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Synthesis of High-Pressure Phases of VCoSb and VFeSb with a Ni_2In ($B8_2$) Type Structure

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The high-pressure transformation of VCoSb and VFeSb from the MgCuSb-type structure ($C1_b$) to the Ni_2In-type structure ($B8_2$) was found to occur under high temperature–pressure conditions. The decrement of unit cell volume associated with the phase transformation was calculated to be about 15% in both cases, and average coordination numbers of the transition metal increased from 6 to 8.5 in the pressure-induced phase transformation.

Introduction

Pnictides with a chemical formula of MM′X (M and M′ are 3d transition metals) are best understood as intermetallic compounds and concepts of classical valency are not easily applied to them. In fact, most of these compounds show metallic behavior in electrical conductivity. On the other hand, they exhibit a variety of magnetic properties such as ferromagnetism, ferrimagnetism, antiferromagnetism, and Pauli paramagnetism. Unlike the phosphides and arsenides, systematic syntheses and investigations of antimonides have rarely been carried out.[1] We have tried to prepare antimonides in order to increase our understanding of the structures and magnetic properties which they exhibit. In the present study, hexagonal new phases of VCoSb and VFeSb with the Ni_2In-type structure ($B8_2$) were synthesized under high pressures. Cubic phases of these compositions with the MgCuSb-type structure ($C1_b$) have been previously prepared.[2] These results indicate that for these compounds polymorphic transformation from the MgCuSb- to the Ni_2In-type takes place under high pressures. This transformation is discussed from the viewpoint of crystal chemistry.

Experimental Section

For the preparation of the low-pressure phases of VCoSb and VFeSb, vanadium (99.9%), cobalt (99.99%), iron (99.99%), and antimony (99.999%) powders were mixed in the desired ratio, sealed in an evacuated silica tube, and heated in an electric furnace at 1200 °C for 24 h. After the reaction was complete, the reacted matter was cooled slowly to room temperature.

For the high-pressure experiments, the starting material obtained in this way was placed into a cylindrical BN capsule, which was thereafter inserted into a carbon tube. This assemblage was placed in a pyrophyllite cube, and the cube was subjected to high temperature–pressure conditions with a cubic anvil device. The cell assemblage is shown in Figure 1. The magnitude of pressure generated inside the cell was calibrated on the basis of the electrical transitions for Bi (2.55 and 7.7 GPa) and Ba (5.5 GPa). The temperature of the sample was determined by using a Pt/Pt/13% Rh thermocouple placed in the center of the cube.

The reaction was carried out at 5.0 GPa and 900 °C for 1 h. The sample was quenched to room temperature prior to the release of applied pressure. The products were identified by X-ray powder diffraction. Silicon was used as an internal standard.

Results and Discussion

Table I. X-ray *d* Spacings for VCoSb-I[a] with the MgCuSb-Type Structure ($C1_b$)

hkl	d_{obsd}/nm	d_{calcd}/nm	I/I_0
111	0.3357	0.3350	61
200	0.2903	0.2901	39
220	0.2053	0.2051	100
311	0.1752	0.1749	18
222	0.1675	0.1675	7
400	0.1451	0.1450	8
331	0.1332	0.1331	3
420	0.1298	0.1297	4
422	0.1185	0.1184	11
440	0.1026	0.1026	3
531	0.09810	0.09807	3
600, 442	0.09672	0.09670	3
620	0.09176	0.09174	4

[a] $a = 0.5802$ nm.

Table II. X-ray *d* Spacings for the High-Pressure Phase of VCoSb-II with the Ni_2In-Type Structure ($C1_b$)[a]

hkl	d_{obsd}/nm	d_{calcd}/nm	I/I_0
101	0.3018	0.3016	97
002	0.2698	0.2697	29
102	0.2166	0.2166	98
110	0.2099	0.2100	100
201	0.1725	0.1723	11
112	0.1658	0.1657	17
103	0.1613	0.1612	10
202	0.1510	0.1508	15
004	0.1347	0.1349	4
211	0.1332	0.1332	4
203	0.1278	0.1279	3
212	0.1225	0.1225	10
300	0.1213	0.1212	5
114	0.1135	0.1135	9

[a] $a = 0.4200$ nm, $c = 0.5398$ nm.

The X-ray diffraction patterns of the low-pressure phase of VCoSb, denoted as VCoSb-I, were completely indexed on the basis of the cubic unit cell (Table I), and the value of the lattice parameter is in good agreement with that previously reported.[2] The crystal structure of this cubic phase is found to be that for MgCuSb (C1b), and atomic distribution of the low-pressure phase of VCoSb is expected to be as follows: Co, A site; V, B site; Sb, D site (Figure 2). This distribution is based on the results of the neutron diffraction analysis of MnCoSb and MnCuSb with the MgCuSb-type structure.[3,4] In the case of VFeSb, however, the product prepared by the same method as that used for VCoSb did not result in a single phase with a MgCuSb-type structure but contained a small

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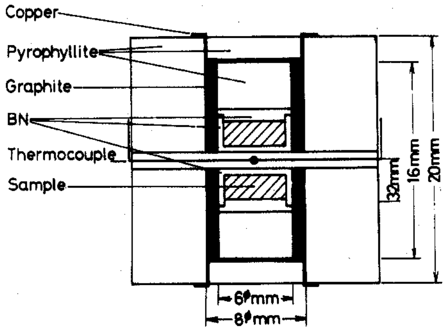

Figure 1. Cell assemblage for the high-temperature–pressure experiment.

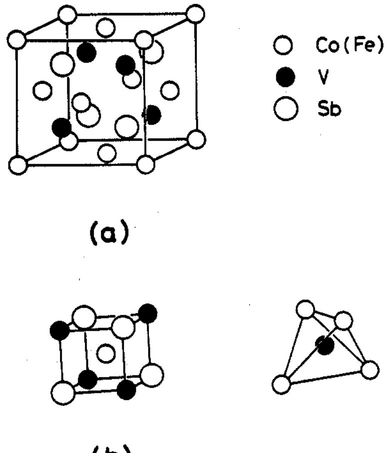

Figure 2. (a) Crystal structure of the MgCuSb type ($C1_b$). (b) Coordination polyhedron of V and Co (Fe) in the MgCuSb-type structure.

Table III. X-ray *d* Spacings for the High-Pressure Phase of VFeSb-II with the Ni_2In-Type Structure ($B8_2$)[a]

hkl	d_{obsd}/nm	d_{calcd}/nm	I/I_0
101	0.3038	0.3033	100
002	0.2698	0.2699	15
102	0.2176	0.2173	72
110	0.2118	0.2117	100
201	0.1737	0.1736	10
112	0.1667	0.1665	10
103	0.1614	0.1615	8
202	0.1517	0.1516	15
211	0.1342	0.1342	5
212	0.1232	0.1233	9
114	0.1137	0.1138	5

[a] $a = 0.4233$ nm, $c = 0.5398$ nm.

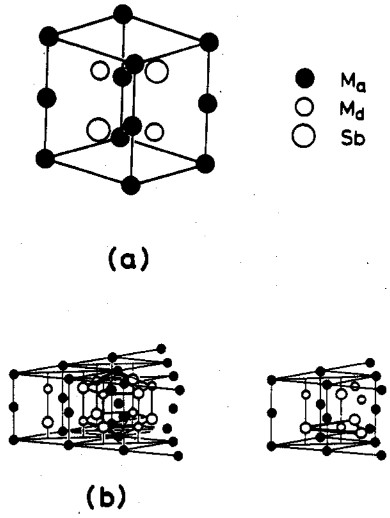

Figure 3. (a) Crystal structure of the Ni_2In type ($B8_2$). (b) Coordination polyhedron of M_a (2(a) site transition metal) and M_d (2(d) site transition metal) in the Ni_2In-type structure.

Table IV. Volume-Change-Ratios of VCoSb and VFeSb

compd	10^3V_I/nm^3	10^3V_{II}/nm^3	$(V_{II} - V_I)/V_I$
VCoSb	48.78	41.23	−0.15
VFeSb	49.44	41.93	−0.15

Table V. Crystallographic Data for VCoSb-I and VCoSb-II Phases

1. VCoSb-I: MgCuSb-Type Structure ($C1_b$)

space group $F\bar{4}3m$ Sb atoms in D site
$Z = 4$ $a = 0.5802$ nm
Co atoms in A site $V_{\mu ni} = 0.1953$ nm^3
V atoms in B site

Interatomic Distances (nm)

	Co	V	Sb
Co		0.2511 (4)[a]	0.2511 (4)
V	0.2511 (4)		0.2901 (6)
Sb	0.2511 (4)	0.2901 (6)	

2. VCoSb-II: Ni_2In-Type Structure ($B8_2$)

space group $P6_3/mmc$ Sb atoms in 2(c) site
$Z = 2$ $a = 0.4200$ nm
M_a atoms in 2(a) site $c = 0.5398$ nm
M_d atoms in 2(d) site $V_{\mu ni} = 0.8246$ nm^3

Interatomic Distances (nm)

	M_a	M_d	Sb
M_a	0.2699 (2)	0.2775 (6)	0.2775 (6)
M_d	0.2775 (6)		0.2425 (3) 0.2699 (2)
Sb	0.2775 (6)	0.2425 (3) 0.2699 (2)	

[a] Numbers in parentheses give numbers of atoms.

amount of an unknown phase.

The X-ray *d* spacings of VCoSb-II and VFeSb-II, synthesized under high pressure–temperature, were indexed on the basis of a hexagonal unit cell of the Ni_2In structure ($B8_2$) (Tables II and III). It is expected that in this structure V and Co (Fe) atoms randomly distribute on both 2(a) and 2(d) sites and that the Sb atom occupies site 2(c) (Figure 3). The only other antimonide with a Ni_2In-type structure that has been reported is CoNiSb.[5]

Our X-ray data on quenched material show that VCoSb and VFeSb transform from the MgCuSb- to the Ni_2In-type structure at high pressure. To our knowledge, this polymorphic transition has not been reported previously. Volume-change ratios for this transformation are summarized in Table IV. As seen in the table, a volume change of 15% for both compounds is found. It must be that the Ni_2In-type structure represents a more dense filling of atoms compared to the MgCuSb-type structure, since it is well-known that pressure favors more efficient packing and the higher density phase.

For these two types of crystal structure, coordination polyhedra of the transition metal are shown in Figure 2. In the MgCuSb-type structure, Co (or Fe) is surrounded by four Sb and four V atoms forming a cube, and V is coordinated by four Co (or four Fe) atoms forming a tetrahedron. On the other hand, for the Ni_2In-type structure, M_d (2(d) site transition metal) is surrounded by three Sb atoms forming a planar triangle, and M_a (2(a) site transition metal) is coordinated by two M_a, six M_d, and six Sb atoms forming a complicated polyhedron. As a result, the average coordination number of the transition metal is 6 (=(4 + 8)/2) for the MgCuSb-type structure, while it is 8.5 (=(14 + 3)/2) for the Ni_2In-type structure. We therefore conclude that the transformation of VCoSb and VFeSb involves an increase of coordination number.

Interatomic distances between the constituent atoms of both MgCuSb- and Ni_2In-type structures are shown in Table V. From these, it is seen that the nearest-neighbor distance between the transition metal and Sb shrinks from D(Co–Sb) = 0.2511 nm to $D(M_d–Sb)$ = 0.2425 nm, while that between the transition metals expands from D(V–Co) = 0.2511 nm to $D(M_a–M_a)$ = 0.2699 nm in the transformation.

In discussing interatomic distances in metal and intermetallic compounds, Pearson pointed out that Pauling's bond-order rule appears to be most reliable[6]

$$D(n) - D(1) = 0.060 \log n \text{ (Pauling's rule)}$$

In this equation n is the number of valence electrons per ligand, $D(1)$ represents the single-bond distance calculated by using Pauling's single-bond radii[7], and $D(n)$ is the observed bond distance.

In VCoSb-I with the MgCuSb-type structure ($C1_b$), D(Co–Sb) = 0.2511 nm is comparable with the sums of Co and Sb single-bond radii ($D(1)$ = 0.2533 nm), while D(Co–V) = 0.2511 nm is larger than the sums of Co and V single-bond radii ($D(1)$ = 0.2386 nm). The bond orders are calculated to be 1.17 for the Co–Sb bond and 0.62 for the Co–V bond. These values of bond order indicate that the Co–Sb bond is much stronger than the Co–V bond. Consequently, the Co atom is coordinated substantially by the four Sb atoms forming a tetrahedron due to the strong Co–Sb bond, although it is surrounded apparently by four Sb and four V atoms. That the bond order is 1.17 for the Co–Sb bond and that there is a tetrahedral bond directionality indicate that covalency between Co and Sb atoms occurs.

In VCoSb-II with the Ni_2In-type structure ($B8_2$), $D(M_d–Sb)$ = 0.2425 nm is much smaller than the sums of M_d and Sb single-bond radii ($D(1)$ = 0.2584 nm), but $D(M_a–M_a)$ = 0.2425 nm is larger than the single-bond separation between M_a atoms ($D(1)$ = 0.2386 nm). The bond orders are calculated to be 1.84 for the M_d–Sb bond and 0.30 for the M_a–M_a bond. Considering the calculated value of n and the triangular bond directionality for the M_d–Sb bond, a strong covalency between M_d and Sb atoms is expected. It is concluded that the metal atom forms the covalent bond with the Sb atom in both MgCuSb- and Ni_2In-type structures and that the strength of the covalent bond increases in the transformation from the MgCuSb- to Ni_2In-type structure.

Registry No. VCoSb, 12526-55-5; VFeSb, 66590-17-8.

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Reactions of Metal–Disulfur Complexes with Nucleophiles and Electrophiles[1]

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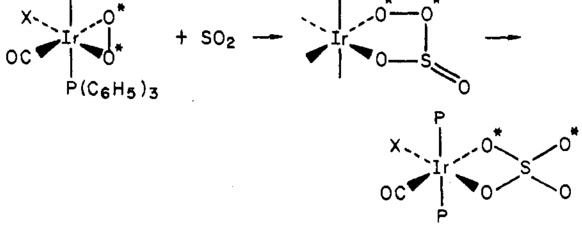
New synthetic methods for the preparation of the disulfur complexes of molybdenum $MoOS_2(S_2CNR_2)_2$ (where R = CH_3, C_2H_5, and n-C_3H_7) are described. The reactions of these disulfur complexes with a series of nucleophiles, N (N = $P(OC_2H_5)_3$, $P(C_6H_5)_3$, CH_3NC, CN^-, and SO_3^{2-}), have been characterized, and in each case the sulfur-substituted nucleophile (S→N) and $MoO(S_2CNR_2)_2$ are produced. Reaction of $MoOS_2(S_2CNR_2)_2$ with C_6H_5SH or $C_6H_5S^-$ yields the dimeric molybdenum(V) complex $Mo_2O_2S_2(S_2CNR_2)_2$. The molybdenum–disulfur complexes do not react with the electrophile CH_3I, but reaction with CH_3SO_3F produces a new complex containing a persulfide ligand, $[MoO(SSCH_3)(S_2CNR_2)_2]^+$. Characteristics of the synthetic molybdenum complexes are compared to those of certain molybdoenzymes which have been found to contain labile sulfur atoms. Reactions of the coordinated disulfur ligand in $IrS_2(dppe)_2Cl$ (where dppe = bis(diphenylphosphino)ethane) have also been studied. In contrast to the molybdenum systems, no reactions occur with the common thiophiles $P(C_6H_5)_3$, $P(OC_2H_5)_3$, and CN^-. Methyl fluorosulfonate reacts to form a persulfide complex of Ir(III), $[Ir(SSCH_3)(dppe)_2]$,$^{2+}$ which has been characterized by ^1H and ^{31}P NMR, conductivity studies, and analytical data.

Introduction

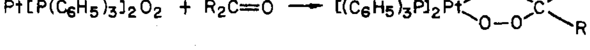
Although examples of mononuclear complexes containing the dioxygen ligand are known for most transition metal ions,[2] few monomeric complexes containing the analogous disulfur ligands have been characterized.[3-10] The latter have been prepared principally by two methods: by the reaction of elemental sulfur with coordinatively unsaturated compounds[4-6a] or by the reaction of hydrogen sulfide with compounds containing basic ligands.[3,6] Two disulfur complexes which have been characterized by X-ray diffraction studies are $[IrS_2(dppe)_2]^+$ (where dppe = bis(diphenylphosphino)ethane)[4b] and $MoOS_2[S_2CN(C_3H_7)_2]_2$.[6] The S_2 ligand is bonded to the metal ion in a side-on orientation in each case, and the S–S bond distances in the molecules are similar (2.066 (6) Å in the former complex and 2.018 (8) Å in the latter).[4b,6]

Studies of analogous side-on bonded dioxygen complexes have revealed no correlation between O–O bond distance and reactivity,[2,11] but a variety of reactions of the coordinated O_2 ligand have been characterized.[11] Labeling studies with ^{18}O have helped to characterize reactions of certain group 8 dioxygen complexes (e.g., reaction 1).[12] In some reactions the



(1)

peroxy linkage remains intact (e.g., reaction 2).[13,14] It has



(2)

been proposed that in reactions of certain four-coordinate

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