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Intercalation of the Niobium–Diselenide Layer Structure by First-Row Transition Metals

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The systems M_xNbSe_2 (where M = Ti, V, Cr, Mn, Fe, Co, Ni) were prepared. It appeared that the limit of solid solution was reached at $x \approx \frac{1}{3}$. Crystallographic ordering and changes in the *c*-axis of $NbSe_2$ were observed. Unit cell parameters and crystallographic orderings are compared with those observed in analogous NbS_2 systems.

Introduction

A recent study (*1*) of the structural behavior of NbS_2 and TaS_2 revealed that the first-row transition metals Mn, Fe, Co, and Ni can be inserted into the octahedral holes between the prismatic sulfur layers, characteristic of NbS_2 and TaS_2. Superstructures, resulting from an ordering of the inserted metals, were formed. A similar behavior could be expected for the selenides. We therefore started an investigation on combinations of the first-row transition metals with $NbSe_2$.

Experimental

The samples $M_xNbSe_2 (x = 0 \rightarrow \frac{1}{2})$ were prepared by firing pressed pellets, of the appropriate mixtures of the elements, in sealed evacuated quartz tubes at 800C for 48 hr. The tubes were allowed to cool in the furnace.

The cell dimensions were calculated from the back reflections of Debye–Scherrer photographs, using a least-squares program. (M. H. Mueller and L. Heaton, report no. ANL-6176). $CuK_{\alpha 1}$ radiation ($\lambda = 1.54051$) was used and the reflections were corrected for shrinkage of the film and absorption, using the Nelson–Riley's extrapolation.

In a number of samples small traces ($\leqslant 5\%$) of first-row transition metal selenides could not be avoided, even after regrinding and annealing. It appeared that this does not influence the lattice constants significantly.

Structural Properties

Diffractometer diagrams (CuK_α radiation) of M_xNbSe_2 showed that the transition metals V, Cr, Mn, Fe, Co, and Ni can be inserted between the prismatic $NbSe_2$ layers; only Ti showed much less tendency to enter the lattice. The inclusion of these metals could be concluded from changes in the *c*-axis of 2*s*-$NbSe_2$ and the observation of weak superlattice reflections, pointing to a possible ordering of the transition-metal atoms. These observations, roughly similar to those in NbS_2, gave us reason to assume that the metal atoms enter the octahedra between the $NbSe_2$ layers (Fig. 1). The stronger reflections could be indexed on the original hexagonal lattice of the 2*s*-$NbSe_2$ type (*2*). At concentrations of x varying from $\frac{1}{4}$ to $\frac{1}{3}$ weak superlattice reflections showed up corresponding to a unit cell with an axis $2a$ and not with an axis $a\sqrt{3}$ as observed in the sulfides for $x = \frac{1}{3}$. The periodicity in the *c*-direction was the same as in 2*s*-$NbSe_2$. From the possible orderings it was found that with this $2a$-supercell a well-defined ordered compound could be expected at $x = \frac{1}{4}$, as shown in Fig. 2. At this concentration one quarter of the octahedra are occupied. For the $2a$-superlattice, the systematic extinctions hhl, $l = 2n + 1$ were observed. Using the space group P63/mmc of 2*s*-$NbSe_2$, the ordered structure for $M_{1/4}NbSe_2$ can be described on the following initial positions:

12 S in $x, 2x, z$ (12*k*) with $x = \frac{1}{6}$, $z = \frac{1}{8}$.
4 S in $\frac{1}{3}, \frac{2}{3}, z$ (4*f*) with $z = \frac{5}{8}$
6 Nb in $\frac{1}{2}, 0, 0$ (6*g*).
2 Nb in 0, 0, 0 (2*a*).
2 M in $0, 0, \frac{1}{4}$ (2*b*).

With M in the position (2*b*) the super-reflections $hkl (l = 2n + 1)$ would be extinguished. It proved

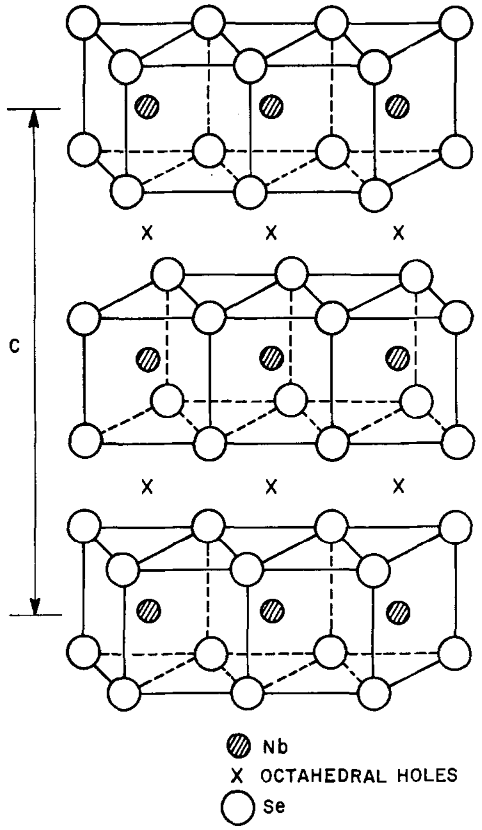

FIG. 1. Stacking of prismatic layers in 2*s*-$NbSe_2$.

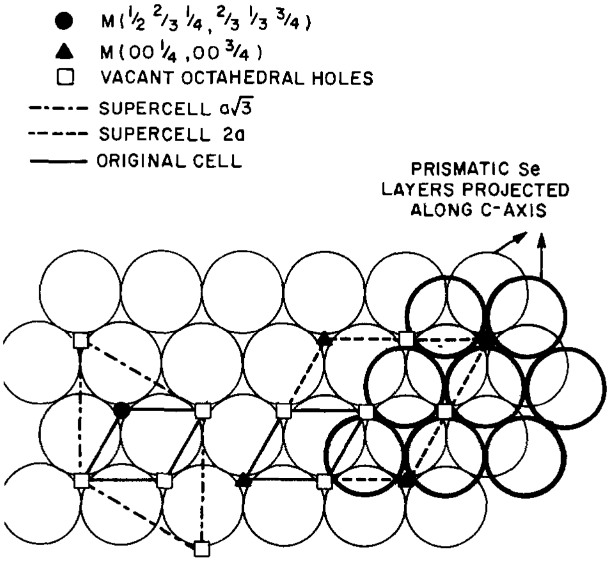

FIG. 2. Possible orderings of inserted metal atoms ($z = \frac{1}{4}$) between two prismatic layers.

more difficult to get all the samples completely ordered at $x = \frac{1}{4}$, and up till now annealing at various temperatures did not change the superlattice reflections significantly. Apparently, a higher concentration made it easier to completely fill one crystallographic position, the rest being randomly distributed. We observed the same phenomenon at $x = \frac{1}{2}$, where in the systems containing Mn, Fe, Co, and Ni superlattice reflections corresponding to an axis $a\sqrt{3}$ were observed. This type of ordering corresponds to the concentration $x = \frac{1}{3}$, and is extensively discussed in a previous paper (*1*). This behavior shows that possibly a concentration higher than $x = \frac{1}{3}$ can be inserted in the four mentioned systems. An example of this is shown in Table III where the low-angle reflections for $Fe_{1/3}NbSe_2$ and $Fe_{1/2}NbSe_2$ are listed. Most of the superlattice reflections were observed below $\theta = 27$.

TABLE I

LATTICE CONSTANTS OF THE SYSTEMS M_xNbSe_2

	a	*c*
$V_{1/4}NbSe_2$	3.451	12.660
$V_{1/3}NbSe_2$	3.454	12.673
$Cr_{1/4}NbSe_2$	3.452	12.570
$Cr_{1/3}NbSe_2$	3.452	12.567
$Mn_{1/4}NbS_2$	3.462	12.899
$Mn_{1/3}NbSe_2$	3.469	13.033
$Mn_{1/2}NbSe_2$	3.476	13.165
$Fe_{1/4}NbSe_2$	3.454	12.623
$Fe_{1/3}NbSe_2$	3.459	12.671
$Fe_{1/2}NbSe_2$	3.468	12.773
$Co_{1/4}NbSe_2$	3.452	12.379
$Co_{1/3}NbSe_2$	3.456	12.384
$Ni_{1/4}NbSe_2$	3.453	12.419
$Ni_{1/3}NbSe_2$	3.456	12.413
$NbSe_2$	3.442	12.54

TABLE II

COMPARISON OF *c*-AXES OF $M_{1/3}NbS_2$ AND $M_{1/3}NbSe_2$; $\Delta = c_{(x=1/3)} - c_{(x=0)}$

M	$NbSe_2$		NbS_2(*1*)	
	c	Δ	*c*	Δ
None	12.54		11.89	
Mn	13.033	0.493	12.629	0.739
Fe	12.671	0.131	12.212	0.322
Co	12.384	−0.156	11.886	−0.004
Ni	12.413	−0.137	11.897	0.007

TABLE III

LOW-ANGLE REFLECTIONS FROM DIFFRACTOGRAMS (CuKα; θ = 10–27°)

$Fe_{1/3}NbSe_2$
Systematic extinctions (hhl), $l = 2n + 1$.
P6₃/mmc, indexed on 2a-supercell

$10^4 \sin^2 \theta_{obs}$	$10^4 \sin^2 \theta_{calc}$	hkl	I_{obs}
311	314	102	w
496	497 499	110 103	vw
592	592	004	w
645	645	112	vw
663	663	200	w
698	699	201	st
756	758	104	w
809	811	202	st
994	996	203	st
1089	1089 1091	114 105	w
1161	1159	210	vw
1252	1255	204	vst
1300	1307	212	vw
1331	1333	006	m
—	1491 1492	300 213	—
1499	1498	106	w
—			
—	1527	301	—
1588	1588	205	mst
1640	1639	302	vw
—	1751	214	—
1818	1824 1829	303 116	w
—	1979	107	—
1988	1987 1995	220 206	st
775		?	w

$Fe_{1/2}NbSe_2$
Systematic extinctions ($00l$), $l = 2n + 1$.
P6₃22; indexed on $a\sqrt{3}$-supercell

$10^4 \sin^2 \theta_{obs}$	$10^4 \sin^2 \theta_{calc}$	hkl	I_{obs}
365	365	102	vw
548	547	103	w
583	583	004	w
659	659	110	mw
695	695	111	st
805	802 804	104 112	st
—	878	200	—
916	915	201	w
987	986	113	st
1024	1024	202	vw
1130	1130	105	w
—	1206	203	—
1242	1241	114	vst
1312	1311	006	mw
—	1461	204	—
—	1531 1537	106 210	— —
1570	1570 1574	115 211	m
—	1683	212	—
—	1789	205	—
1866	1865	213	vw
1977	1970 1976	116 300	st
609		FeSe	w

The intensities of $Fe_{1/2}NbSe_2$ show roughly the same trend as those of $Fe_{1/3}NbS_2$ (*1*). A largely similar pattern was observed for the rest of the systems.

In order to determine the influence of the inclusion of metal atoms on the $NbSe_2$ lattice, the cell constants of the subcell were calculated. For those systems, where the concentration $x = \frac{1}{2}$ did not show any change in axes compared to the lower concentrations, these calculations were omitted.

From the results listed in Table I it appears that in the Mn and Fe system the concentration is indeed higher than $x = \frac{1}{3}$, as in these cases there is an expansion of the lattice up to $x = \frac{1}{2}$. As the sample $Fe_{1/2}NbSe_2$ contains an excess of ferromagnetic iron, the maximum concentration with our experimental conditions must be somewhere between $x = \frac{1}{3}$ and $\frac{1}{2}$. As a check, a number of samples Fe_xNbSe_2 ($x > \frac{1}{2}$) were prepared. The lattice constants appeared to be the same as for $Fe_{1/2}NbSe_2$ and an increase of ferromagnetic iron as function of concentration was observed. From the fact that the samples $V_{1/2}NbSe_2$ and $Cr_{1/2}NbSe_2$ contained a considerable amount of V and Cr selenides, a maximum concentration of

$x \leqslant \frac{1}{3}$ may be concluded. This is also evident from the much slower increase of the c-axis after an initial expansion at $x = \frac{1}{4}$.

The lattice constants of the compounds $M_{1/3}NbSe_2$ ($M = Mn$, Fe, Co, Ni) are compared with those of the corresponding sulfides (Table II). In NbS_2, Mn, and Fe cause an expansion of the lattice in the c-direction. Ni causes a small expansion and Co causes a slight contraction of the lattice. In the selenides (as compared to the sulfides) Mn and Fe bring about smaller expansions of the lattice. For Co, a larger contraction of the lattice is observed and for Ni a change from a small expansion in the sulfide to a contraction of the lattice in the selenide. These differences are undoubtedly caused by the presence of larger octahedral holes in $NbSe_2$ than in NbS_2. The effective paramagnetic moment of Mn in $Mn_{1/3}NbSe_2$ as obtained from magnetic measurements (inverse susceptibility vs. temperature) is $4.90\mu_B$. This is in good agreement with the spin-only moment $4.91\mu_B$, calculated for Mn^{3+}. Room-temperature Mössbauer spectra indicate the iron in $Fe_{1/3}NbSe_2$ is Fe^{2+}. Crystal growth of these materials is being carried out by vapour transport methods in order to further study their crystallographic and magnetic properties.

Summary

Combinations of $NbSe_2$ with first-row transition metals were prepared. Of the latter the metals V, Cr, Mn, Fe, Co, and Ni enter the octahedral holes between the prismatic layers of $NbSe_2$. Two types of ordered distributions ($2a$- and $a\sqrt{3}$-supercells of $2s - NbSe_2$) were observed. The influence of inclusion of the transition metals on the lattice was consistent with the difference in anion sizes of NbS_2 and $NbSe_2$.

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