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Void Channels in the Nb_3Te_4, Ta_2S, and Nb_2Se Structure Types; The Structure of Nb_3Se_4

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The crystal structure of Nb_3Se_4 has been determined and refined by single-crystal X-ray methods. The final unweighted R factor of the hexagonal unit cell (space group $P6_3/m$, $a = 10.007_4 \pm 1_5$ and $c = 3.4667 \pm 8$ Å) equaled 0.058. The phase Nb_3Se_4 is isostructural with Nb_3S_4 and Nb_3Te_4. The existence of similar void channels in the Nb_3Te_4 structure type and the Ta_2S and Nb_2Se structures and a rationale for the nonexistence of a phase exhibiting the Nb_3Te_4 structure type in which another Group VB transition metal is substituted for Nb are discussed.

Introduction

In an investigation of the Nb–Se and Nb–Te systems Selte and Kjeshus (*1*) reported phases of the stoichiometries Nb_3Se_4 and Nb_3Te_4, respectively, and determined the structure of Nb_3Te_4 by single crystal techniques. These investigators were unable to establish the structure of Nb_3Se_4 by single-crystal X-ray techniques, but concluded on the basis of the X-ray powder diffraction patterns that the two phases were isostructural. Ruysink, Kadijk, Wagner, and Jellinek (*2*) recently reported a single-crystal X-ray diffraction study of the phase Nb_3S_4, and report it to be isostructural with Nb_3Te_4. The purpose of this paper is to correlate the Nb_3Te_4 structure with those of Ta_2S and Nb_2Se and to rationalize the nonexistence of the Nb_3Te_4 structure type when either vanadium or tantalum is substituted for Nb. In addition, structural parameters of the isostructural Nb_3Se_4, as determined by single-crystal X-ray techniques, are reported.

Experimental

The Nb_3Se_4 samples were prepared from selenium (Fairmount Chemical Co., Newark, N.J., 99.99%) and powdered niobium (Apache Chemicals, Benson, Ariz., 99.9%) in a manner similar to that described previously (*3*), but modified by use of a closed crucible. The final annealing temperature was 1550°C. The space group, $P6_3/m$, and an initial set of lattice parameters were determined from Weissenberg, rotation and precession photographs. Single-crystal intensity data were collected from a rectangular prism (about $10 \times 20 \times 70$ μ) using a multiple film Weissenberg technique. Intensities were measured by visual comparison with a calibrated scale. Nickel-filtered CuK_α radiation was used to collect 92 independent reflections from the HK0 and K1 levels; the crystal cracked before further data could be collected.

The raw data were corrected for the usual effects, including absorption [$\mu = 790$ cm^{-1}] using Busing and Levy's method (*4*) for a general polyhedron. Lattice parameters determined from a Guinier powder photograph at 25°C using Pt, $a = 3.9237 \pm 3$ Å (5) as an internal standard follow: $a = 10.007_4 \pm 1_5$ Å, $c = 3.4667 \pm 8$ Å, $V = 300.7 \pm 2$ Å^3. With $Z = 2$ (cf. below), $D_x = 6.57$ gcm^{-3}.

Structure Refinement

Since Nb_3S_4, Nb_3Se_4, and Nb_3Te_4 have been reported to be isostructural, the positions of the atoms in Nb_3Te_4 were used as initial positions for those in the Nb_3Se_4 structure. In addition to the four positional parameters ($Z = 2$), three independent isotropic temperature factors and two scale factors were refined using the computer program ORFLS (*6*). The structure was thus refined with

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more than ten reflections per refined variable. The atomic scattering factors were those given by Hanson, Herman, Lea, and Skillman (*7*). The real and imaginary parts of the dispersion correction were applied to the scattering factors of both Nb and Se according to the relationship $f = f_0 + \Delta f' + (\Delta f'')^2/(2(f_0 + \Delta f'))$, where f, f_0, $\Delta f'$ and $\Delta f''$ are respectively the scattering factor corrected for dispersion, the scattering factor uncorrected for dispersion, and the real and anomalous dispersion corrections (*8*, *9*). The weights, w, were taken as unity for all reflections. The quantity minimized in the least-squares computation was $\Sigma w(|F_{\text{obsd}}| - |F_{\text{calcd}}|)^2$. An unweighted R value of 0.058 was obtained after several cycles, and additional cycles of computation did not result in further refinement of the structure; all parameter shifts were <1% of the e.s.d.'s of the parameters. The parameters obtained are listed in Table I. The interatomic distances implied by these parameters were calculated using the program DISTAN (*10*) and may be found in Table II.

TABLE II

INTERATOMIC DISTANCES IN Nb_3Se_4

Reference atom	Coordinated atom	Number of coordinated atoms	Distance (Å)
Nb	Nb	2	2.885 ± 7
	Nb	2	3.467 ± 1
	Nb	2	3.567 ± 7
	Se-II	2	2.577 ± 5
	Se-II	1	2.612 ± 6
	Se-I	2	2.692 ± 3
	Se-II	1	2.781 ± 7
Se-I	Nb	6	2.692 ± 3
	Se-I	2	3.467 ± 1
	Se-II	6	3.511 ± 5
	Se-II	3	3.896 ± 5
Se-II	Nb	2	2.577 ± 5
	Nb	1	2.612 ± 6
	Nb	1	2.781 ± 7
	Se-II	2	3.467 ± 1
	Se-I	2	3.511 ± 5
	Se-II	4	3.583 ± 5
	Se-I	1	3.896 ± 5

Discussion

The isomorphism of Nb_3S_4, Nb_3Se_4, and Nb_3Te_4 is expected in view of the fact that S, Se, and Te all exhibit similar valence electron configurations and that the Se/Nb radius ratio is between that of S/Nb and Te/Nb.

Ruysink et al. (*2*) have commented on a distinctive feature of the Nb_3Te_4 structure type, namely, the presence along the *c* direction of empty channels which run through the lattice and which are wide enough to accommodate additional atoms. Similar empty channels have been found recently in the Ta_2S (*11*) and Nb_2Se (*12*) structures. The phases Ta_2S, Nb_2Se and others isotypic with Nb_3Te_4 are similar in many respects. All exhibit high metallic luster, good electrical conductivity (*2*, *13*), and a high degree of brittleness. In addition, all of these structures exhibit a significant number of short metal–metal contacts. In the Nb_3Te_4 structure type, one chalcogen atom is situated in a trigonal prism formed by six metal atoms, a common coordination polyhedron in transition metal–chalconide phases, while the second chalcogen atom may be considered coordinated in a trigonal prism in which two of the metal atoms forming one of the triangular faces are missing. A similar coordination polyhedron is observed for one of the S atoms in the Ta_2S structure. It has been argued that the empty channels present in the Ta_2S and Nb_2Se structures are not truly void, but rather contain regions of localized nonbonded electrons (*12*). In view of the decided similarity in physical properties and structural characteristics between Ta_2S, Nb_2Se and the phases isostructural with Nb_3Te_4, it seems plausible to suggest that in the Nb_3Te_4 structure type the channels devoid of atomic centers are similarly regions of localized nonbonding electrons.

TABLE I

THE PARAMETERS OF THE CRYSTAL STRUCTURE OF Nb_3Se_4 FROM THE LEAST-SQUARES REFINEMENT

	$10^4\ X/a$	$10^4\ Y/b$	$10^4\ Z/c$	$B(\text{Å}^2)^{a,b}$
Nb	4876 ± 4	1085 ± 5	2500	$2.5_6 \pm 1_7$
Se-I	3333	6667	2500	$4.1_3 \pm 2_8$
Se-II	3385 ± 6	2800 ± 6	2500	$4.0_3 \pm 1_6$

[a] Scale factor zero level = $0.429_4 \pm 5_8$

[b] Scale factor first level = $0.511_2 \pm 6_9$

It is most interesting that the Nb_3Te_4 structure type has not been found for any metal except Nb, not even for the other Group VB transition metals, vanadium or tantalum. Brewer (*14*) has discussed the ideas of Engle which correlate the tendency of a metal to be found in a given coordination polyhedron in the condensed state with the promotion energy required to obtain the gaseous metal atom in a given electronic configuration. This rule states that, if two excited states have the same number of unpaired electrons available for bonding and if their bond energies are comparable, then the states with the lowest promotion energy will be favored in the condensed state. In Table III are listed the promotion energies for V, Nb, and Ta (*15*) for the lowest d^3s^2, d^4s, d^5, and d^3sp states with the maximum electronic multiplicity for the gaseous atoms.

Consistent with the Brewer–Engle correlation (BEC), the lowest lying valence electron bonding configuration for all Group VB metals is the d^4s state. For vanadium and niobium the next energy states are 41 and 32 kcal/mole higher, respectively, and accordingly the d^4s state should make important contributions to bonding with little or no contribution from higher energy states. However the d orbitals in the first row transition series are not as effective in bonding as they are in the second and third row transition metals (*16*). Accordingly, if the transition metal d orbitals are substantially involved in bonding in these phases, thereby stabilizing a given structure, then V_3X_4, with X = S, Se and Te, may well be expected to exhibit a structure different from that of Nb_3Te_4. This is precisely what is found; namely, vanadium is known to form the phases V_3S_4 (*17*), V_3Se_4 (*18*) and, V_3Te_4 (*19*), all of which exhibit the Fe_3Se_4 (*20*) structure type which is also exhibited by a large number of other first row transition metal chalconides: Ti_3Se_4 (*18*), Ti_3Te_4 (*19*), Cr_3S_4 (*21*), Cr_3Se_4 (*22*), Cr_3Te_4 (*19*), Fe_3Te_4 (*23*), Co_3Se_4 (*18*), and Ni_3Se_4 (*18, 24*). In addition, the fact that so many of the first row transition metals from Ti to Ni (with the exception of Mn) form phases isostructural with Fe_3Se_4 suggests that the bonding in this structure type is relatively insensitive to the electronic population of metallic d orbitals.

Tantalum forms a phase 2H-$Ta_{1+x}Se_2$, $0.2 \leqslant x \leqslant 0.64$ (*25, 26*), which exhibits the M_3X_4 stoichiometry when $x = 0.50$ and which is isostructural with 2H-$Nb_{1+x}Se_2$, $0 \leqslant x \leqslant 0.29$ (*25, 26*) and 2H-$Nb_{1+x}S_2$, $0.30 \leqslant x \leqslant 0.43$ (*27*). In addition Nb forms the phases 3R-$Nb_{1+x}S_2$, $0.12 \leqslant x \leqslant 0.35$ at 1000°C and $0.12 \leqslant x \leqslant 0.50$ at 800°C, which when, at 1000°C, $x = 0.25$ is $Nb_{2.50}S_4$ and when, at 800°C, $x = 0.50$ is $Nb_{3.00}S_4$ (*27*). The valence electron concentrations (VEC) calculated on the basis of an $M_{2+y}X_4$ stoichiometry for these phases along with that for the hypothetical M_3X_4, M = V, Nb, and Ta and X = S, Se, and Te, are listed in Table IV.

TABLE III

PROMOTION ENERGIES IN kcal/mole FOR THE GROUP V B METALS

Metal	$d^3s^2(^4F)$	$d^4s(^6D)$	$d^5(^6S)$	$d^3sp(^6G)$
V	0	6	58	47
Nb	3	0	32	48
Ta	0	28	34	50

With regards to the BEC it is noteworthy to observe that for Nb and Ta the differences between the d^4s state, the lowest lying interesting bonding state, and the d^5 state are 32 kcal/mole and 6 kcal/mole, respectively. Accordingly, a possible reason for the existence of the Nb_3Te_4 structure type for niobium alone is that as metal atoms are added to a hypothetical $M_{2+y}X_4$ phase to reach the M_3X_4 stoichiometry a critical VEC is reached at or below 39. Above this limiting VEC either the additional electron must be placed into an additional orbital necessitating configuration interaction between two valence electron configurations if this is energetically feasible (the case for Ta but not Nb), or the structure must change, (the situation for Nb). Consequently tantalum availing itself of both the d^4s and d^5 configurations in bonding can form a phase 2H-$Ta_{1+x}Se_2$ which with a VEC >39 does not exhibit the Nb_3Te_4 structure type. On the other hand Nb with only the d^4s configuration energetically available is forced at a VEC <39 [36.9 for 2H-$Nb_{1+x}Se_2$, $x = 0.29$, and 36.5 for 3R-$Nb_{1+x}S_2$, $x = 0.25$ (1000°C), and 38.3 for 2H-$Nb_{1+x}S_2$, $x = 0.43$] to form another structure type, namely that of Nb_3Te_4. The existence of phase 3R-$Nb_{1+x}S_2$, $x = 0.50$ (800°C), with a VEC equal to 39, can be accounted for as either due to the existence of a phase boundary between 3R-$Nb_{1+x}S_2$ and Nb_3S_4 as x in the limit

TABLE IV

VALENCE ELECTRON CONCENTRATION (VEC) FOR VARIOUS GROUP V B METAL CHALCONIDES

Phase	VEC
M_3X_4 (M = Group V B Metal, X = S, Se or Te)	39.0
2H-$Ta_{1+x}Se_2$ $x = 0.64$	40.4
2H-$Nb_{1+x}Se_2$ $x = 0.29$	36.9
3R-$Nb_{1+x}Se_2$ $x = 0.25$ (1000°C)	36.5
3R-$Nb_{1+x}Se_2$ $x = 0.50$ (800°C)	39.0
2H-$Nb_{1+x}S_2$ $x = 0.43$	38.3

approaches 0.50 or to the fact that 3R-$Nb_{1+x}S_2$, $x \leqslant 0.50$, may be a thermodynamically stable low temperature phase (800°C) while all the other phases discussed here, including 3R-$Nb_{1+x}S_2$, $x \leqslant 0.25$, are thermodynamically stable only at substantially higher temperatures (>1000°C). In either case the arguments for the existence and uniqueness of the Nb_3Te_4 structure type remain cogent.

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