Details have been noted in the Experimental and Section; e.g. the conversion to Na_2S_4 appears complete after 0.5 h at 220 °C. This does not rule out the possible existence of S_5^{2-} in the molten state, but the very marked band broadening on fusion does not make the melt spectra (Figure 2) very informative. Some further thoughts on this follow.

Aqueous Solutions and Molten Polysulfides. The present work was limited to some careful investigation of the Raman spectrum of aqueous Na_2S_4. A comparison of the Raman spectra for the skeletal modes of polycrystalline and molten Na_2S_4 with the aqueous solutions is illustrated in Figure 4; the numerical values of the frequencies and depolarization results are in Table I. The spectra are the average results of repeated scans (four to ten) to increase the signal to noise ratio. The aqueous spectra show the same marked line broadening that accompanies the melting of the polysulfides (cf. Figures 2 and 4). While the band contour for the aqueous solutions shows more structure than for the molten-phase spectra, the unusually large broadening in the aqueous and molten states is such that the band contour virtually overlaps completely the skeletal frequencies for the individual di-, tri-, tetra-, and pentapolysulfides as crystalline solids (Table I and Figures 3–5). While factors such as rotational, conformational, and anharmonicity contributions undoubtedly feature in this band broadening, the magnitude is more in accord with contributions due to the equilibrium coexistence of a series of polysulfide species. From this viewpoint the results of Schwarzenbach and Fischer[10] are informative. It was thus shown that for the tetrasulfide the equilibrium properties of the aqueous solution may be ascribed to 64% S_4^{2-}, 27% S_5^{2-}, and 9% of S^{2-} and that the equilibrium composition is established rapidly (10^{-2} s). Similarly, rapid disproportionation of the di- and trisulfides, with the formation of S_5^{2-} and S_4^{2-} species, was noted. Tegman[17,24] has shown that the assumption of an equilibrium distribution of several polysulfide species is required to account for the thermodynamic equilibria between the molten polysulfides and sulfur vapor at high temperatures. The magnitude of the Raman band broadening (aqueous solutions; molten polysulfides) is additional support for these observations.

Acknowledgment. We wish to thank J. L. Katz (Physics), and H. W. Wiedemeier (Chemistry) for assistance with the x-ray diffraction studies. The studies reported in this publication are part of a program supported at Rensselaer Polytechnic Institute by a National Science Foundation–RANN contract with the Ford Motor Co. for sodium–sulfur battery research.

Registry No. Na_2S_2, 22868-13-9; Na_2S_3, 37488-76-9; Na_2S_4, 12034-39-8; Na_2S_5, 12034-40-1; Na_2S, 1313-82-2.

References and Notes

(1) Research Assistant, 1974–1975.
(2) Research Assistant, 1973–1974.
(3) Visting Professor, 1974–1975; on leave from Lake Forest College, Lake Forest, Ill.
(4) Postdoctoral Associate, 1972–1973.
(5) E. Rosen and R. Tegman, *Chem. Scr.*, **2**, 221 (1972).
(6) N. K. Gupta and R. Tischer, *J. Electrochem. Soc.*, **119**, 1033 (1972).
(7) D. G. Oei, *Inorg. Chem.*, **12**, 435, 438 (1973).
(8) R. Tegman, *Acta Crystallogr., Sect. B*, **29**, 1463 (1973).
(9) A. T. Ward, *Mater. Res. Bull.*, **4**, 581 (1969).
(10) G. Schwarzenbach and A. Fischer, *Helv. Chem. Acta*, **43**, 1365 (1960).
(11) G. J. Janz, E. Roduner, J. W. Coutts, and J. R. Downey, Jr., *Inorg. Chem.*, **15**, 1751 (1976).
(12) G. J. Janz, J. W. Coutts, J. R. Downey, Jr., and E. Roduner, *Inorg. Chem.*, **15**, 1755 (1976).
(13) E. Rosen and R. Tegman, *Acta Chem. Scand.*, **25**, 3329 (1971).
(14) G. J. Janz et al., unpublished work.
(15) Sodium disulfide exists in two crystalline modifications. The α form may be synthesized by a low-temperature process in alcohol but converts irreversibly to the β form between 150 and 250 °C. The β form is obtained by cooling the melt. All further references to Na_2S_2 in the present communication are to the β form of this compound.
(16) F. Feher and H. J. Berthold, *Z. Anorg. Allg. Chem.*, **273**, 144 (1953).
(17) R. Tegman, Ph.D. Thesis, University of Umea, Umea, Sweden, 1974.
(18) H. Foeppel, E. Busmann, and F. K. Frorath, *Z. Anorg. Allg. Chem.*, **314**, 12 (1962).
(19) K. Venkateswarlu and P. Thirugnanasambandam, *Trans. Faraday Soc.*, **55**, 1993 (1959).
(20) H. Bottger, *Justus Liebigs Ann. Chem.*, **224**, 335 (1884).
(21) G. Herzberg, "Molecular Spectra and Molecular Structure", Van Nostrand, New York, N.Y., 1945.
(22) H. Stamreich and R. Forneris, *Spectrochim. Acta*, **8**, 46 (1956).
(23) K. S. Pitzer, *J. Chem. Phys.*, **5**, 469, 473, 752 (1937).
(24) R. Tegman, *Chem. Scr.*, **2**, 63 (1972).

Contribution from Baker Laboratory of Chemistry,
Cornell University, Ithaca, New York 14853

Synthesis and Structural Aspects of the Vanadium-Substituted Niobium Diselenides[1]

MICHEL BAYARD, BERNARD F. MENTZEN, and M. J. SIENKO*

Received February 9, 1976 AIC601030

Solid solutions of formula $Nb_{1-x}V_xSe_2$ ($0 < x < 1$) have been prepared by direct synthesis from the elements under minimum-gradient conditions. Single crystals of $NbSe_2$ and VSe_2 have been made by chemical transport using iodine as transporting agent. X-ray studies by single-crystal and Debye–Scherrer techniques have been used to define regions of homogeneity. Monophasic regions occur for $0 \le x \le 0.01$ (where the structure is that of the 2H-$NbSe_2$ polytype), $0.11 \le x \le 0.20$ (structure 4Hb), and $0.30 \le x \le 1.00$ (structure 1T). It is proposed that vanadium substitutes for niobium in trigonal-prismatic coordination in only the first of these regions; otherwise, the vanadium goes into octahedral coordination and produces the 4Hb polytype by enhancing octahedral coordination of the niobium. The variation of structural parameters with composition is described in terms of a pure size effect attendant on the vanadium-for-niobium substitution.

Introduction

The layered dichalcogenides are of great interest as model compounds for study of electrical interactions and critical phenomena in quasi-two-dimensional systems. Excellent summaries of the structural and physical properties have been given by Wilson and Yoffe[2] and by Yoffe.[3] Two distinguishing characteristics of the compounds are metallic vs. nonmetallic behavior and trigonal-prismatic vs. octahedral coordination. As an approximate rule, groups 4 and 6 dichalcogenides are semiconductors, whereas group 5 compounds are metals; however, there is not a 1:1 correlation between metallic behavior and coordination. The principles that govern adoption of trigonal-prismatic rather than octahedral coordination have not been definitively worked out, but Gamble[4] and Madhukar[5] have had considerable success in correlating trigonal-prismatic preference within a given group with large metal-to-chalcogen radius ratio and small bond ionicity. The fact that it does not seem to matter whether covalent or ionic radii are used in the classification suggests that relative sizes are more important than bond ionicity in setting the coordination.

One possible way to get more precise information on the factors that influence coordination is to look in detail at a

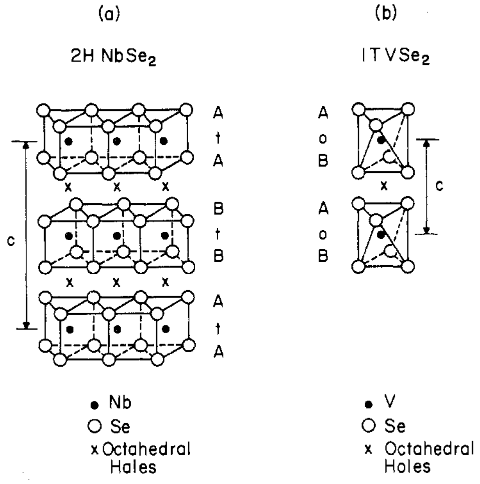

Figure 1. Idealized structural arrangements in (a) 2H-$NbSe_2$ and (b) 1T-VSe_2. In the 2H-$NbSe_2$ structure the niobium atoms occupy trigonal-prismatic holes (t) between hexagonal-packed selenium layers that are stacked A over A or B over B. In the 1T-VSe_2 structure the vanadium occupies octahedral holes (o) between selenium layers A and B.

mixed system in which coordination changes from trigonal prismatic to octahedral on substitution of one element for another of the same group. An attractive system for such a study is $NbSe_2$–VSe_2. The one end member $NbSe_2$ crystallizes with a 2H structure (trigonal prismatic, as shown in Figure 1a); the other, with a 1T structure (octahedral, Figure 1b). Both end members are metallic, so any effect of itinerant electrons can be discounted. Vanadium and niobium have the same Pauling electronegativity (1.6), which is not far from that of selenium (2.4), so the fraction of ionic character[6] is constant at 15%. In a covalent model, appropriate radii would be 1.25 Å for V and 1.36 Å for Nb. In the mixed system $Nb_{1-x}V_xSe_2$, average metal atom radius is the only apparent variable being affected by replacement of vanadium for niobium, so it is of interest to ask how the evolution of structural parameters proceeds on change of composition.

Crystallographic studies[7-9] have shown Nb_xSe_2 ($1.00 \leq x \leq 1.25$) to exist in several polytypes, depending upon the stacking sequence of the trigonal-prismatic Se–Nb–Se slabs. However, we are concerned here only with the two-layer 2H modification, represented in Figure 1a, which was the only one obtained for $NbSe_2$ under the experimental conditions described below.

A further motivation for examining the structural modifications in carefully prepared specimens of $Nb_{1-x}V_xSe_2$ is that $NbSe_2$ is a superconductor with critical temperature around 7.2 K whereas VSe_2, although a metal, does not superconduct even at temperatures as low as 0.05 K.[10] Preliminary experiments carried out in this laboratory[11] indicated that vanadium in vanadium-substituted niobium disulfide develops a magnetic moment, presumably as a result of localizing a conduction electron. Since such a "localized" moment would be expected to destroy the superconductivity, it became of interest to investigate the effect of vanadium substitution on superconducting critical temperature. As niobium disulfide is notoriously difficult to prepare with exact 1:2 stoichiometry, it was more expedient to study the effect in $NbSe_2$ instead. The magnetic susceptibility and electron transport properties are described in a separate communication.[12] Here we detail the preparation of the materials and their structural characterization.

Experimental Section

Preparation of Materials. The starting materials were 99.99% niobium wire and 99.98% vanadium wire from Leico Industries and 99.999% selenium from Alfa Inorganics. The $Nb_{1-x}V_xSe_2$ solid solutions were prepared by allowing the elements to react in evacuated (less than 10^{-3} Torr) silica tubes. The tubes, approximately 15 cm long, were inserted in metallic coils in order to minimize any temperature gradient, heated at 15 °C/h to 750 °C, and then held at this temperature for 8 days. It was found that without the coils some selenium would condense in the coldest part of the tube at the end of the reaction. The samples were opened in a drybox filled with nitrogen, ground in an agate mortar, and resealed in silica tubes. The samples were refired for 8 days at 750 °C and allowed to cool at the rate of 100 °C/h.

Single crystals of $NbSe_2$ ($10 \times 3 \times 0.1$ mm^3) and of VSe_2 ($2 \times 1 \times 0.1$ mm^3) were prepared by chemical transport using a concentration of 1 mg/cm^3 of iodine as transporting agent. The iodine, which was 99.98% pure from Mallinckrodt, was resublimed under vacuum and was kept in sealed Pyrex tubes between experiments. The concentration was rigorously limited, since Huntley and Frindt[13] have shown that appreciable amounts of iodine enter the structure for higher concentrations. The preparations of the sample and the design of the three-zone furnace used were similar to those described by Kershaw, Vlasse, and Wold.[14] At the start of the transport run, the charge end was kept at 120 °C, the other end at 810 °C, and the growth zone also at 810 °C. This arrangement of temperature zones minimizes the number of nuclei in the growth zone. After 24 h, the charge zone was raised to 798 °C, the other end maintained at 805 °C, and the growth zone programmed to 734 °C at a rate of 1 °C/h. Transport was allowed to continue for 8 days in the case of $NbSe_2$ and 11 days in the case of VSe_2 after the growth zone had reached the desired temperature. All the heaters were then shut off and the tube was allowed to cool to room temperature.

Chemical transport is not a suitable method for the growth of solid solutions such as $Nb_{1-x}V_xSe_2$. The intermediary niobium and vanadium iodides do not form and diffuse at the same rate, so inhomogeneous crystals are usually obtained by this method. Therefore, the mixed crystals were grown from a polycrystalline charge using essentially no temperature gradient and long periods of time (e.g., 3 weeks). The charge, placed at one end of the silica tube, was maintained at 798 °C, while the temperature increased linearly along the tube to 805 °C at the other end. Before the reaction, 1 mg/cm^3 of iodine, as mineralizer, was introduced in the tube as described in ref 14. The product crystals (3×1 mm) were removed from the reaction tube by snapping it inside an evacuated transparent plastic hose. After air was slowly bled in, the crystals were removed and freed of excess iodine by heating them up to 150 °C under vacuum for 3 h and condensing the iodine in a liquid nitrogen trap.

Chemical Analysis. Chemical analysis of $NbSe_2$ powders and crystals was carried out by igniting the selenides in a stream of dry oxygen to Nb_2O_5. The composition was found to be $NbSe_{1.998}$. Such a method is not suitable for VSe_2 or $Nb_{1-x}V_xSe_2$ since V_2O_5 has some tendency to be oxygen deficient. The vanadium content of these phases was determined by neutron activation analysis both on the product powders and on single crystals taken from those same powders.

X-Ray Analysis. X-ray diffraction patterns were taken with Cu Kα radiation in a Debye–Scherrer camera of nominal diameter 114.6 mm. Direct diffraction lines were used following correction for line shift due to absorption of the cylindrical specimen. Back-diffraction lines were also used when not broad. Figure 2 shows the evolution of cell parameters as a function of x in an "idealized" representation based on a least-squares fit of the observed data. All phases were indexed on the basis of a hexagonal cell. Weissenberg photographs were also taken for some of the crystal specimens.

Results

As shown in Figure 2, there are three domains of homogeneity in the system $Nb_{1-x}V_xSe_2$ corresponding to 2H ($0 < x \leq 0.01$), 4Hb ($0.11 \leq x \leq 0.20$), and 1T ($0.30 \leq x \leq 1.00$) polytypes, respectively. Very little vanadium can be substituted for niobium in 2H-$NbSe_2$ without changing its structure. Since very large amounts of vanadium can be intercalated in the octahedral holes between the prismatic layers of 2H-$NbSe_2$,[15] it is very likely that in the very dilute vanadium region the vanadium atoms substitute for niobium within the layer. There is no observable modification in the intensity of the lines or the cell parameters in the narrow domain of existence of 2H-$Nb_{1-x}V_xSe_2$, which belongs to the same space

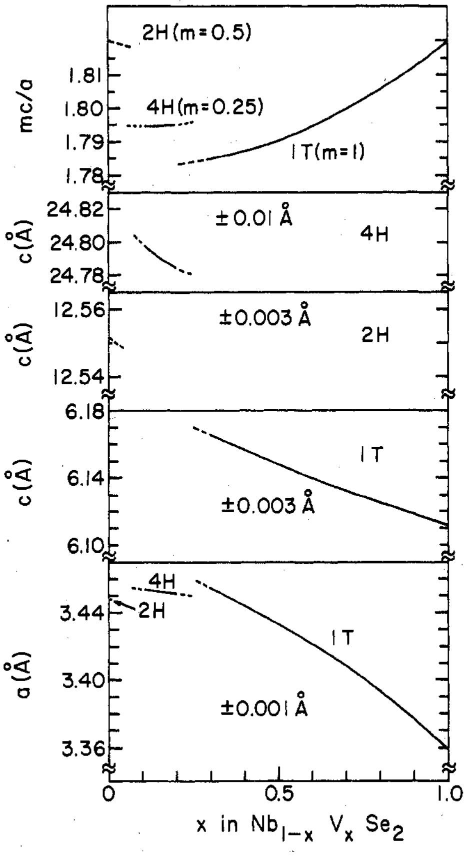

Figure 2. Idealized structural parameters as a function of composition in the system $Nb_{1-x}V_xSe_2$.

Table I. X-Ray Intensities for $Nb_{1-x}V_xSe_2$ ($x = 0.15$)

d, Å	Intens	*hkl*
6.191	Strong	004
3.099	Weak	008
2.8132	Medium	103
2.6939	Strong	104
2.5651	Medium	105
2.4294	Very very weak	106
2.2870	Weak	107
2.1526	Very strong	108
2.0671	Medium	0,0,12
1.8003	Weak	1,0,11
1.7268	Medium	110
1.6979	Weak (broad)	1,0,12
1.6632	Very weak	114
1.6079	Weak	1,0,13
1.5489	Weak	0,0,16
1.4709	Very weak	203
1.4306	Very weak	205
1.3464	Medium	208
1.3242	Medium	1,1,12
1.1533	Strong	1,1,16
1.1445	Weak	1,0,20

group ($P6_3/mmc$) as 2H-$NbSe_2$.

When more vanadium is substituted for niobium ($0.01 < x < 0.11$), a second phase appears together with 2H-$Nb_{1-x}V_xSe_2$. We call it 4Hb-$Nb_{1-x}V_xSe_2$ since its *c* parameter is approximately twice as large as that of 2H-$NbSe_2$ and since the x-ray pattern corresponds to what has been suggested[16] for the direct stacking of metal atoms over each other that is characteristic of the 4Hb polytype. As shown by the typical data of Table I, the *h*0*l* lines for $l = 4n$ are strong and the 10*l* lines for $l = 4n + 2$ are not observed. The 4Hb-$Nb_{1-x}V_xSe_2$ is found as a single phase for $0.11 \leq x \leq 0.20$ and belongs to the space group $P6_3/mmc$, as revealed by single-crystal Weissenberg pictures of first and second layers.

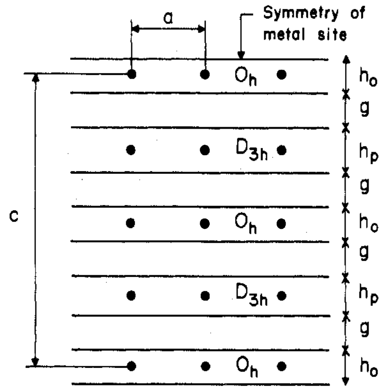

Figure 3. Proposed stacking in the 4Hb polytype observed for $Nb_{1-x}V_xSe_2$ ($0.11 \leqslant x \leqslant 0.20$). The precise sequence O_h, D_{3h}, O_h, D_{3h}, O_h, . . . for the symmetry of the metal site is irrelevant to our calculation.

Since V^{4+} is encountered in octahedral but never trigonal-prismatic coordination whereas Nb^{4+} can be found in both, it is suggested that one layer out of two contains only niobium atoms in trigonal-prismatic coordination, the other layer being forced into octahedral symmetry by the presence of an appreciable amount of vanadium (~22% of the sites, as deduced from the lower limit of the homogeneity range). Keeping in mind that each gap between the Se–(Nb,V)–Se slabs is made of a hexagonal packing of selenium atoms, a systematic analysis of different possible stackings to get $c \simeq 24.79$ Å reveals that this is the only alternative (Figure 3). More conclusive evidence for such a stacking is given in the Discussion.

For $0.20 < x < 0.30$ we again find a two-phase region where 4Hb-$Nb_{1-x}V_xSe_2$ and 1T-$Nb_{1-x}V_xSe_2$ occur together. The 1T phase is isotypic with VSe_2 and is therefore characterized by cations in octahedral coordination.[17] It is found alone for $0.30 \leq x \leq 1.00$.

There was a question as to whether the heat treatment would affect the domains of homogeneity shown in Figure 2. For example, it was thought that partial quenching might retain a high-temperature phase while a low-temperature phase was starting to form, resulting in a two-phase domain. Fast quenching experiments from a variety of temperatures ranging from 950 to 600 °C at 50 °C intervals were carried out for $x = 0.03$, which ostensibly lies in a two-phase region. Samples were heated to the desired temperature overnight and then dropped in cold water. X-ray photographs were taken after each quench. The same mixture of 4Hb-$Nb_{1-x}V_xSe_2$ and 2H-$Nb_{1-x}V_xSe_2$ was observed throughout the series, except for the sample heated to 950 °C, which showed a loss of selenium and was not analyzed. In order to clarify conflicting data found in the literature, similar experiments were done on pure 2H-$NbSe_2$. Neither the 3H- nor the 4H-$NbSe_2$ as reported by Kadijk et al.[8] and Revolinsky et al.,[7] respectively, was found. As the authors themselves suggest, these phases are probably the result of poor stoichiometry or low purity of the starting materials or both. Our results seem to confirm the hypothesis. The authors also mention some difficulty in making the same phase twice under similar experimental conditions. We never experienced such a problem.

Discussion

One of the basic issues to be understood and resolved about layered dichalcogenides is the reason for the occurrence of octahedral or trigonal-prismatic coordination. In Madhukar's covalent model,[5] consideration is given to relative size, polarization of bonding orbitals, and ionicity of the metal–chalcogen bond. Figure 4 shows the relative placing of $NbSe_2$ and VSe_2 with respect to the relevant parameters. R_T and R_X are single-order covalent radii for metal T and chalcogen X,

Table II. Comparison of Apparent Bond Lengths D (all data in Å)

Compd	a	c	h^a	g^a	D(X-ray)	D(eq 3)	Ref
			Trigonal Prismatic-2H Polytype				
NbS_2	3.31	11.89	3.14	2.80	2.47	2.47	20
MoS_2	3.160	12.293	3.19	2.96	2.41	2.42	21
$NbSe_2$	3.444	12.544	3.333	2.939	2.595	2.594	22
$TaSe_2$	3.436	12.692	3.35	3.00	2.59	2.59	23
α-$MoTe_2$	3.517	13.955	3.63	3.35	2.73	2.72	24
			Octahedral-1T Polytype				
TiS_2	3.407	5.696	2.64	3.05	2.32	2.36	25
PtS_2	3.543	5.038	2.289	2.750	2.34	2.34	26
$PtSe_2$	3.728	5.081	2.592	2.489	2.513	2.512	26
$PtTe_2$	4.026	5.221	2.653	2.568	2.676	2.676	26

[a] See Figure 3.

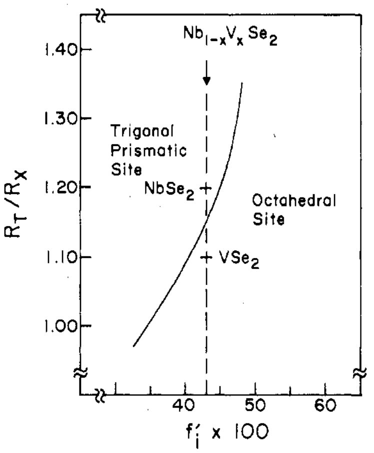

Figure 4. Comparison of $NbSe_2$ and VSe_2 with respect to parameters that determine type of coordination. R_T and R_X are covalent radii and f_i' is resonating bond ionicity (after Madhukar[5]).

and f_i' is the resonating-bond ionicity. The latter is defined by $1 - f_i' = n(1 - f_i)$ where n is the bond order (equal to $^2/_3$ for octahedral or trigonal-prismatic coordination) and f_i is the ionicity as given by Pauling,[6] viz., $1 - \exp[-^1/_4(\chi_T - \chi_X)^2]$, χ being the electronegativity. Because niobium and vanadium have the same electronegativity, all of the $Nb_{1-x}V_xSe_2$ phases fall on the same vertical line (shown dashed in Figure 4). The problem then is to calculate an apparent R_T for a composition-weighted $Nb_{1-x}V_x$ "atom" and see for what value of x the ratio R_T/R_X crosses the threshold that separates trigonal-prismatic from octahedral coordination.

Assuming that

$$R_T = (1 - x)R_{Nb} + xR_V \qquad (1)$$

with R_{Nb} = 1.362 Å and R_V = 1.254 Å, R_T so calculated can be used to extract a bond length D from

$$D = D_S - 0.26 \ln n \qquad (2)$$

where D_S is the single-order bond length, given by $D_S = R_T + R_X - C\,|\chi_T - \chi_X|$, and n is the bond order.[18] The expression for D_S includes a correction term for the partial ionic character that arises from electronegativity difference between atoms T and X. The empirical constant C is given a value of 0.04 for selenium.[19] Values of D thus obtained can be compared as a function of x with those calculated on a hard-sphere model from observed a and c cell parameters. Assuming that the metal atom is smaller or just fills the site size defined by the coordination shell and that the chalcogen spheres are not overly deformed, it can be shown that ideally (i.e., z = 0.250, c/a = 1.633) D should be given by

$$D = [(a^2/3) + (h^2/4)]^{1/2} \qquad (3)$$

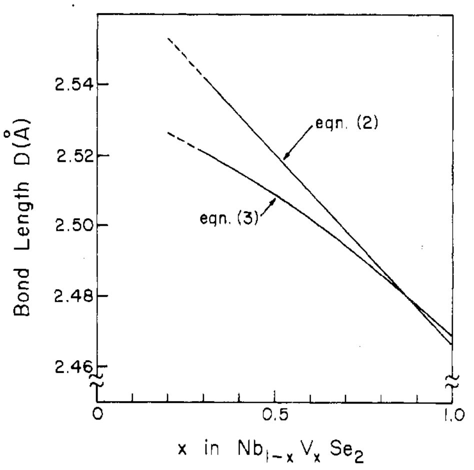

Figure 5. Bond length change as a function of x in $Nb_{1-x}V_xSe_2$ as computed by eq 2, which is based on Pauling's bond ionicity model, and by eq 3, which is based on a hard-sphere packing model.

Table III. Apparent Covalent Radii and Radii Ratios in $Nb_{1-x}V_xSe_2$

x	R_T, Å	R_T/R_X	x	R_T, Å	R_T/R_X
1.0	1.256	1.102	0.5	1.295	1.136
0.9	1.265	1.109	0.4	1.301	1.141
0.8	1.273	1.117	0.3	1.307	1.146
0.7	1.281	1.124	0.2[a]	1.312	1.151
0.6	1.288	1.130			

[a] For x = 0.2 we have extrapolated the results obtained for higher values of x.

where a is the unit-cell parameter and h, the thickness of the X–T–X slab, is approximately equal to $c/2$ for the 1T phases.

The assumptions used to establish eq 3 can be tested with dichalcogenides for which the structure has been fully determined. Table II shows a comparison of D values observed and calculated with eq 3. The agreement is quite good.

Figure 5 shows how the value of D changes with x in $Nb_{1-x}V_xSe_2$ ($0.30 \leq x \leq 1.00$), first as computed from eq 2 and also as computed from eq 3. The agreement between the two sets of values is well within the limits of uncertainty of Pauling's estimates as compared to observed bond lengths in dichalcogenides. It suggests that both Pauling's bond ionicity model and the hard-sphere model adequately describe the T–X bond in $Nb_{1-x}V_xSe_2$.

By substituting D from eq 3 into eq 2 one can calculate a better "apparent" value of R_T than that obtained from eq 1. Table III shows these "apparent" values of R_T together with the ratio R_T/R_X. It is seen that for $x < 0.3$ R_T/R_X reaches the critical ratio 1.15 (see Figure 4) at which the cations in $Nb_{1-x}V_xSe_2$ should change from purely octahedral coordination. The results thus conform to the fact that for $x < 0.3$

Table IV. Apparent Covalent Radii and Radii Ratios Deduced for Trigonal-Prismatic Layers of $Nb_{1-x}V_xSe_2$

x	D_o,[a] Å	h_o, Å	h_p, Å	D_p, Å	R_{T_p}, Å	R_{T_p}/R_X
0.11	2.525	3.096	3.108	2.528	1.315	1.153
0.15	2.520	3.085	3.141	2.538	1.324	1.162
0.20	2.515	3.068	3.187	2.551	1.337	1.173

[a] From D at $2x$ in 1T.

the 1T structure has with it some 4Hb structure, which most certainly contains cations in trigonal-prismatic as well as octahedral coordination.

Additional evidence for the existence of trigonal-prismatic sites in the 4Hb structure can be deduced from gap height relations for 4H stacking as shown in Figure 3. Assuming that h_o, the thickness of the octahedral X–T–X slab, is equal to the gap height, g, where the X arrangement is also octahedral, we can write for the ideal c lattice parameter

$$c = 6h_o + 2h_p \tag{4}$$

with h_p being the thickness of the prismatic X–T–X layer. The T–X bond length in the octahedral layers, D_o, given by $D_o = [(a^2/3) + (h_o^2/4)]^{1/2}$, can be used to calculate a value of h_o since in the 4Hb polytype one layer out of two contains vanadium atoms. D_o at a given x in the 4Hb structure thus corresponds to D for $2x$ in the 1T structure. Knowing h_o, we can use eq 4 to get h_p, which in turn can be used to calculate D_p, the T–X bond length in the trigonal-prismatic layers, $D_p = [(a^2/3) + (h_p^2/4)]^{1/2}$. The same approach used above for the 1T structure can be applied to the 4Hb structure by calculating an "apparent" covalent radius for the metal in the trigonal-prismatic layers, R_{T_p}, using the Pauling bond length between niobium and selenium atoms. We expect the trigonal-prismatic layers to be characterized by $R_T/R_X \geq 1.15$, which is confirmed by the results shown in Table IV.

Conclusions

The most favorable conditions under which chalcogens can arrange themselves in trigonal-prismatic coordination so as to make full use of the greater stabilizing strength of d^4sp bonding orbitals occur when the ionicity of the bonds is small, the cation:anion ratio is large, and the number of nonbonding d electrons is small. Otherwise, octahedral coordination is preferred. In the $Nb_{1-x}V_xSe_2$ phases, the ionicity of the bonds and the number of nonbonding d electrons stay constant. The only variable is the cation:anion ratio, which should be the dominant factor governing the structure of these phases. This is completely borne out by our results which show that realization of trigonal-prismatic vs. octahedral coordination is mostly a size effect.

Acknowledgment. The authors are grateful to Lynn Schneemeyer for performing the quenching experiments and to the Analytical Facility of the Cornell Materials Science Center for the neutron activation analysis.

Registry No. $NbSe_2$, 12034-77-4; VSe_2, 12299-51-3.

References and Notes

(1) This research was sponsored by the Air Force Office of Scientific Research (AFSC) under Grant No. AFOSR-74-2583 and was supported in part by the National Science Foundation and the Materials Science Center at Cornell University.
(2) J. A. Wilson and A. D. Yoffe, *Adv. Phys.* **18**, 193 (1969).
(3) A. D. Yoffe, *Festkoerperprobleme*, **13**, 1 (1973).
(4) F. R. Gamble, *J. Solid State Chem.*, **9**, 358 (1974).
(5) A. Madhukar, *Solid State Commun.*, **16**, 383 (1975).
(6) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 98.
(7) E. Revolinsky, G. A. Spiering, and D. J. Beerntsen, *J. Phys. Chem. Solids*, **26**, 1029 (1965).
(8) F. Kadijk, R. Huisman, and F. Jellinek, *Recl. Trav. Chim. Pays-Bas*, **83**, 768 (1964).
(9) K. Selte, E. Bjerkelund, and A. Kjekshus, *J. Less-Common Met.*, **11**, 14 (1966).
(10) M. H. Van Maaren and G. M. Schaeffer, *Phys. Lett. A*, **24**, 645 (1967).
(11) J. Pivnichny, private communication.
(12) M. Bayard and M. J. Sienko, to be submitted for publication.
(13) D. J. Huntley and R. F. Frindt, *Can. J. Phys.*, **52**, 861 (1974).
(14) R. Kershaw, M. Vlasse, and A. Wold, *Inorg. Chem.*, **6**, 1599 (1967).
(15) J. M. Voorhoeve-van den Berg and M. Robbins, *J. Solid State Chem.*, **1**, 134 (197).
(16) F. J. di Salvo, B. G. Bagley, J. M. Voorhoeve, and J. V. Waszczak, *J. Phys. Chem. Solids*, **34**, 1357 (1972).
(17) E. Hoschek and W. Klemm, *Z. Anorg. Allg. Chem.*, **242**, 49 (1939).
(18) Reference 8, p 255.
(19) Reference 8, p 229.
(20) F. Jellinek, G. Brauer, and H. Muller, *Nature (London)*, **185**, 376 (1960); B. Morosin, *Acta Crystallogr., Sect. B*, **30**, 551 (1974).
(21) R. Dickinson and L. Pauling, *J. Am. Chem. Soc.*, **45**, 1466 (1923); J. C. Wildervanck and F. Jellinek, *Z. Anorg. Allg. Chem.*, **328**, 309 (1964).
(22) M. Marezio, P. D. Dernier, A. Menth, and G. W. Hull, Jr., *J. Solid State Chem.*, **4**, 425 (1972).
(23) E. Bjerkelund and A. Kjekshus, *Acta Chem. Scand.*, **21**, 513 (1967).
(24) D. Puotinen and R. E. Newnham, *Acta Crystallogr.*, **16**, 1183 (1963).
(25) M. S. Whittingham and A. H. Thompson, *J. Chem. Phys.*, **62**, 1588 (1975).
(26) S. Furuseth, K. Selte, and A. Kjekshus, *Acta Chem. Scand.*, **19**, 257 (1965).