be $P\,6_322$ or $P\,6_3/m$. As the rather strong additional reflections are caused by an ordering of the extra metal atoms and the space group $P\,6_322$ showed a better possibility for an ordering of these atoms than $P\,6_3/m$, the former was chosen.

Solution and Refinement. The intensities were measured from powder diffractograms. To obtain random orientation the substance was mixed with dry Canada balsam. Only the observed peaks which could be indexed unambiguously were used in the refinement. From the crystal data and the positions in 2s-NbS_2 the following initial positions were assumed:

12 S	in x, y, z (12 i) with $x=1/3$, $y=0$, $z=3/8$
4 $Nb_I(Ta_I)$	in 1/3, 2/3, z (4 f) with $z=0$
2 $Nb_{II}(Ta_{II})$	in 0, 0, 0, (2a)
2 M	in 1/3, 2/3, 1/4 (2c) or 2/3, 1/3, 1/4 (2d) or 0, 0, 1/4 (2b)

Considering that the extra reflections point to a superstructure, there are three possibilities for the position of the atoms M: 2c (≡2d) or 2b, or a statistical distribution over 2c and 2b. Calculation of the structure factors for the different possibilities showed that the best fit to experimental data could be obtained for 2 *M* in (2c), and this one was used in the least-squares refinement. The results are listed in Table II.

The shifts of the x- and y-parameters were not significant. The R factor was calculated for all the structure factors observed. Experimental and calculated structure factors are listed in Table VII.

In order to justify a unique conclusion that only (2c) is occupied, we tried the following procedure.* By

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(1) F. Jellinek, *Arkiv Kemi*, *20*, 447 (1963).
(2) K. Koerts, *Acta Cryst.*, *16*, 432 (1963).
(3) J. M. van den Berg, *J. Less-Common Metals*, *13*, 363 (1967).

(*) The statistical analysis was kindly performed for us by J. Meisner.

Table I. Cell dimensions with standard deviations

	a	c		a	c
$MnNb_3S_6$	5.782 (0)	12.629 (0.001)	$MnTa_3S_6$	5.757 (0)	12.697 (0.001)
$FeNbS_3S_6$	5.766 (0)	12.212 (0.000)	$FeTa_3S_6$	5.739 (0)	12.289 (0.001)
$CoNb_3S_6$	5.768 (0)	11.886 (0.001)	$CoTa_3S_6$	5.740 (0)	11.932 (0.000)
$NiNb_3S_6$	5.758 (0)	11.897 (0.000)	$NiTa_3S_6$	5.737 (0)	11.942 (0.001)
2s-NbS_2	$5.74 = a\sqrt{3}$	11.89	2s-TaS_2	$5.74 = a\sqrt{3}$	12.10

Table II. Atomic parameters with standard deviations

	x(S)	y(S)	z(S)	z(Nb_I)	B	R(%)
$MnNb_3S_6$	0.333	0	0.375 (0.002)	−0.001 (0.001)	1.20 (0.19)	17.9
$FeNb_3S_6$	0.333	0	0.375 (0.002)	−0.002 (0.001)	0.60 (0.34)	16.9
$CnNb_3S_6$	0.333	0	0.370 (0.002)	−0.003 (0.001)	0.38 (0.14)	11.3
$NiNb_3S_6$	0.333	0	0.365 (0.001)	−0.001 (0.001)	0.11 (0.06)	5.0
$MnTa_3S_6$	0.333	0	0.375 (0.004)	−0.000 (0.005)	0.76 (0.33)	6.7
$FeTa_3S_6$	0.333	0	0.371 (0.002)	−0.003 (0.002)	0.65 (0.28)	3.7
$CoTa_3S_6$	0.333	0	0.366 (0.003)	−0.002 (0.002)	0.10 (0.38)	9.1
$NiTa_3S_6$	0.333	0	0.369 (0.002)	−0.003 (0.001)	0.83 (0.22)	6.2

Table III. Occupation numbers with standard deviations

	x (2c)	x (2d)	x (2b)
$MnNb_3S_6$	0.272 (0.071)	0.008 (0.070)	0.050 (0.129)
$FeNb_3S_6$	0.190 (0.160)	0.000 (16.10^{-2})	0.140 (0.310)
$NiNb_3S_6$	0.212 (0.075)	0.046 (0.072)	0.072 (0.136)
$MnTa_3S_6$	0.250 (0.110)	0.050 (0.110)	0.030 (0.200)
$FeTa_3S_6$	0.172 (0.089)	0.000 (89.10^{-3})	0.158 (0.153)
$CoTa_3S_6$	0.213 (0.080)	0.048 (0.078)	0.069 (0.144)
$NiTa_3S_6$	0.259 (0.085)	0.013 (0.84)	0.058 (0.154)

introducing the occupation number x for the extra metal atoms M over the three positions (2c), (2d), and (2b) and subsequent least-squares refinement we followed the behaviour of x. This attempt failed because different minima could be calculated for x. The final R values were slightly larger (about 2-5%) than those in Table II for (2c) fully occupied, but no unique conclusion could be drawn. We therefore did a statistical calculation assuming that the sum of the occupation numbers is 1/3. The results in Table III show that our initial assumption of x (2c) = 1/3 is a reasonable one in most cases.* For some unknown reason the calculation was unsuccessful for $CoNb_3S_6$. Meanwhile we succeeded in isolating single crystals of some of the compounds. The preliminary results of analyses of these crystals completely support the ordering of M in (2c).**

Magnetic Measurements. The magnetic susceptibilities were measured on powder samples in a temperature range 100-1000 °K at different field strengths using the Faraday method. For compounds which showed a field dependence due to ferromagnetic impurities, the measured values were extrapolated to infinite field strength; otherwise the values were averaged.

Results and Discussion

Structures. When the disulfides in question are combined with extra metal atoms of the first-row transition elements these atoms are inserted into the octahedral holes between the layers of the 2s-NbS_2 type compounds (NbS_2 and TaS_2. The compounds MNb_3S_6 and MTa_3S_6 have one third of the available octahedra occupied. In the discussion we assume that position (2c) is fully occupied. The ordering of the metal atoms in the (001) planes is drawn in Figure 1. In Figure 2 we see that linear Nb_IMNb_I and Ta_IMTa_I groups are formed along the c-axis. As expected, the Nb_I and Ta_I atoms are shifted slightly to the vacant octahedra.

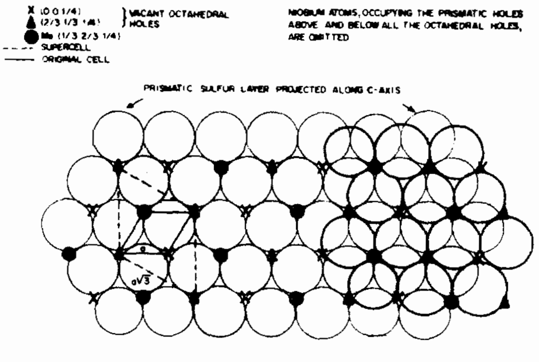
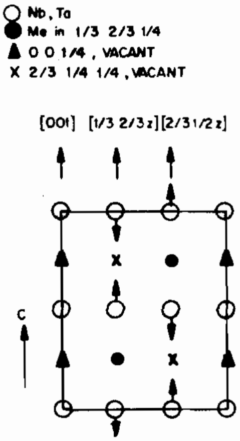


Figure 1. Ordering of the metal atoms.

The distances indicated in Figure 3 are listed in Table IV. From Tables I and III we see that the cell axis a is determined by the sulfur contacts (3) and the niobium and tantalum distances in the prismatic slabs. The c-axis is determined by the intermetallic M–Nb or M–Ta distance and the M–S distance; Mn and Fe expand the lattice, while Co and Ni have little influence on the NbS_2 lattice and even contract that of TaS_2. This influence on the lattice is mainly reflected in the S–S distances (5) between the prismatic layers. The M–S distances decrease in the order Mn, Fe, Co, Ni.

(*) Neutron diffractions carried out by the University of Leyden and R. C. N. Petten also support this conclusion according to discussion remarks made by D. J. W. Ydo and B. van Laar at the Second International Conference on Solid Compounds of Transition Elements, Enschede, June 12-16, 1967.

(**) Results will be published elsewhere.



Figur 2. Diagonal section (110) of $MNb_3(Ta_3)S_6$ (arrows indicate deviations from the ideal positions).

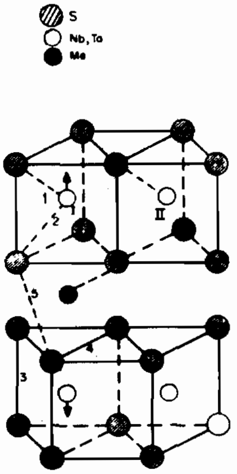


Figure 3. Interatomic distances calculated.

Table IV. Interatomic distances

	2s-NbS_2	$MnNb_3S_6$	$FeNb_3S_6$	$CoNb_3S_6$	$NiNb_3S_6$
M–S	(2.42)	2.491	2.454	2.394	2.357
M–Nb_I	(2.97)	3.170	3.077	3.008	2.984
Nb_{II}–S	2.47	2.491	2.454	2.467	2.502
Nb_I–S(1)	2.47	2.483	2.493	2.445	2.494
Nb_{II}–S(2)	2.47	2.499	2.470	2.489	2.510
Nb_I–Nb_{II}	3.31	3.338	3.329	3.330	3.324
S–S(3)	3.14	3.157	3.053	3.091	3.210
S–S(4)	3.31	3.338	3.329	3.330	3.324
S–S(5)	3.40	3.699	3.607	3.441	3.341

	2s-TaS_2	$MnTa_3S_6$	$FeTa_3S_6$	$CoTa_3S_6$	$NiTa_3S_6$
M–S	(2.44)	2.488	2.423	2.361	2.380
M–Ta_I	(3.03)	3.171	3.108	3.007	3.019
Ta_{II}–S	2.44	2.488	2.484	2.493	2.468
Ta_I–S(1)	2.44	2.488	2.461	2.478	2.446
Ta_I–S(2)	2.44	2.488	2.508	2.509	2.491
Ta_I–Ta_{II}	3.32	3.322	3.314	3.314	3.310
S–S(3)	3.03	3.171	3.170	3.198	3.126
S–S(4)	3.32	3.322	3.314	3.314	3.310
S–S(5)	3.58	3.706	3.535	3.365	3.422

Figure 4 shows that the occupied octahedral holes share faces with the occupied prismatic holes, resulting in short intermetallic distances. This points to intermetallic bonding between the two different metal atoms, which apparently plays an important role in the stability of this type of compound. We may compare them with the structure of $Cu2/3NbS_2$ and $Cu2/3TaS_2$, which have one third of the tetrahedra occupied in a statistical distribution (Figure 4). The preference of Cu for tetrahedral co-ordination and of Mn, Fe, Co, and Ni for octahedral co-ordination together with their tendency to intermetallic bonding with Nb or Ta may explain why copper compounds of NbS_2 and TaS_2 change into the 2s-MoS_2 type, while the other compounds preserve the 2s-NbS_2 type; in 2s-MoS_2 it is the tetrahedra and in 2s-NbS_2 the octahedra which are just above the occupied prismatic holes.

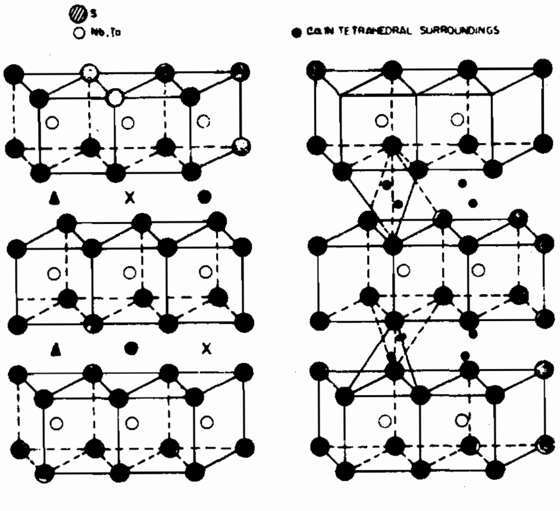


Figure 4. (a) Diagonal section (110) of $MNb_3(Ta_3)S_6$ with sulfur surroundings. (b) Diagonal section of Cu_xNbS_2 (≡ ($\bar{1}$10) section of 2s-MoS_2).

Magnetism. Plotting the experimental susceptibilities χ_{Mol} against the reciprocal temperature T^{-1}, we found that the χ values showed a linear dependence at temperatures above ~350 °K (Figure 5). This points to a normal Curie-Weiss behaviour with rather low values of θ, which causes a deviation from the linear curve at lower temperatures.

From an observation of the resulting curves it is immediately clear that in many instances a positive temperature-independent component will remain at infinite temperature, which in some cases even adopts an unusually high value we take into account that diamagnetic corrections have not yet been introduced in the curves shown.

An obvious method to analyse magnetic data such as the ones obtained here is to try whether the susceptibility can be described by a formula

$$\chi_{Mol} = A_M + \frac{C_M}{T-\theta}$$

Such an analysis gives inherently large uncertainties in A_M and θ, but a reasonable first approximation can be obtained for C_M.

The values of C_M, θ and A_M in Table V have been obtained by using a least-squares anlysis of the susceptibilities at 273°K and higher temperatures. It appeared that in a number of instances the values of χ at lower temperatures, especially liquid-nitrogen temperatures, were not easily incorporated in the series of measurements at higher temperatures. Therefore these points have been omitted systematically, which seems justified in view of the fact that magnetic interactions and the influence of impurities are becoming more important at lower temperatures. Considering the values of θ, all compounds are antiferromagnetic except those with manganese.

Table V. Magnetic parameters for $x = 1/3$ with standard deviations

	A_M (10^{-3} c.g.s.)	C_M	θ (°K)	$\mu = \sqrt{8C_M}$
$MnNb_3S_6$	0.48 (0.07)	2.88 (0.03)	68 (3)	4.80
$FeNb_3S_6$	0.33 (0.03)	2.39 (0.02)	− 67 (6)	4.36
$CoNb_3S_6$	0.82 (0.01)	0.55 (0.01)	− 72 (4)	2.09
$NiNb_3S_6$	0.21 (0.02)	0.44 (0.01)	− 21 (9)	1.87
$MnTa_3S_6$	0.29 (0.20)	2.91 (0.06)	112 (4)	4.82
$FeTa_3S_6$	0.30 (0.05)	2.65 (0.02)	− 11 (3)	4.60
$CoTa_3S_6$	−0.32 (0.02)	1.72 (0.02)	−136 (5)	3.71
$NiTa_3S_6$	−0.59 (0.03)	1.11 (0.01)	−190 (10)	2.98

Table VI. Magnetic parameters of $M_{0.2}NbS_2$

	A_M (10^{-3} c.g.s.)	C_M	θ	$\mu = \sqrt{8C_M}$
$MnNb_5S_{10}$	0.05 (0.02)	3.22 (0.04)	126 (3)	5.08
$FeNb_5S_{10}$	−0.13 (0.13)	2.67 (0.07)	50 (8)	4.62
$CoNb_5S_{10}$	0.83 (0.01)	0.69 (0.01)	− 95 (4)	2.35
$NiNb_5S_{10}$	0.11 (0.02)	0.48 (0.01)	− 44 (10)	1.95

We realize that this is a rather rough approximation (for example, by doing so we neglect the possibility of a temperature-dependent magnetic moment) and Table V certainly does not pretend to cover the only solution. If impurities are present which mainly influence the low-temperature measurements, and consequently the curvature in that region, the extrapolation on the other side of the curve where A_M is important becomes very uncertain.

That we are indeed also concerned with this kind of effect in the present case is demonstrated by the influence of small variations in the preparative procedures, which cause changes in θ and rather drastic ones in A_M. For further confirmation we carried out a series of measurements on the systems M_xNbS_2 with $x = 0.2$, which could be obtained more easily. Long reaction times were needed for the compounds with $x = 1/3$ to pass into the ordered modification. Comparing the results listed in Table VI with those of Table V, we found that A_M approximated the diamagnetic correction ($\sim 0.5 \times 10^{-3}$) more closely in a number of cases, where the temperature and reaction time during preparation were lower. Only in the system Co_xNbS_2 did the excessively large A_M value persist. This suggests that reaction of the samples with the silica tubes is responsible for impurities, which is reflected most clearly in A_M. Of course, this is also reflected in C_M, but its value is less sensitive to the uncertainties mentioned and can in most cases be reasonably approximated.

It is interesting to compare these compounds with the disulfides; NbS_2 shows a weakly temperature-dependent paramagnetism of the order of 0.1×10^{-3}, pointing to Pauli paramagnetism.[4] Evidently the interaction of the new metal atoms with a pair of niobium (or tantalum) atoms in adjacent layers causes the formation of a centre {NbMNb} or {TaMTa} where localized electrons can be stored, accompanied by a rearrangement of the electrons in niobium (and tantalum) layers.

We arrive at the following assignment for the valencies and configuration of the inserted transition elements:

Mn in NbS_2	Mn^{3+}	high spin d^4
Fe in NbS_2	Fe^{2+}	high spin d^6
Co in NbS_2	Co^{2+}	low spin d^7
Ni in NbS_2	Ni^{3+}	low spin d^7
Mn in TaS_2	Mn^{3+}	high spin d^4
Fe in TaS_2	Fe^{2+}	high spin d^6
Co in TaS_2	Co^{2+}	high spin d^7
Ni in TaS_2	Ni^{2+}	d^8

Judging from this evidence, only Mn can attain the trivalent state in both NbS_2 and TaS_2 compounds, whereas the other elements are incorporated as M^{2+}. If Mn becames trivalent the centres can be described as Nb^{3+} M^{3+} Nb^{3+} (or Ta^{3+} M^{3+} Ta^{3+}) with Nb^{3+} and Ta^{3+} in the diamagnetic state as observed in the isoelectronic MoS_2. With M^{2+} the same centres are found. However, the third Nb (or Ta) which is not coupled to inserted metal atoms remains in this way formally quadrivalent. The fact that only Mn is trivalent in both NbS_2 and TaS_2 compounds may be seen in the light of its lower ionization potential for d-electrons. The only exception seems to be Ni which in the NbS_2 compound is incorporated as Ni^{3+}. In this connection it is of interest to note another difference: Co and Ni are in a high-spin state in the TaS_2 compounds and in a low-spin state in the NbS_2 compounds. As matters

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(4) C. F. van Bruggen and F. Kadijk, private communication.

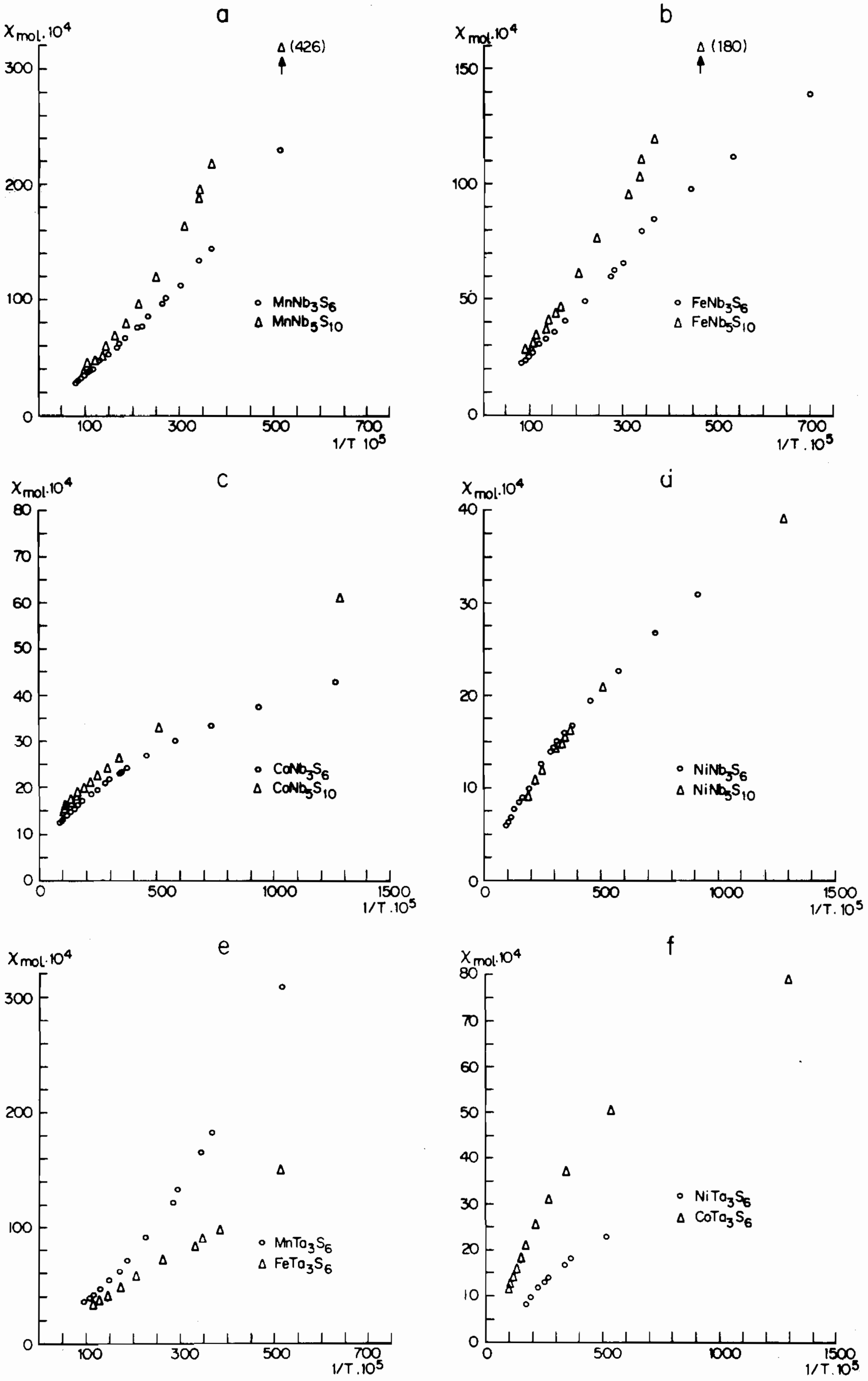

Figure 5. Magnetic susceptibilities *vs.* reciprocal temperature.

Table VII. Experimental and calculated structure factors

$MnNb_3S_6$		
h k l	F_o	$\sqrt{p} \times F_c$
1 0 0	86	67
1 0 1	138	158
1 0 2	73	89
1 0 3	180	155
1 1 0	442	482
1 1 1	343	373
1 0 4	119	78
1 1 2	591	642
2 0 1	128	127
1 1 3	312	334
2 0 2	91	73
1 0 5	166	111
2 0 3	136	129
1 1 4	1186	1123
1 1 5	314	295
1 2 0	86	66
1 2 1	135	154
1 2 3	145	159
1 1 5	626	523
1 0 7	145	120
3 0 0	772	834
2 1 4	80	82
3 0 2	497	504
2 0 6	57	58
1 1 7	314	243
2 1 5	120	120
3 0 4	354	290
2 0 7	172	107
2 2 0	349	338
2 2 1	257	237
2 2 2	481	451
2 1 6	78	73
1 3 0	75	51
1 1 8	685	461
1 3 1	181	121
2 2 3	226	226
1 3 3	131	127
2 2 4	829	800
3 0 6	435	417
2 1 7	142	136
2 2 5	205	216
4 0 2	107	45
1 0 10	107	45
2 0 9	147	62
2 2 6	374	392
4 0 4	74	43
3 1 6	104	60
1 1 10	647	372
2 3 0	55	42
3 0 8	1117	864
2 3 1	129	100
1 4 0	341	360
1 4 1	357	267
2 3 4	53	55
1 4 2	492	493
4 0 6	38	39
1 1 11	241	178
2 2 8	472	349
1 4 4	862	884
1 0 12	33	36
4 0 7	72	74
2 3 6	72	50
3 0 10	475	331
2 2 9	256	178
1 4 5	284	248
5 0 2	79	35
1 1 12	1334	591
3 1 9	151	67
2 0 12	42	33
1 4 6	528	437
2 3 7	1167	96
3 3 0	447	500

$FeNb_3S_6$		
h k l	F_o	$\sqrt{p} \times F_c$
1 0 0	56	67
1 0 1	117	155
1 0 2	78	90
1 0 3	163	164
1 1 0	401	482
1 1 1	301	371
1 1 2	612	642
1 0 4	74	78
2 0 1	112	126
1 1 3	324	338
2 0 2	89	74
1 0 5	133	98
2 0 3	152	139
1 1 4	1145	1131
1 2 0	73	67
1 0 6	73	67
1 2 1	144	155
1 1 5	274	294
1 2 3	159	174
3 0 0	778	862
1 1 6	476	527
1 0 7	180	139
3 0 2	452	518
1 2 4	74	85
1 2 5	150	109
1 1 7	352	256
3 0 4	273	303
1 0 8	51	55
2 2 0	293	356
2 2 1	203	249
2 0 7	103	126
2 2 2	418	477
2 2 3	194	241
1 3 2	111	75
1 1 8	709	478
1 3 3	212	143
1 0 9	78	53
2 2 4	780	851
2 0 8	46	51
3 0 6	538	448
1 2 7	164	164
1 1 9	242	227
2 2 6	455	419
2 3 3	88	64
3 0 8	1283	935
1 1 10	553	403
4 0 5	72	60
2 2 7	253	213
1 4 0	352	399
1 4 1	268	295
1 3 7	129	141
1 0 11	103	114
1 4 2	505	550
2 3 4	57	61
1 4 3	276	289
2 2 8	439	382
2 3 5	172	78
1 1 11	444	202
1 4 4	807	991
1 3 8	47	57
1 2 10	47	60
5 0 0	33	28
2 3 6	69	57
1 0 12	47	38
5 0 1	81	66
1 4 5	336	276
2 2 9	234	194

$CoNb_3S_6$		
h k l	F_o	$\sqrt{p} \times F_c$
1 0 0	50	47
1 0 1	113	105
1 0 2	80	63
1 0 3	134	123
1 1 0	336	369
1 1 1	270	282
1 1 2	477	534
1 0 4	75	54
2 0 1	107	85
1 1 3	271	289
2 0 2	93	52
1 0 5	118	55
2 0 3	147	105
1 1 4	831	875
1 2 1	119	105
1 1 5	209	192
2 0 5	89	48
1 2 3	164	132
3 0 0	662	679
1 1 6	394	395
3 0 2	402	403
1 2 4	80	59
1 2 5	71	61
1 1 7	265	242
3 0 4	249	233
2 2 0	286	278
2 2 1	190	193
1 0 8	35	37
2 0 7	117	103
2 2 2	453	404
2 2 3	183	212
1 1 8	479	372
2 2 4	647	673
3 0 6	439	427
2 0 9	40	17
1 2 8	120	45
2 2 6	300	321
3 0 8	742	736
1 1 10	458	375
2 3 3	118	95
2 2 7	252	206
1 4 0	238	317
1 4 1	266	235
1 2 9	19	21
1 4 2	513	478
2 3 4	46	42
1 4 3	249	259
2 2 8	355	304
2 3 5	47	43
1 4 4	744	800
1 1 11	189	210
1 3 8	33	39
3 0 10	245	218
5 0 3	66	59
3 3 0	465	470
1 4 6	385	386
2 3 7	102	104
3 3 2	306	280
5 0 4	26	26
1 2 11	166	124
1 1 12	632	512
2 2 10	393	322
2 4 3	98	78
1 4 7	313	257

$NiNb_3S_6$		
h k l	F_o	$\sqrt{p} \times F_c$
1 0 0	46	85
1 0 1	166	200
1 0 2	69	113
1 0 3	196	193
1 1 0	626	594
1 1 1	441	425
1 1 2	809	835
1 0 4	85	94
2 0 1	156	156
1 1 3	469	486
2 0 2	121	90
1 0 5	145	133
2 0 3	199	159
1 1 4	1384	1383
1 2 1	168	193
1 0 6	87	80
1 1 5	257	234
2 0 5	174	118
1 2 3	191	200
3 0 0	1078	1078
1 1 6	563	565
1 0 7	151	148
3 0 2	607	592
1 2 4	107	103
1 1 7	419	430
3 0 4	401	398
2 2 0	494	453
2 2 1	278	298
2 0 7	131	135
2 2 2	632	651
2 2 3	341	364
1 1 8	638	636
1 3 3	197	167
2 2 4	1083	1087
1 0 9	75	85
2 0 8	55	62
3 0 6	682	769
2 2 5	179	191
2 0 9	78	79
1 2 8	82	82
2 2 6	472	472
3 0 8	1182	1171
2 3 3	140	145
1 1 10	647	675
2 2 7	360	375
1 4 0	533	527
1 4 1	376	370
1 2 9	105	104
2 0 10	54	55
1 3 7	154	155
1 4 2	784	791
2 3 4	76	76
1 4 3	467	455
2 2 8	580	531
1 4 4	1290	1321
1 3 8	66	72
1 1 11	352	380
5 0 3	110	91
3 0 10	290	241
3 3 0	818	788

$MnTa_3S_6$		
h k l	F_o	$\sqrt{p} \times F_c$
1 0 1	126	174
1 0 2	96	96
1 0 3	139	157
0 0 4	469	431
1 1 0	868	968
1 1 1	373	402
1 0 4	75	85
1 1 2	1204	1315
2 0 1	131	140
1 1 3	320	368
2 0 3	126	132
1 1 4	1740	1807
0 0 6	483	497
1 1 5	291	321
1 2 3	161	165
1 1 6	1081	1098
1 0 7	114	116
3 0 0	1208	1290
3 0 2	1042	1063
0 0 8	857	725
1 1 7	244	279
3 0 4	760	805
2 0 7	99	104
2 2 0	656	714
2 2 1	219	266
1 2 6	78	83
2 2 2	924	975
1 1 8	974	986
1 3 1	144	140
2 2 3	153	258
1 3 3	129	135
2 2 4	1304	1354
3 0 6	895	926
1 2 7	129	134
0 0 10	430	370
1 3 4	88	75
1 1 9	286	246
2 2 5	184	244
2 2 6	837	861
1 1 10	895	844
4 0 4	51	49
1 3 6	75	70
3 0 8	1400	1406
2 3 0	48	49
2 3 1	119	119
1 4 0	755	801
1 4 1	294	312
2 3 4	63	65
4 0 6	42	46
1 4 2	1060	1110
1 1 11	208	218
2 2 8	769	784
0 0 12	318	246
1 4 4	1472	1555
3 0 10	819	737
2 2 9	230	207
2 3 6	66	60
1 4 5	234	291
5 0 0	33	30
5 0 1	81	72
1 1 12	1176	1059
1 3 9	113	102
5 0 3	73	70
1 4 6	1053	999
2 3 7	104	99
3 3 0	810	837
2 2 10	708	694
5 0 4	42	40
3 3 2	703	692

$FeTa_3S_6$		
h k l	F_o	$\sqrt{p} \times F_c$
1 0 0	47	59
1 0 1	118	128
1 0 2	101	80
1 0 3	178	171
0 0 4	357	350
1 1 0	793	788
1 1 1	301	319
1 0 4	65	68
1 1 2	104	108
2 0 1	188	103
1 1 3	288	320
2 0 2	68	66
2 0 3	139	145
1 1 4	1425	1463
0 0 6	421	426
1 2 0	98	59
1 1 5	220	225
1 2 1	125	127
1 2 3	190	182
1 1 6	845	855
3 0 0	1052	1055
1 0 7	169	170
1 2 4	76	74
3 0 2	877	849
0 0 8	565	579
1 1 7	250	262
1 2 5	49	52
3 0 4	718	659
2 2 0	595	586
2 0 7	157	154
2 2 1	218	213
2 2 2	830	808
2 2 3	227	227
1 1 8	793	794
1 3 2	66	66
1 3 3	147	151
2 0 8	42	42
2 2 4	1091	1108
3 0 6	792	803
1 2 7	198	200
0 0 10	265	262
2 2 6	665	679
2 3 1	86	86
1 1 10	716	713
3 0 8	1139	1148
2 3 2	55	56
1 4 0	634	664
1 3 7	165	173
1 4 1	240	252
2 3 4	54	52
1 4 2	955	931
4 0 6	42	39
1 4 3	256	271
2 2 8	609	639
1 1 11	191	219
1 2 10	57	57
1 3 8	47	47
0 0 12	198	198
1 4 4	1290	1286
2 0 11	146	144
5 0 0	27	25
1 4 5	207	209
5 0 1	60	53
2 2 9	138	128
3 0 10	568	526
5 0 2	147	34
5 0 3	82	80
4 0 8	33	31
1 1 12	869	842
1 2 11	198	192
1 4 6	822	796
3 3 0	721	697
2 3 7	156	152
2 0 12	26	27
5 0 4	32	32
3 3 2	585	564
2 2 10	606	595

$CoTa_3S_6$		
h k l	F_o	$\sqrt{p} \times F_o$
1 0 0	51	51
1 0 1	100	114
1 0 2	64	68
1 0 3	118	135
0 0 4	343	309
1 1 0	640	691
1 1 1	252	270
1 1 2	858	964
1 0 4	53	59
2 0 1	140	93
1 1 3	272	303
2 0 2	93	57
2 0 3	171	116
1 1 4	1164	1288
0 0 6	459	407
1 2 1	120	116
1 1 5	158	157
3 0 0	893	957
1 1 6	769	739
1 0 7	136	127
3 0 2	744	752
1 2 4	65	66
0 0 8	602	511
1 2 5	98	66
1 1 7	254	267
3 0 4	589	608
2 2 0	507	539
1 0 8	41	42
2 2 1	259	190
2 2 2	745	759
2 2 3	190	227
1 1 8	783	741
1 3 3	144	125
2 2 4	963	1027
1 0 9	16	19
2 0 8	37	39
3 0 6	751	808
1 2 7	144	154
1 3 5	73	55
0 0 10	280	211
1 2 8	54	52
2 2 6	645	619
1 0 10	40	40
3 0 8	1057	1057
4 0 5	37	36
1 1 10	767	723
2 2 7	248	233
2 3 3	117	110
1 4 0	519	639
1 2 9	19	21
1 4 1	192	236
1 4 2	802	923
2 3 4	42	49
2 2 8	577	628
1 4 4	1139	1253
1 1 11	217	239
1 3 8	43	45

$NiTa_3S_6$		
h k l	F_o	$\sqrt{p} \times F_c$
1 0 0	57	84
1 0 1	157	182
1 0 2	91	112
1 0 3	215	235
0 0 4	494	447
1 1 0	1012	1074
1 1 1	392	427
1 1 2	1393	1473
1 0 4	86	90
2 0 0	110	64
2 0 1	174	137
1 1 3	430	445
2 0 2	115	87
1 0 5	100	62
2 0 3	266	192
1 1 4	1887	1959
0 0 6	653	587
1 2 1	150	165
1 0 6	72	79
1 1 5	256	275
1 2 2	98	106
1 2 3	202	238
3 0 0	1387	1416
1 1 6	1123	1122
1 0 7	261	220
3 0 2	1114	1131
1 2 4	94	95
0 0 8	777	752
1 1 7	368	365
3 0 4	861	873
2 2 0	779	780
1 0 8	58	58
2 2 1	229	280
2 0 7	193	198
2 2 2	1075	1089
2 2 3	254	312
1 1 8	1106	1039
1 3 3	190	192
2 2 4	1450	1460
2 0 8	53	52
3 0 6	1132	1096
1 2 7	241	254
0 0 10	326	320
1 3 5	48	47
1 2 8	67	67
2 2 6	890	881
1 0 10	58	57
3 0 8	1462	1460
1 1 10	1018	949
4 0 5	32	29
2 2 7	321	298
2 3 3	174	161
1 4 0	884	865
1 2 9	19	18
1 4 1	334	326
1 3 7	189	216
1 4 2	1276	1236
2 3 4	66	63
1 4 3	270	365
2 2 0	849	823
2 3 5	171	37
1 4 4	1725	1662
1 1 11	311	300
1 3 8	257	56
0 0 12	191	255
2 3 6	54	61
1 4 5	219	249
3 0 10	677	636

Accolades: overlapping reflections.

stand, with the difficulties possibly related to impurities, we do not feel justified in attempting a more detailed description. We hope that measurements on single crystal samples will throw more light on this matter.

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