$FeNb_3Se_{10}$: A new structure type related to $NbSe_3$

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Employing single-crystal x-ray-diffraction techniques, the crystal structure of $FeNb_3Se_{10}$ was found to consist of two $NbSe_6$ trigonal prismatic chains of the type found in $NbSe_3$ and a double chain of edge-shared MSe_6 octahedra, both running parallel to the monoclinic b axis. The metal-atom disorder, critical to the interpretation of previously observed electronic properties, is confined to the octahedral chains.

I. INTRODUCTION

The groups IV B and V B transition-metal trichalcogenides have been the subject of many studies in recent years. Of particular interest has been $NbSe_3$, for which two incommensurate charge density waves (CDW's) have been observed, with onset temperatures of 144 and 59 K.[1,2] Its basic structural units are $NbSe_6$ trigonal prisms sharing triangular faces to form infinite chains of three types running parallel to one crystallographic direction (the monoclinic b axis).[3] Substantial cross linking occurs between chains through Nb—Se bonds that are only slightly longer than those within the prisms. The resulting two-dimensional slabs are weakly bonded to neighboring slabs, through Se-Se van der Waals interactions.

Several studies have appeared which have shown CDW's to be suppressed by dilute doping with foreign atoms.[4–6] Recently, a compound of Fe and $NbSe_3$, originally reported with composition $Fe_{0.25}Nb_{0.75}Se_3$, but here shown to be $FeNb_3Se_{10}(Fe_{0.25}Nb_{0.75}Se_{2.5})$ was found to become highly resistive below the onset of a CDW at about 140 K.[7] The resistivity of $FeNb_3Se_{10}$ increases by nine orders of magnitude between 140 and 3 K, suggesting that atomic disorder produces this increase through Anderson localization.[7,8] X-ray scattering showed the CDW to be incommensurate, with a $\bar{q}$ of (0.0, 0.27, 0.0) at onset. The CDW wave vector is only slightly different from the high-temperature CDW in $NbSe_3$, where $\bar{q} = (0.0, 0.24, 0.0)$ with an onset of 144 K.[1,2] $FeNb_3Se_{10}$ is unusual in that a large proportion of Fe is incorporated without quenching the CDW. The present structural study in fact shows $FeNb_3Se_{10}$ to be of a new structure type, composed of two $NbSe_6$ trigonal prismatic chains and a double chain of edge-shared $(Fe,Nb)Se_6$ octahedra.

The Fe-Nb disorder is confined to the octahedral chains, explaining the relatively small perturbation of the CDW, which likely occurs in the trigonal prismatic chains as in pure $NbSe_3$.

II. EXPERIMENTAL

The crystals employed in this study were from the same batch as those employed in the previous studies.[7] They were synthesized from a mixture of the pure elements, in the proportion $FeNb_3Se_{12}$, heated in a sealed, evacuated quartz tube in a 700−650 °C thermal gradient. The present study shows such crystals to be prepared in the presence of excess selenium. Powders were prepared at the compositions $FeNb_3Se_8$, $FeNb_3Se_{10}$, and $FeNb_3Se_{12}$ in small evacuated quartz tubes and heated at 600 °C for one week. Only the powder with composition $FeNb_3Se_{10}$ gave a single-phase product. The powder deficient in Se formed some $(Fe,Nb)Se_2$, while the third powder yielded a product containing Se as a separate phase. A very small sample (3.7 mg) from the original batch of crystals was available for chemical analysis. The approximate composition was found to be (wt. %): Fe, 3.4(3); Nb, 22.5(2.0); and Se, 73.1(3.0); compared with the calculated Fe, 4.97; Nb, 24.8; Se, 70.2.

The precession technique indicated that the crystal employed in the structural study was not twinned. However, inspection under a polarizing microscope and slight peak-shape anomalies noted on the diffractometer indicated that a small amount of twinning may be present. The crystal was studied at room temperature with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation, and intensities were gathered on an automated four-circle diffrac-

tometer to $\sin\theta/\lambda = 0.661$. The sample had dimensions $0.007 \times 0.02 \times 1.042$ mm^3. Of the 810 independent structure factors observed in the bisecting mode, 689 had intensities greater than three times their standard deviation (σ) and were employed in the structural refinement. Refinements were carried out in the x-ray 76 series[9] of programs on $\sum w(|F_0| - |F_c|)^2$, where $w = \sigma^{-2}$. Lorentz-polarization corrections were applied to the data, but absorption corrections were omitted owing to the small size of the crystal. Scattering factors for neutral atoms were employed[10] with corrections for anomalous dispersion.[11]

III. RESULTS

Systematic extinctions observed on the diffractometer established the space group as $P2_1$ or $P2_1/m$. Statistics of the normalized structure factors supported the assignment of the centrosymmetric space group $P2_1/m$. Monoclinic cell parameters determined by a least-squares refinement of the setting angles of 15 reflections were in reasonable agreement with those reported earlier: monoclinic crystal system, 1 formula unit per cell: $a = 9.235(7)$, $b = 3.478(2)$, $c = 10.271(8)$ Å, and $\beta = 114.18(5)$. The measured density, 6.15(5) g/cm^3, is in good agreement with the theoretical, 6.20 g/cm^3. The structure was determined by a combination of direct methods[12] and successive Fourier syntheses. All atoms were found to occupy special positions of the type $2e(x,\frac{1}{4},z)$, $(\bar{x},\frac{3}{4},\bar{z})$. With 1 formula unit per cell, there are five independent Se and two independent metal positions. The metal atoms were found to have both trigonal prismatic and octahedral coordination to selenium. Owing to the possibility of (Fe,Nb) disorder at either site, a systematic series of refinements was carried out in which different values of x and y in the expressions ($Nb1_x$, $Fe1_{1-x}$; $Fe2_{1-y}$, $Nb2_y$) were assigned and held fixed. In the various models, metal

atoms occupying the same site were constrained to have identical parameters and all positional and thermal parameters were allowed to vary. The results indicated, within the limits of experimental error, that the trigonal prismatic chains contain only niobium atoms (the limit of Fe detectability was approximately 3%) and that iron and niobium randomly occupy the octahedral chains such that the fractional iron content is 0.5(1). Thus the metal disorder is confined to the octahedral chains. The final agreement factor for this model, including anisotropic thermal parameters for all atoms was 0.041. The agreement is defined as $R(F) = (\sum||F_0| - |F_c||)/\sum|F_0|$. Analysis of the final difference Fourier map revealed no peak greater than approximately $2e$ Å^{-3}. A table of observed and calculated structure factors may be obtained from the authors. Final structural parameters are presented in Table I. Selected interatomic distances are presented in Table II.

A projection of the structure down the monoclinic b axis is presented in Fig. 1. Selenium and metal atoms are represented by large and small circles, respectively, and the trigonal prisms and octahedra are emphasized by solid lines along their edges. The $NbSe_6$ prismatic chains run parallel to b and involve the atoms Nb1, Se1, Se2, and Se3. In addition to being bonded to the Se atoms within the trigonal prisms (at distances of 2.66, 2.65, and 2.63 Å) the Nb1 atoms are bonded to an Se3 atom shared by a neighboring prismatic chain and octahedron (2.75 Å), and an Se4 atom in a neighboring octahedron (2.72 Å), and thus the true coordination is eightfold. These bonds are represented by dotted lines in Fig. 1. The Nb coordination in this prism is virtually identical to the Nb coordination in one of the prisms (about Nb III) in $NbSe_3$ (Ref. 3) where the intraprism distances are 2.66, 2.65, and 2.62 Å, and the interprism distances 2.77 and 2.72 Å. Further, the Se1-Se2 separation of 2.34 Å for one set of edges in the prism indicates the presence of an Se—Se bonded pair, as occurs in the Nb III prism in $NbSe_3$ at 2.37 Å.

TABLE I. Positional and anisotropic thermal parameters (Å^2) for $FeNb_3Se_{10}$. Estimated standard deviations are given in parentheses. The form of the thermal parameter is
$T = \exp[-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23})]$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{13}
Nb1	0.2759(2)	0.75	0.8644(1)	0.0117(7)	0.0078(7)	0.0056(6)	0.0050(5)
Nb2,Fe2[a]	0.4493(4)	0.25	0.5918(3)	0.0192(15)	0.0187(17)	0.0159(15)	0.0071(13)
Se1	0.0407(2)	0.25	0.7424(2)	0.0155(8)	0.0072(8)	0.0116(8)	0.0026(6)
Se2	0.1607(2)	0.25	0.9925(2)	0.0176(8)	0.0067(8)	0.0110(7)	0.0094(6)
Se3	0.4890(2)	0.25	0.8638(2)	0.0129(7)	0.0057(7)	0.0059(7)	0.0050(6)
Se4	0.2448(2)	0.75	0.5894(2)	0.0232(9)	0.0101(8)	0.0065(7)	0.0079(6)
Se5	0.6618(2)	0.75	0.6659(2)	0.0199(8)	0.0105(8)	0.0177(8)	0.0042(7)

[a] The population parameter, x, in the expression ($Fe2_x$, $Nb2_{1-x}$) = 0.5(1).

TABLE II. Selected interatomic distances (Å) with estimated standard deviations in parentheses.

Atoms	Distances	Symmetry codes[a]	Atoms	Distances	Symmetry codes[a]
Nb1-Nb1	3.478(2)	(c),(e)	Se2-Se2	3.478(2)	(c),(e)
Nb1-Nb1	4.298(4)	(m),(o)	Se2-Se2	3.498(3)	(f),(h)
Nb1-Nb2Fe2	4.135(5)	(d),(e)	Se2-Se3	3.428(3)	(k),(m)
Nb1-Se1	2.661(2)	(d),(e)	Se2-Se3	3.771(4)	(d)
Nb1-Se2	2.652(2)	(d),(e)	Se2-Se5	3.207(4)	(m)
Nb1-Se3	2.628(2)	(d),(e)			
Nb1-Se3	2.746(3)	(m)			
Nb1-Se4	2.719(3)	(d)			
			Se3-Se3	3.229(3)	(k),(m)
Nb2Fe2-Nb2Fe2	2.984(5)	(j),(l)	Se3-Se3	3.478(2)	(c),(e)
Nb2Fe2-Nb2Fe2	3.478(2)	(c),(e)	Se3-Se4	3.293(3)	(c),(d)
Nb2Fe2-Se3	2.665(5)	(d)	Se3-Se5	3.516(3)	(c),(d)
Nb2Fe2-Se4	2.560(3)	(c),(d)			
Nb2Fe2-Se5	2.416(4)	(l)	Se4-Se4	3.478(2)	(c),(e)
Nb2Fe2-Se5	2.497(3)	(c),(d)	Se4-Se4	4.477(4)	(g),(i)
			Se4-Se5	3.535(3)	(l),(n)
Se1-Se1	3.478(2)	(c),(e)	Se4-Se5	3.601(4)	(d)
Se1-Se2	2.344(3)	(d)			
Se1-Se2	4.249(4)	(f),(h)			
Se1-Se3	3.803(4)	(d)			
Se1-Se4	3.347(4)	(g)			
Se1-Se4	3.387(3)	(c),(d)	Se5-Se5	3.478(2)	(c),(e)
Se1-Se5	3.692(3)	(a),(b)	Se5-Se5	3.903(3)	(l),(n)

[a] Symmetry codes for second atom in pair:

(a)	$-1+x$	$-1+y$	z	(i)	$-x$	$2-y$	$1-z$
(b)	$-1+x$	y	z	(j)	$1-x$	$-y$	$1-z$
(c)	x	$-1+y$	z	(k)	$1-x$	$-y$	$2-z$
(d)	x	y	z	(l)	$1-x$	$1-y$	$1-z$
(e)	x	$1+y$	z	(m)	$1-x$	$1-y$	$2-z$
(f)	$-x$	$-y$	$2-z$	(n)	$1-x$	$2-y$	$1-z$
(g)	$-x$	$1-y$	$1-z$	(o)	$1-x$	$2-y$	$2-z$
(h)	$-x$	$1-y$	$2-z$				

The $(Fe,Nb)Se_6$ octahedra are in the center of the cell projection. Each shares four edges with neighboring octahedra, and one corner Se atom with the $NbSe_6$ trigonal prisms. The octahedrally coordinated Nb and Fe atoms form a double chain parallel to b: their separation is 3.48 Å along b but only 2.98 Å
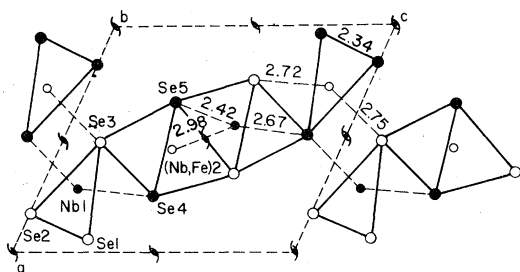

FIG. 1. The structure of $FeNb_3Se_{10}$ projected onto the ac plane, b axis into paper. Small circles are Nb and Fe, while large circles are Se. Filled and open circles are at $y = 0.25$ and $y = 0.75$, respectively.

with metal atoms in the neighboring octahedral chain. For cases when two Nb atoms are neighbors across chains, the 2.98-Å separation implies the existence of a metal-metal bond, as for instance, occurs in NbS_2Cl_2 and Nb_2Se_3 where the distances are 2.90 and 2.97 Å, respectively.[13,14] Iron-niobium bonding may also occur. The average displacement of the metal atoms from the centers of the Se coordination octahedra, decreasing the metal separation between chains, is apparent in Fig. 1, and a view emphasizing the metal-selenium coordination polyhedra is presented as Fig. 2.

Iron occurs in octahedral coordination in several selenides.[15] Iron-selenium bond distances assume a wide range of values, between about 2.28 and 2.65 Å. The average bond distance found in $FeNb_3Se_{10}$, 2.53 Å, is in good agreement with those values. The presence of a significant proportion of iron has induced $\frac{1}{3}$ of the niobium in the structure into octahedral coordination, where the average Nb—Se bond length is shorter than that in the trigonal prisms. The same
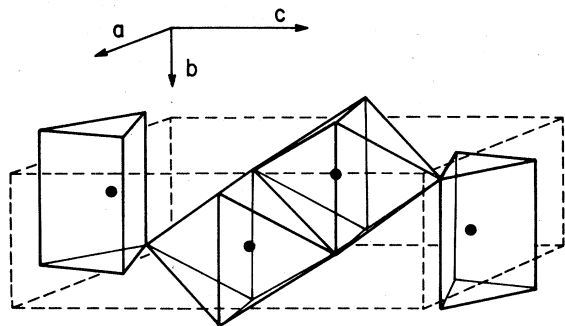
FIG. 2. The structure of $FeNb_3Se_{10}$ viewed 10° from the ac plane, emphasizing the metal-selenium coordination polyhedra. Metal atoms are represented by filled circles, and selenium atoms are at the vertices of the polyhedra.

effect has been observed in Ti- or V-substituted $NbSe_2$ where the $1T$ octahedrally coordinated phases are formed instead of the usual trigonal prismatic phases found when no dopant is present.[4,16,17]

The interpolyhedra metal-selenium bonding is such that two-dimensional slabs are formed which are parallel to the yz plane. As in $NbSe_3$, the two-dimensional slabs are held together by van der Waals bonds between Se atoms. The Se-Se distances across the van der Waals gap are comparable to those in $NbSe_3$.

IV. CONCLUSIONS

$FeNb_3Se_{10}$ occurs in a previously unobserved structure type, consisting of a set of two $NbSe_3$-like trigonal prismatic chains and a double chain with metals in octahedral coordination, both forming parallel to

one crystallographic axis. The disorder among the metal atoms occurs solely on the double octahedral chains. The near equivalence of the CDW wave vectors for $FeNb_3Se_{10}$ and $NbSe_3$ with onset near 140 K indicates that the CDW in $FeNb_3Se_{10}$ occurs on the trigonal prismatic chains, explaining why the relatively large iron content does not quench the CDW. Further, the results suggest that the CDW in $NbSe_3$ with onset at 144 K occurs on the $NbSe_6$ chain whose Nb-Se and Se-Se coordination and local structural environment are the same as the $NbSe_6$ chain we have found in $FeNb_3Se_{10}$. This chain in $NbSe_3$ is about the Nb III atom.[3] Wilson[18] has proposed that the first CDW in $NbSe_3$ should occur on this chain.

Two types of structural disorder occur in $FeNb_3Se_{10}$ that might effect the CDW occurring on the trigonal prismatic chains: the randomly arranged Fe and Nb atoms in the nearby octahedral chains, and the random small displacements of the Se atoms actually bonded to the Nb atoms in the chains (Se3 and Se4) from their mean positions, due to differences in the sizes of the $FeSe_6$ and $NbSe_6$ octahedra. These differences in size are implied by the relatively large anisotropic thermal parameters for the Se atoms in the octahedra. Efforts are currently underway to synthesize other compounds in this structure type, in particular those of stoichiometry $M_2Nb_2Se_{10}$ which would not display metal-atom disorder on the octahedral chains.

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