metal ion. There is no suggestion at this time as to what the nature of that barrier is.

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Structure and Properties of Nickel Vanadium Selenide, NiV_2Se_4[1]

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The structure of NiV_2Se_4 was determined by X-ray analysis of a powder sample. The structure is based on the monoclinic space group I2/m. The cell dimensions are $a = 6.142 \pm 0.006$, $b = 3.437 \pm 0.004$, $c = 11.55 \pm 0.01$ A, and $\beta = 91.5 \pm 0.1°$. There appear to be two V–V distances that are less than 3.44 A, and, according to Goodenough, metal–metal d-orbital overlap can occur and may account for the observed metallic behavior of this compound.

Introduction

Recently, a series of monoclinic chalcogenides of the type NiM_2X_4 was prepared and characterized[2] where M was V^{3+} or Cr^{3+} and X was sulfur or selenium. The vanadium compounds were reported to be metallic with positive temperature coefficients of resistivity and low Seebeck voltages. The corresponding chromium compounds appeared to be semiconductors. Unit cell volumes of the vanadium compounds should have been larger than those of the corresponding isostructural chromium compounds since both the ionic and covalent radii of vanadium exceed those of chromium. However, the reverse was true (Table I). An examination of several metal–metal distances and interactions has been carried out in order to investigate this anomaly.

TABLE I
UNIT CELL DIMENSIONS OF SOME ISOSTRUCTURAL MONOCLINIC CHALCOGENIDES

Formula	a, A	b, A	c, A	β, deg	V, A³
Cr_3S_4[a]	5.95	3.42	11.24	91.5	229
$NiCr_2S_4$[a]	5.90	3.41	11.10	91.4	223
NiV_2S_4	5.82	3.28	11.05	92.0	211
$NiCr_2Se_4$	6.23	3.59	11.52	91.1	258
NiV_2Se_4	6.14	3.44	11.55	91.6	244

[a] Refined cell dimensions are in close agreement with those reported by Jellinek.[4]

Goodenough[3] has indicated that direct interaction of the d orbitals of metal atoms and consequent delocalization of the t_{2g} electrons can occur only if metal–metal distances are less than ≈3.34 A for the thiochromites and ≈3.44 A for the thiovanadites. For the compounds $NiCr_2S_4$ and NiV_2S_4 these metal–metal distances, measured along the *b* axes, are 3.41 and 3.28 A, respectively, and so this type of bonding could occur in NiV_2S_4 and account for the small unit cell size and metallic properties of this compound.

In order to extend studies of the effect of vanadium–vanadium interactions in these compounds, a powder sample of NiV_2Se_4 has been subjected to X-ray crystal structure analysis.

Experimental Section

NiV_2Se_4 was prepared by reaction of the elements in an evacuated silica tube. The tube was slowly heated to 500° and kept at this temperature until most of the selenium had reacted. The temperature was then raised to 1000° after the sample had been ground under dry nitrogen. Firings were continued at this temperature until no change was observed in the X-ray diffraction pattern and no impurity peaks were present. This diffraction pattern could be indexed approximately on the basis of a monoclinic unit cell of the type ascribed by Jellinek[4] to Cr_3S_4. Subsequent refinement of these parameters by a conventional least-squares procedure,[5] in which the differences between observed and calculated values of $\sin^2 \theta$ were minimized for the indexed reflections, resulted in the values $a = 6.142 \pm 0.006$, $b = 3.437 \pm 0.004$, $c = 11.55 \pm 0.01$ A, and $\beta = 91.5 \pm 0.1°$, where maximum errors in these quantities are indicated.

X-Rays from a high-intensity copper source were diffracted by the powder, then monochromatized (AMR-202 focusing monochromator) and detected by electronic pulse counting using a Norelco diffractometer. Relative intensities (I_o) for the various multiple reflections were obtained by fixed time scans from background to background on either side of each peak and then by subtracting the appropriate portions of an established curve of background intensity *vs.* angle. Lorentz and polarization[6,7] corrections were applied to these intensities, and the absolute

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[1] This work has been supported by ARPA and Grant No. AF 19(628)-3837.

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values of the observed structure factors (F_o) were derived for those peaks which could be indexed unambiguously [$F_o = \sqrt{\{(LP^{-1})I_o/p\}}$], where p is the multiplicity[8] of a particular reflection. Only 22 out of 74 observed peaks could be classed as unambiguous in that each had a unique set of Miller indices, no visible overlap with adjacent peaks, and a peak/background ratio greater than 0.5.

Because all peaks in the diffractogram could be indexed on the basis of the Cr_3S_4-type lattice, the "ideal structure" used by Jellinek[4] for this compound was also used to initiate refinement of the structural parameters of NiV_2Se_4. This trial structure is shown in Figure 1 and is based on the monoclinic space group I2/m which is the body-centered equivalent of the conventional monoclinic space group C2/m.

Throughout the least-squares refinement, structure factors (F_c) were calculated using best known atomic positions, scattering factors for the neutral atoms with real anomolous dispersion corrections applied,[9] and isotropic temperature factors. Hence the values of six positional parameters, four isotropic temperature factors, and one scale factor (applied to every F_o) were adjusted to minimize the sum of the squares of the differences between observed and calculated structure factors for the 22 unambiguous reflections. These reflections were weighted equally except for 002 and 004 which were included in the refinement at one-fourth this weight because their intensities appeared to be enhanced by preferred orientation, which is known to be characteristic behavior of these materials. After 13 cycles using a block-diagonal approximation refinement program,[10] the value of the conventional reliability index $R = (\sum||F_o| - |F_c||/\sum F_o)$ was 6.1%. At this stage the maximum shift in a positional parameter as a fraction of the esd was 0.027. Final values of all structural parameters are given in Table II, and Table III contains the observed and calculated structure factors derived from these parameters.

Table II

Atomic Coordinates and Isotropic Thermal Parameters from Least-Squares Refinement of NiV_2Se_4[a]

Atom	x	$10^4\sigma(x)$	z	$10^4\sigma(z)$	B
Ni	0.0000		0.0000		2.12 (1.02)[b]
V	−0.0457	(42)[b]	0.2592	(29)[b]	2.47 (0.91)
Se	0.3355	(30)	0.3625	(15)	0.48 (0.37)
Se	0.3380	(26)	0.8892	(20)	0.34 (0.34)

[a] $y = 0.0000$ for each atom. [b] Digits in parentheses are standard deviations of variable parameters estimated from the diagonal elements of the normal equations matrix.

It is not convenient to include any ambiguous peaks in an R-index calculation because of the difficulty of dividing an observed intensity between two or more reflections. Nevertheless, calculated intensities (pF_c^2) for all reflections which could contribute to such peaks are additive. Therefore, a measure of the over-all agreement of any group of recorded intensities in a powder pattern is afforded by the disagreement factor[4] $D = \sum(I_o' - I_c')/\sum I_o'$, where $I_o' = (LP)^{-1}I_o$ and is the observed intensity of the multiple reflection. Also $I_c' = \sum pF_c^2$ and is the sum of the calculated intensities of all of the reflections which could contribute to this observed intensity. The D factor for the 22 unambiguous reflections used in the refinement was 10.0%, and the best value for all 74 peaks measured in the powder pattern was 11.5%.[11] Observed and calculated intensities for all 74 peaks and 111 contributing reflections are recorded in Table IV.

Interatomic distances, in angstroms, were calculated from the refined coordinates of neighboring atoms and are listed in Table V. Except where these distances were identical with the b cell constant, standard deviations have been calculated from the standard deviations of coordinates listed in Table II and range from 0.03 A for selenium–selenium pairs to 0.04 A for metal–metal pairs. These comparatively high values reflect the low number of observations per refinable parameter but in no way affect the main conclusion of this paper.

Table III

Observed and Calculated Structure Factors Using Parameters in Table II

H	K	L	$\lvert F_o\rvert$	F_c
0	0	2	41.3	−33.8
1	0	1	35.2	41.7
0	1	1	43.9	48.9
1	0	3	37.1	44.3
0	0	4	125.6	−99.2
−2	0	2	164.5	169.9
1	1	2	140.1	146.8
0	1	3	85.2	82.9
2	1	1	64.8	66.6
−1	1	4	181.3	169.3
3	0	1	82.3	82.8
−2	1	3	78.9	79.6
2	1	3	41.9	−37.2
−3	0	3	105.4	97.4
−3	1	0	226.6	233.9
0	2	0	244.0	247.4
−1	1	6	136.6	119.8
−3	0	5	65.5	−62.1
−4	0	4	110.5	108.1
0	1	9	71.1	67.5
−5	1	2	129.2	135.8
4	2	2	105.3	106.4

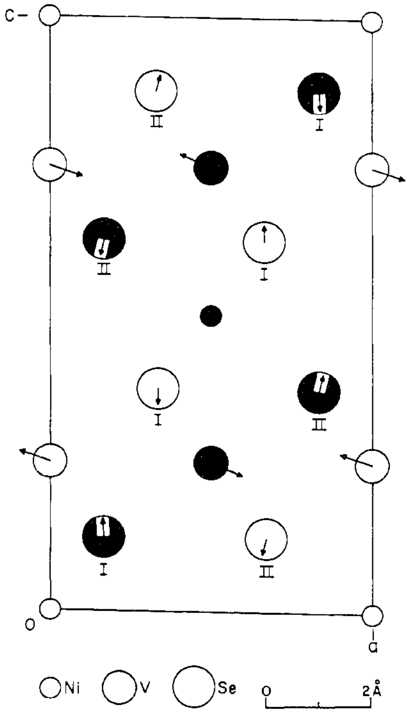

Figure 1.—Trial structure of NiV_2Se_4 and shifts (arrows doubled for emphasis) made in refinement. Dark circles represent atoms at $y = 1/2$; open circles represent atoms at $y = 0$. I and II distinguish the crystallographically independent sets of selenium atoms (from Jellinek[2]).

Discussion

The final refined structure can be derived from the trial structure, shown in Figure 1, by shifting the atoms

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[8] "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, pp 31, 32.

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[10] G. B. Carpenter, "Brown Crystallographic Least-Squares Program, BXLS," Brown University, 1962.

[11] Jellinek obtained a D factor of 11.0% for the 47 measured peaks in the powder pattern of the isomorphous compound Cr_3S_4.

TABLE IV

OBSERVED AND CALCULATED INTENSITIES FOR NiV_2Se_4

hkl	$10^{-2}pF_o^2$	$10^{-2}I_o'$	*hkl*	$10^{-2}pF_c^2$	$10^{-2}I_o'$	*hkl*	$10^{-2}pF_c^2$	$10^{-2}I_o'$
002	23	30	215	9		512	500	
101	35	22	−107	400	1698	−219	364	
011	96	68	−123			−130	34	
103	39	24	−314	513		−422	418	
−202	577	475	123	34	376	−318	650	2014
004	197	277	220	13		219	85	
112	862	688	−402	296		−132	583	
013	275	255	017	28		−309	56	
211	177	147	314	366	708	132	387	
−114	1147	1154	024	330		318	753	
301	137	119	402	337	533	028	774	2823
−213	254	219	−222	685		−514	164	
213	55	62	222	921		+11·10	253	
−303	190	195	008	647	2323	−417	442	983
−310	2188	1802	125	260		309	123	
020	1224	1045	−224	511		−424	288	
−116	574	654	404	310	1174	231	29	
−305	77	75	217	356		−231	3	
−404	234	214	224	512		11·10	140	
019	182	178	−208	11	782	505	5	
−512	738	586	−118	6		−424	289	751
422	453	389	413			424	378	
202	836		321	119		417	8	
−112	1605	2335	−307		148	−134	336	
105	240		316	21		134	397	
−204	503	973	026	12	131	−228	28	1122
301	137		307	72		−129	14	
−301			−109	10	192	327	103	
204	521		−323	172		−600	339	417
114	1328	2200	109	152	347	−521	7	
006	12		−406	292		01·11	363	
015	56	113	501	52	343	−516	259	
−215	124		−226	466		602	17	
−206	351		415	383		−507	2	
022	11	617	406	196	1115	−330	838	1535
206	262		−127	456		−426	395	
116	798		226	372	758	521	49	378

TABLE V

INTERATOMIC DISTANCES IN ANGSTROMS FOR NiV_2Se_4

V–S, Ni–Ni (parallel to *b*): 3.44
Ni–V: 3.00
V–V: 3.05, 4.02
Ni–Si^I: 2.57
Ni–Se^{II}: 2.41
V–Se^I: 2.55, 2.66
V–Se^{II}: 2.38, 2.52
Se^I–Se^I: 3.44, 3.72, 3.27
Se^{II}–Se^{II}: 3.23, 3.44, 3.75

Around each Se^I
2Se–Ni: 2.57
2Se–V: 2.65
1Se–V: 2.55

Around each Se^{II}
2Se–V: 2.38
1Se–V: 2.52
1Se–Ni: 2.41

half the distances indicated by arrows. It is isostructural with Cr_3S_4 and can be described as approximately hexagonal close-packed arrangement of selenium atoms with metal atoms occupying three-fourths of the available octahedral holes in an ordered fashion. This ordering produces a slight monoclinic distortion in the parent hexagonal lattice. It is worth noting that, because of the particular ordering of the ions among the available sites, no hexagonal space group can be used to describe the structure even if this distortion is ignored.

The most significant features of the structure are the possibilities for d-orbital overlap between vanadium atoms. In particular, those located close to the plane at $z = {}^1/_4$ are shown in projection on this plane in Figure 2 with four crystallographically independent vanadium–vanadium distances. Two of these distances are less than or equal to 3.44 A, and, therefore, according to the Goodenough[3] model, metal–metal d-orbital overlap can occur. It should be noted that in Cr_2S_3, the metal ions do not show this tendency to move more closely together. Since any vanadium–vanadium band will be only partially filled, this provides an

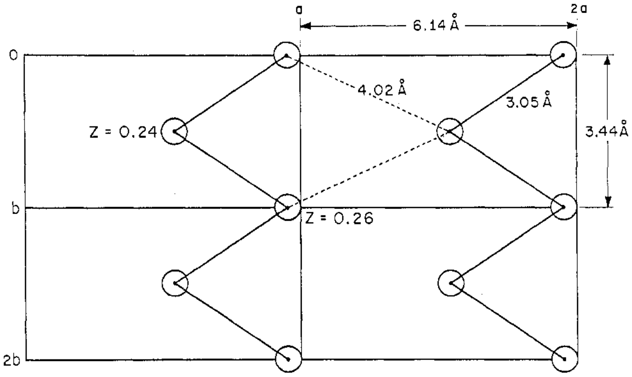

Figure 2.—Vanadium atoms near the plane $z = {}^1/_4$ projected on that plane.

explanation for the metallic properties of NiV_2Se_4. Also, the smaller unit cell size noted earlier for NiV_2Se_4 is apparently primarily the result of metal–metal interactions affecting the *a* and *b* axial lengths.

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Vibrational Analysis of Some Oxyanion–Metal Complexes

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Normal coordinate calculations have been performed for metal complexes of the oxyanions nitrate, carbonate, sulfate, perchlorate, and phosphate. Force fields determined to give satisfactory frequencies for the uncomplexed oxyanions were perturbed in ways corresponding to metal binding and oxyanion polarization, and the effects on observable infrared and Raman vibrational frequencies were calculated. Comparisons are made between our calculated frequencies for the complexed oxyanions and experimental frequencies, enabling conclusions to be drawn about the relative importance of metal–oxygen bond formation and oxyanion polarization effects.

A considerable amount of experimental data has become available recently concerning the changes in infrared and Raman spectra of oxyanions such as carbonates, nitrates, phosphates, sulfates, and perchlorates upon metal complex formation. In order to extract from the reported frequency shifts and intensity changes some information about the physical nature of the interaction between metal ions and oxyanion ligands, we have undertaken a series of normal coordinate analyses of the molecular vibrations in complexes of these polyatomic ligand anions.

These calculations, the results of which we present here, were performed in the simplest permissible fashion, in order to show the trends of molecular deformation parameters, especially of the bond-stretching force constants, in a variety of forms and strengths of metal–ion association.

Normal Coordinate Calculations

The method of approach was identical for all molecules and consisted of first finding the simplest set of force constants which could give a set of frequencies for the normal modes of the free (uncomplexed) oxyanion in close agreement with observed frequencies.[2] A simple valence force field with one or two off-diagonal interaction force constants was found satisfactory in all cases. The calculations for the free oxyanions were all performed assuming symmetry point groups corresponding to the symmetries of the metal–oxyanion complexes investigated, but force constants for all modes involving metal motion were equated to zero. Thus, the factored secular determinants were divided into blocks corresponding to the irreducible representations of the point groups of the complexes, but these blocks contained identical eigenvalues owing to the artificial separation of degenerate modes. The oxyanion bond-stretching force constants were then changed so that the bond to the oxygen atom interacting with a metal ion was weakened, while the others were strengthened. This was done in such a way that the sum of the stretching force constants for all of the oxyanion bonds remained constant in all cases. This situation is believed to represent closely simple polarization of the oxyanions. Next the metal–oxygen bond force constant was increased from zero, leaving the oxyanion force constants at their values for the free anion. Finally, the metal–oxygen bond was given a finite force constant, and the polarization effect on the anion bonds to the oxygen atoms was redetermined.

Changes in off-diagonal elements of the force constant matrices, in bending force constants of the ligands, and in the Z–O–M bending force constants have been neglected. The directions and magnitudes of the first two effects are hardly predictable, even in a more elaborate force field approach, without a more detailed knowledge of charge distributions. For Z–O–M bending force constants also, it is virtually impossible to predict their behavior as M–O bond strength and ligand polarization increase. Certainly, it is likely that such effects will be small compared with the changes in stretching force constants considered in detail above. Incorporation of a Z–O–M bending force constant of 0.2 mdyne/A into the force field of C_{2v} nitrate complexes, for example, leaves all of the A levels unchanged and results mainly in an upward shift of the two B levels by only 10–15 cm^{-1}.

The standard Wilson *F–G* matrix method[3] of analyzing the normal modes of vibration was used throughout although several of the results could alternatively have been obtained by a simpler first-order perturba-

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