

CONTRIBUTION NO. 1539 FROM THE CENTRAL RESEARCH DEPARTMENT,
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The Synthesis, Crystal Structure, and Superconducting Properties of Niobium Phosphorus Sulfide, Niobium Phosphorus Selenide, and Tantalum Phosphorus Sulfide

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Received February 17, 1969

The new ternary compounds NbPS, NbPSe, and TaPS were prepared by reaction of the elements in 1:1:1 atomic ratio in a tetrahedral anvil press at 1200° and 65 kbars. The compounds are isostructural, with orthorhombic cells and space group Immm. The cell dimensions at 1 atm and 25° are: for NbPS, $a = 3.438 \pm 0.002 \text{ \AA}$, $b = 11.88 \pm 0.01 \text{ \AA}$, $c = 4.725 \pm 0.002 \text{ \AA}$; for NbPSe, $a = 3.462 \pm 0.002 \text{ \AA}$, $b = 12.33 \pm 0.01 \text{ \AA}$, $c = 4.821 \pm 0.005 \text{ \AA}$; for TaPS, $a = 3.430 \pm 0.005 \text{ \AA}$, $b = 11.85 \pm 0.01 \text{ \AA}$, $c = 4.728 \pm 0.005 \text{ \AA}$. The crystal structures of NbPS and NbPSe were solved from X-ray powder diffraction data by the use of three-dimensional Patterson and least-squares refinement techniques. The R factors, based on F^2 , were reduced to 0.093 for NbPS and 0.086 for NbPSe. The coordination around each Nb is a bicapped trigonal prism comprised of four P and four S (Se) atoms. These share faces in pairs through the four P atoms with $2.93 \pm 0.02 \text{ \AA}$ between the Nb atoms. The P atoms are paired at $2.21 \pm 0.05 \text{ \AA}$ in NbPS and $2.13 \pm 0.04 \text{ \AA}$ in NbPSe. Solid solutions have been prepared in the systems $\text{Nb}_{1-x}\text{Ta}_x\text{PS}$ and $\text{NbPS}_{1-x}\text{Se}_x$ where $1 > x > 0$. All compounds show metallic behavior, and NbPS is superconducting with the maximum $T_c = 12.5^\circ\text{K}$. NbPSe and TaPS do not show superconductivity down to 1.25°K .

Introduction

The Nb-S, Nb-Se, and Nb-P systems have been extensively studied. Several interesting compounds are known; e.g., NbS₂ and NbSe₂ are superconducting at 6.2°K .¹ Both compounds have crystal structures based on close-packed sheets of anions^{2,3} with the Nb atoms in either octahedral or trigonal prism coordination. In the Nb-P system, the compounds NbP and NbP₂ have been reported.^{4,5} The crystal structure of NbP₂ is reported to be similar to that of NbAs₂,⁶ in which the Nb atoms are eightfold coordinated and half of the arsenic atoms are present as single anions and half are paired at 2.44 \AA . The NbP₂ structure has not yet been refined, and superconducting properties have not been described.

This paper describes the synthesis and properties of the new compounds NbPS, NbPSe, and TaPS.

Experimental Section

All reactions were carried out using a tetrahedral anvil press of National Bureau of Standards design.⁷ The operating procedure is explained elsewhere.⁸ The reactants were 2N+ pure Nb powder, 3 N pure Ta powder, 5 N pure red phosphorus, and 6 N pure sulfur obtained from Electronics Space Products, Inc., Los Angeles, Calif. Selenium of 5 N purity was obtained from American Smelting and Refining Co. of New Jersey. The elements were ground together in the desired ratio, pressed into a pellet, and contained in a boron nitride crucible. The crucible was surrounded by a graphite-sleeve resistance heater and heated in the tetrahedral anvil press. The temperature was measured using a 30% Rh-Pt—6% Rh-Pt thermocouple, uncorrected for pressure effects, which was placed at the center of the surface of the heater. The temperature at the ends of the pellet is approximately 30% lower.

(1) E. Revolinisky, *et al.*, *J. Phys. Chem. Solids*, **26**, 1029 (1965).

(2) F. Jellinek, G. Brauer, and H. Müller, *Nature*, **185**, 376 (1960).

(3) B. E. Brown and D. J. Beerntsen, *Acta Cryst.*, **18**, 31 (1965).

(4) N. Schönberg, *Acta Chem. Scand.*, **8**, 226 (1954).

(5) F. Hulliger, *Nature*, **204**, 775 (1964).

(6) S. Furuseth and A. Kjekshus, *Acta Cryst.*, **18**, 320 (1965).

(7) E. C. Loyd, U. O. Hutton, and D. P. Johnson, *J. Res. Natl. Bur. Std.*, **C63**, 59 (1959).

(8) T. A. Bither, J. L. Gillson, and H. S. Young, *Inorg. Chem.*, **5**, 1559 (1966).

Several ratios of reactants and conditions of temperature and pressure were used. The optimum conditions were 1200° and 65 kbars, held for 1 hr, cooling over 3 hr to 900°, and quenching. During quenching, the sample was cooled from operating temperature to room temperature in less than 1 min while maintaining pressure. The optimum starting ratio of Nb:S (or Se):P is 1:1.1:1.3 since excess of the lower melting reactant enhances crystal growth and excess P impedes the formation of NbS or NbSe. The products, because of the temperature gradient, generally form at the ends of the boron nitride crucible, leaving the lower melting material, usually black phosphorus, in the center. The products of all reactions were examined by Debye-Scherrer X-ray powder diffraction using nickel-filtered Cu K α radiation ($\lambda 1.5418 \text{ \AA}$). Films were read on a David Mann film reader, Model No. 1222. Unit cell dimensions were refined by a least-squares technique which utilizes an extrapolation of the Nelson Riley function.⁹

NbPS.—Reactions to prepare NbPS were carried out at various elemental ratios and conditions (Table I). When excess P was used, crystals of NbPS were often separable from excess black P. When it was not used, traces of NbS₂ were always seen in the X-ray powder diffraction patterns. Chemical analyses of the phase were only approximate because of the difficulty in obtaining sufficient separable material. They do serve to indicate the approximate formula. *Anal.* Calcd for NbPS: Nb, 59.6; S, 20.6; P, 19.9. Found: Nb, 63.1, 53.5; S, 25.4, 22.2; P, 20.39, 19.73. The density was measured pycnometrically: found, 5.29 g/cm³; calculated for four molecules of NbPS per unit cell, 5.37 g/cm³.

The variation in cell constants as given in Table I indicates a narrow range of stoichiometry in NbPS. When excess phosphorus was used in the reactants, the b axis showed the greatest change indicating a small excess of phosphorus in the product. When excess sulfur was used, little or no change occurred indicating that the compound tolerates very little deviation in sulfur content. The cell constants of stoichiometric NbPS may be indicated by an average of the values from the experiments with excess sulfur. They are $a = 3.439 \pm 0.001 \text{ \AA}$, $b = 11.875 \pm 0.002 \text{ \AA}$, and $c = 4.725 \pm 0.002 \text{ \AA}$. The Debye-Scherrer pattern is shown in Table II. The unit cell dimensions of NbPS indicating the range with composition are $a = 3.438 \pm 0.002 \text{ \AA}$, $b = 11.88 \pm 0.01 \text{ \AA}$, and $c = 4.725 \pm 0.002 \text{ \AA}$. The range of composition to which these values correspond cannot be very large.

(9) H. B. Nelson and D. P. Riley, *Proc. Phys. Soc. (London)*, **57**, 160 (1945).

TABLE I

Reactants	Conditions	EXPERIMENTAL RESULTS ^a					Superconducting Transition Temp.
		Products Identified by X-Ray Powder Diffraction		Unit Cell Dimensions in Å			
		Major Phase	Minor Phase	a	b	c	
Nb + P + S	1100°C/65 kb hold 1 hr/ cool to 900°C/quench	NbPS	NbS ₂ , P	3.439(1)	11.875(2)	4.725(2)	10-12°K
Nb + 1.25P + 0.75S	1300°C/65 kb hold 1 hr/ cool to 1100°C/quench	NbPS	Black P	3.436(1)	11.897(2)	4.724(2)	7.5-9.5°K
Nb + 1.15P + 0.85S	1300°C/65 kb hold 1 hr/ cool to 1100°C/quench	NbPS	Black P	3.439(1)	11.875(2)	4.726(2)	7.5-12°K
Nb + 0.85P + 1.15S	1300°C/65 kb hold 1 hr/ cool to 1100°C/quench	NbPS	NbS ₂	3.439(1)	11.874(2)	4.723(2)	11-12°K
Nb + 0.75P + 1.25S	1300°C/65 kb hold 1 hr/ cool to 1100°C/quench	NbPS	NbS ₂	3.439(1)	11.875(2)	4.727(2)	11.5-12.5°K
*Nb + 1.3P + .9S	1300°C/65 kb hold 2 hr/ cool to 1100°C/quench	NbPS	Black P	3.437(1)	11.888(2)	4.724(2)	8-11°K
Nb + 1.2P + 0.9 Se	1200°C/65 kb hold 1 hr/ cool to 1000°C/quench	NbPSe	NbSe ₂ , NbP ₂	3.462(1)	12.33(1)	4.826(5)	None to 1.25°K
Ta + 1.2P + 1.0S	1200°C/65 kb hold 1 hr/ cool to 1000°C/quench	TaPS	TaS, TaP ₂	3.430(5)	11.85(1)	4.728(5)	None to 1.25°K
Nb + 1.3P + .75S + .25Se	1200°C/65 kb hold 2 hr/ quench	NbPS type	NbP, NbS ₂ type	3.446(1)	11.985(2)	4.749(2)	1-5°K
Nb + 1.3P + .45S + .45Se	1200°C/65 kb hold 2 hr/ quench	NbPS type	NbP ₂	3.452(1)	12.103(2)	4.775(2)	1.2-2.3°K
.5Ta + .5Nb + 1.2P + S	1200°C/65 kb hold 1 hr/ quench	NbPS type	Unidentified	3.429(2)	11.861(1)	4.728(5)	4.2-5.8°K

*This run is the sample on which the crystal structure analysis and density determination were performed.
aFigures in parenthesis are standard deviations.

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR NbPS

I/2θ*	Powder Pattern			Observed and Calculated F ² **	
	h	k	l	F ² obs	F ² cal
90	0	1	1	4.3855	4.3870
50	1	1	0	3.2959	3.2976
40	0	3	1	3.0304	3.0358
20	4	0	1	2.9666	2.9726
60	1	0	1	2.7732	2.7758
100	1	3	0	2.5913	2.5949
30	1	2	1	2.5107	2.5153
50	0	0	2	2.3564	2.3599
30	0	2	2	2.1907	2.1935
70	0	5	1	2.1206	2.1243
100	1	4	1	2.0267	2.0291
30	1	5	0	1.9525	1.9551
80	1	1	2	1.9170	1.9191
60	0	4	2	1.8461	1.8485
20	1	3	2	1.7442	1.7459
50	2	0	0	1.7148	1.7160
40	2	1	1	1.5967	1.5981
20	0	6	2	1.5680	1.5697
10	2	0	6	1.5166	1.5179
10	2	3	1	1.4930	1.4939
20	2	4	0	1.4855	1.4863
2	0	3	3	1.4616	1.4623
5	1	0	3	1.4293	1.4301
20	2	0	2	1.3877	1.3879
10	2	2	2	1.3499	1.3516
40	2	5	1	1.3344	1.3349
40	1	0	1	1.3100	1.3106
30	1	4	2	1.2882	1.2885
10	1	7	2	1.2792	1.2795
30	2	4	2	1.2574	1.2576
5	1	9	0	1.2331	1.2333
10	0	0	4	1.1798	1.1799
10	2	7	1	1.1696	1.1697
20	2	1	3	1.1536	1.1542

* Read using the David Mann film reader Model No. 1222.

** Obtained from a diffractometer tracing.

The possible space groups determined by a Buerger precession camera are I222, I2₁2₁2, Imm2, or Immm. Zero-level and first-level pictures were taken of the *b* and *c* axis directions. Only systematic absences indicating body centering (*i.e.*, *h* + *k*, *h* + *l*, and *k* + *l*, all even for *hkl* reflections) were observed. The minimum pressure for formation of NbPS was found to be somewhere between 30 and 45 kbars from 900 to 1200°.

NbPSe and TaPS.—The reaction of Nb + 0.9Se + 1.2P at 1200° (65 kbars), held 1 hr, followed by cooling over 2 hr to 1000° and quenching, yielded black microcrystals at the center of the pellet and a gray material at the ends. The Debye-Scherrer pattern of the center region (Table III) was similar to that of NbPS, and refinement of the data gave orthorhombic cell dimensions: *a* = 3.462 ± 0.001 Å, *b* = 12.33 ± 0.01 Å, *c* =

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR NbPSe

I/2θ*	Powder Pattern			Observed and Calculated F ² **	
	h	k	l	F ² obs	F ² cal
20	0	2	0	6.1499	6.1643
60	0	1	1	4.4888	4.4904
<2	0	3	1	-	-
<2	0	4	0	-	-
40	1	1	0	3.3272	3.3327
2	1	0	1	2.8045	2.8119
100	1	3	0	2.6450	2.6475
75	1	2	1	2.5548	2.5583
60	0	0	2	2.4091	2.4108
35	0	2	2	2.2434	2.2452
90	0	5	1	2.1940	2.1953
95	1	4	1	2.0760	2.0773
10	1	5	0	2.0106	2.0083
85	1	1	2	1.9518	1.9533
30	0	4	2	1.8991	1.8979
30	1	3	2	1.7800	1.7825
50	2	0	0	1.7279	1.7308
30	0	7	1	1.6535	1.6543
10	0	1	1	1.6142	1.6150
10	0	1	3	1.5917	1.5937
10	0	6	2	1.5655	1.5653
10	0	8	2	1.5407	1.5411
2	2	3	1	1.5138	1.5144
5	1	2	3	1.4191	1.4186
20	2	0	2	1.4049	1.4060
5	2	2	2	1.3702	1.3698
20	2	5	1	1.3587	1.3592
20	1	8	1	1.3513	1.3514
50	1	4	3	1.3182	1.3178
20	2	6	1	1.2768	1.2765
5	0	10	0	1.2334	1.2328
5	0	0	4	1.2051	1.2054
10	2	7	1	1.1960	1.1959
5	1	6	3	1.1886	1.1889
2	2	1	3	1.1722	1.1724
2	2	6	2	1.1598	1.1603
2	3	1	0	1.1491	1.1488
30	1	9	2	1.1268	1.1262

* Read using the David Mann film reader Model No. 1222.

** Obtained from a diffractometer tracing.

4.821 ± 0.005 Å. The Debye-Scherrer pattern of the end region of the pellet showed the presence of NbP₂ and NbSe₂.

Pure TaPS was not obtained. The reaction of Ta + S + 1.2P at conditions similar to those described produced a black crystalline material which gave a Debye-Scherrer pattern with diffraction lines of an NbPS-type phase plus lines of TaS₂ and TaP₂. The orthorhombic unit cell dimensions are *a* = 3.430 ± 0.005 Å, *b* = 11.85 ± 0.01 Å, and *c* = 4.728 ± 0.005 Å.

Solid solutions in the systems NbPS_{1-x}Se_x and Nb_{1-x}Ta_xPS were prepared by reaction of the elements at high pressure. The reaction conditions and products are shown in Table I.

TABLE IV
 REFINED PARAMETERS FOR NbPS AND NbPSe (SPACE GROUP Immm)

Atom	Wyckoff notation	NbPS				NbPSe			
		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ^b	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ^b
Nb	4h	0	0.1232 (8) ^a	1/2	0.0 (2)	0	0.1188 (7)	1/2	0.3 (2)
S (Se)	4g	0	0.212 (2)	0	1.0 (6)	0	0.211 (1)	0	0.6 (3)
P	4j	1/2	0	0.235 (5)	1.0 (8)	1/2	0	0.221 (4)	0.2 (6)

^a Figures in parentheses are standard deviations; none is given for positions fixed by symmetry. ^b Isotropic temperature factors (\AA^2).

Crystal Structure Determination.—The end region of the pellet of the sixth reaction listed in Table I was easily separable and showed a single-phase X-ray diffraction pattern. The density of NbPS was measured and X-ray powder intensity data were taken on this material. The exact stoichiometry of this phase is not known, but from the unit cell dimensions, it appears that it contains a slight excess of phosphorus. This pure material was used for the structure determination because some powder diffraction lines of inseparable NbS₂ overlap those of NbPS.

The material was ground to 325 mesh and sprinkled on a glass slide coated with Vaseline to avoid preferred orientation. The powder diffraction pattern was taken using a Norelco diffractometer using Cu K α radiation and an LiF bent crystal monochromator. A scanning rate of 0.25°/min was used with the chart scaled to 1 in./deg. Integrated intensities of the peaks were measured by drawing a smooth background curve on the chart and tracing the peaks onto Cronaflex No. IDF4 drafting film. The peaks were cut out and weighed to obtain relative intensities. The data were corrected for Lorentz and polarization effects to obtain F_o^2 , and for the purpose of calculating a three-dimensional Patterson map, their respective multiplicities were also taken into account. Overlapping peaks were not used in the Patterson calculation.

A three-dimensional Patterson map was calculated¹⁰ using 26 reflections. All of the peaks could be explained by assuming the structure to have space group Immm and atoms at the following sites: four Nb at 4h with $y = 1/8$; four S or P at 4g with $y = 9/40$; four S or P at 4j with $z = 1/4$.

The structure was refined using a full-matrix least-squares method,¹¹ in which all reflections, including overlapping non-equivalent reflections, were refined. Atomic scattering factors of neutral atoms were used, corrected for both the real and imaginary anomalous dispersion effects.¹² Thirty-one reflections were used to refine three positional parameters, one scale factor, and three isotropic temperature factors. Unit weights were used throughout, and the function minimized was $\sum w|F_o|^2 - |F_c|^2|^2$.

At first an average scattering factor of S and P was applied to the anion positions. Then the scattering factors of S and P were applied separately to each position. In each case six cycles were required to reach convergence; the final positional parameters were the same within experimental error. The *R* factor, defined as $R = \sum |F_o|^2 - F_c^2 / \sum F_o^2$, in the case where P was placed in positions 4g and S was placed in the other anion position, was reduced to 9.3%. The temperature factors were refined to 1.0 ± 0.8 for P and 1.0 ± 0.7 for S. When the positions were reversed, the *R* factor refined to 10.0% and the temperature factors were 0.7 ± 0.6 and 1.7 ± 0.8 . The lower *R* factor and similar temperature factors in the former model suggest that it is correct. The final positional parameters, temperature factors, and *R* factor for this model are shown in Table IV. Structure factor data are shown in Table II. One refinement was done using space group Immm2. Parameters restricted by equivalence in space group Immm were allowed to vary separately; however, no changes greater than their respective standard deviations were observed.

(10) C. Fritchie and L. Guggenberger, local unpublished computer program, 1967.

(11) C. T. Prewitt, local unpublished computer program, 1967.

(12) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202, 213; Tables 3.3.1A, 3.3.2A.

Bond distances and angles and their standard deviations (Table V) were calculated.¹³ The numbering of the atoms is shown in Figure 1.

 TABLE V
 BOND DISTANCES AND ANGLES FOR NbPS AND NbPSe

Atoms*	Distance in \AA	
	NbPS	NbPSe
Nb(1)-S(1)	2.60(2)	2.71(1)
-S(2)	2.59(1)	2.668(7)
-P(1)	2.58(1)	2.63(1)
-Nb(3)	3.437(1)	3.462(1)
Nb(4)-Nb(2)	2.93(2)	2.93(2)
S(1)-P(3)	3.25(2)	3.30(1)
P(1)-P(2)	2.51(5)	2.69(4)
P(3)-P(4)	2.21(5)	2.13(4)

Angle in Degrees		
P(1)-Nb(1)-P(2)	58.1(9)	61.4(5)
P(2)-Nb(1)-S(2)	77.9(6)	77.1(4)
S(2)-Nb(1)-S(1)	72.1(3)	70.7(2)
P(3)-Nb(2)-P(5)	83.4(5)	82.0(5)
S(3)-Nb(1)-S(2)	131.6(1.0)	129.2(5)
Nb(1)-S(1)-Nb(2)	107.8(3)	109.3(2)
Nb(1)-S(1)-Nb(3)	82.7(7)	79.2(4)
Nb(2)-S(1)-Nb(5)	131.6(1.0)	129.2(6)
Nb(4)-P(3)-Nb(2)	69.1(5)	67.4(5)
Nb(1)-P(1)-Nb(3)	83.4(5)	82.1(5)

*The numbers of the atoms correspond to the numbers of the atoms in Figure 1.

The crystal structure of NbPSe was verified as being similar to that of NbPS by the techniques described for NbPS. The *R* factor, when P and Se were placed in the positions which gave the best results for NbPS, was reduced to 8.6%. When the positions were reversed, the *R* factor did not refine below 51%, thus confirming the stoichiometry and proper placement of the anions. Parameters are shown in Table IV, bond distances and angles in Table V, and powder diffraction data in Table III.

Electrical Properties.—The electrical properties of NbPS, NbPSe, and several solid solutions were studied by resistivity measurements and the Meissner effect. Resistivities were measured on single crystals of NbPS and NbPSe by a four-point probe technique (Figure 2).

Superconductivity.—Superconductivity was measured observing the self-inductance of a coil containing the specimen (the Meissner effect). The ac field was about 1 Oe peak to peak at a frequency of 1000 Hz. The samples were placed in glass capillary tubes 1 mm in diameter. The temperatures were determined using a 2.1 atom % CoAu vs. copper thermocouple for temperatures above 4.2°K. Below 4.2°K the temperatures were obtained from measurements of the vapor pressure in equilibrium with the liquid helium reservoir. Pumping on this reservoir permitted measurements down to 1.25°K.

The superconducting transition temperatures (T_c) are shown in Table I. The ranges of T_c are probably the result of small variations in stoichiometry.

Additional information was obtained by measuring the resistivity of a crystal of NbPS as the temperature was lowered

(13) L. W. Finger, "University of Minnesota Program for Computing Bond Angles and Distances with Error Analysis, UMBADTEA," 1965.

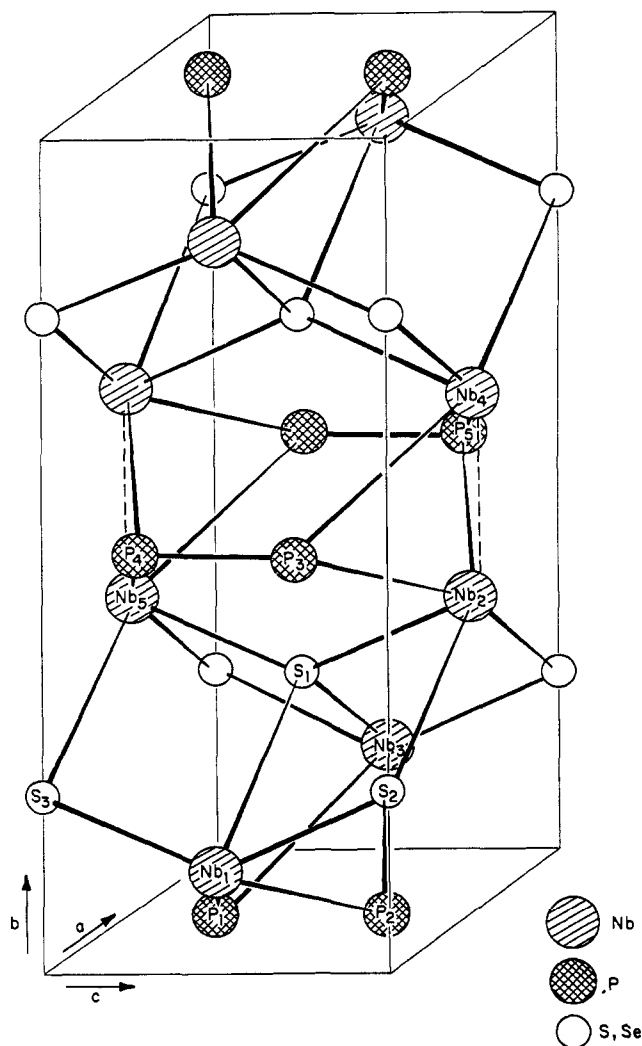


Figure 1.—Crystal structure of NbPS and NbPSe.

through the critical region. It was observed that the resistance decreases to zero at 12.0°K and this transition was complete within an interval of less than 0.1°K. In addition, a magnetic field of 5 kOe decreased the critical temperature by 0.4°K. Such behavior indicates that NbPS is a type II super conductor.

Discussion

The formula NbPS is established as the ideal composition of the phase by density and crystal structure analysis. The sulfur to phosphorus ratio may deviate slightly from unity toward smaller values, by partial substitution of P for S. A consequent lengthening of the *b* axis and lowering of T_c are observed (Table I). The data also indicate that S does not replace P.

The formula NbPSe for the analogous selenium compound is established from the crystal structure analysis. The comparison of *R* factors for NbPSe calculated with exchange of anion sites established the positions of the anions and the fact that these compounds are genuine ternary phases with S (Se) and P occupying distinct positions.

The crystal structure shows several interesting features. The Nb atoms are eightfold coordinated by four P and four S or Se atoms at the corners of a bicapped trigonal prism. The prisms share faces, in pairs,

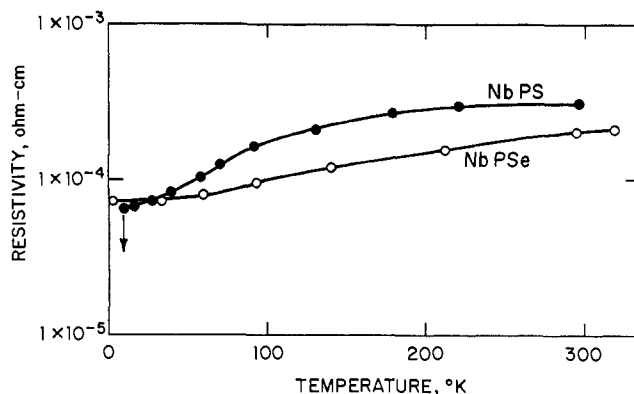


Figure 2.—Electrical resistivity vs. temperature of NbPS and NbPSe.

through the four P atoms, resulting in an Nb–Nb distance of 2.93 (2) Å. This distance suggests the presence of a metal–metal bond. The pairs of bicapped trigonal prisms share triangular faces in the *a*-axis direction, with this Nb–Nb distance being that of the *a* axis.

The S or Se atoms are coordinated by four Nb atoms at the corners of a distorted tetrahedron. The P atoms are coordinated to four Nb atoms and one P atom.

The coordination of Nb is nearly identical with that in NbP₂, NbAs₂, and NbS₂Cl₂.¹⁴ In NbS₂Cl₂ the bicapped trigonal prisms share four S atoms. The S atoms are bonded in pairs at the usual S–S covalent bond distance, and consequently Nb is tetravalent by assignment of valences: Nb⁴⁺, (S₂)²⁻, 2Cl⁻. The distance between the Nb atoms across the shared face is 2.91 Å. The NbPS structure can be considered as a condensed or polymerized version of NbS₂Cl₂ with P in place of S, and S in place of Cl.

The formal valence of Nb in NbPS and NbPSe is determined in part by the P–P distances. The P atoms form continuous strings in the *c*-axis direction with alternating short and long distances. In NbPS the short distance is 2.22 ± 0.05 Å, and the long distance is 2.51 ± 0.05 Å. In NbPSe these distances are 2.13 ± 0.04 and 2.69 ± 0.04 Å, respectively. The short distances are within the normal P–P covalent bond distances found in many other compounds.¹⁵ The long P–P distances are longer than the normal P–P covalent bond distance but may still represent some degree of bonding. If only the P atoms separated by the short distance are considered bonded, then Nb is tetravalent by assignment of valences: 2Nb⁴⁺, (P₂)⁴⁻, 2S²⁻. If the long distance contains bonding character, then the valence of Nb would be lower. This may be the case in NbPS since there is not so much difference between the long and short distances as in NbPSe. The possible difference in formal valence may somehow be related to the difference in superconducting properties.

The metallic electrical conductivity is not surprising since Nb⁴⁺ has one electron for conduction. It might be expected that this electron would be used to form a

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metal-metal bond, but apparently it lies in a band available for conduction. Partial substitution of P for S in NbPS raises the valence of Nb toward +5, and the superconducting transition temperature is lowered. From the limited number of experiments, it appears that the T_c also decreases in direct proportion to the amount of Se or Ta substituted in NbPS.

The superconducting transition temperature of NbPS is the highest known for a compound of anion:cation ratio of 2. A fundamental physical study of these com-

pounds should lead to a greater understanding of conditions permitting the occurrence of superconductivity.

Acknowledgments.—Mr. H. S. Young and Dr. T. A. Bither are thanked for helpful discussions. Dr. C. T. Prewitt is thanked for helpful discussions and for help in the Patterson calculation. Mr. J. L. Gillson is thanked for measuring electrical resistivity. Mr. C. Hoover supervised the high-pressure experiments, and Mr. K. R. Babcock determined the space group.

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The Structure and Spectrum of Potassium Hexafluoromolybdate(III)¹

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Received December 12, 1968

The compound K_3MoF_6 (mp of $734 \pm 10^\circ$ and macroscopic $\rho_{25} 3.23 \pm 0.03$ g/cm³) was prepared in the form of pale yellow cubic crystals by fusing KF and MoF₃ in a sealed platinum tube at 800°. The crystals belong to the space group Fm3m with $a_0 = 8.7839 \pm 0.0009$ Å at 23° and contain octahedrally coordinated MoF₆³⁻ complex anions with an Mo-F bond length of 2.00 (2) Å. The diffuse reflectance spectrum shows three bands—one at 262 mμ, assigned to a charge-transfer transition, and the following ligand field bands: ${}^4T_{2g}(t_{2g}^2e_g) \leftarrow {}^4A_{2g}(t_{2g}^3)$ at 425 mμ and ${}^4T_{1g}(t_{2g}^2e_g) \leftarrow {}^4A_{2g}(t_{2g}^3)$ at 337 mμ with a Dq of 2350 cm⁻¹ and a Racah B parameter of 570 cm⁻¹.

Introduction

The absorption spectrum of a 0.01–1.0 wt % solution of Mo(III) in molten LiF–BeF₂ (66–34 mol %²) contains ligand field bands that are reasonably attributed to octahedrally coordinated³ MoF₆³⁻. We wished to check this result by obtaining the spectrum of this complex ion in a crystalline system where the geometry had been determined by X-ray diffraction. In the compound MoF₃, Mo(III) is surrounded by a slightly irregular octahedral array of F⁻ ions⁴ but we were unable to obtain a satisfactory ligand field spectrum of this material. Therefore, we allowed MoF₃ to react with KF to produce K₃MoF₆, used X-ray diffraction to demonstrate that Mo(III) in this compound is present as octahedrally coordinated MoF₆³⁻, and measured the diffuse reflectance spectrum from 600 to 210 mμ. These results are reported here.

The synthesis of K₃MoF₆ has been reported previously by Peacock⁵ and Aleonard.⁶ Peacock described the reaction of K₃MoCl₆ with molten KHF₂ to produce brown cubic K₃MoF₆ while Aleonard describes the reduction-exchange reaction of MoO₃ with a solution of KF–KBF₄ (50:50 wt %) at 900° in a graphite crucible. However, no chemical analyses nor properties of the compound have ever been given to characterize it fur-

ther. Aleonard was unable to isolate a pure K₃MoF₆ compound from the reaction mixture but a Debye-Scherrer powder pattern of the solid mixture revealed weak reflections, which were presumed to be cubic K₃MoF₆, in addition to the strong fluoroborate lines. Babel⁷ has examined this cubic pattern and points out that it is identical with the pattern given for the oxide-fluoride compound K₃MoO₃F₃. Therefore, it is not clear that K₃MoF₆ has been prepared previously.

Experimental Section

Synthesis.—Stoichiometric quantities of KF and MoF₃ were weighed and mixed in an inert-atmosphere drybox of <1 ppm by volume water content. The KF had been crystallized from its melt and clear crystalline pieces were hand-picked. The MoF₃ was prepared by the reduction of MoF₆ with Mo in a Pyrex system. An oxide analysis on the KF revealed 240 ppm oxide. *Anal.* Calcd for MoF₃: Mo, 62.7; F, 37.3. Found: Mo, 62.7; F, 37.9. Major cation impurities were (in ppm): Al, ≤200; Ca, <100; Li, <500; Na, <300; Si, <300; W, ≤500. A Debye-Scherrer powder pattern of the MoF₃ starting material agreed with the previously reported pattern.⁴

Approximately 200 mg of the K₃MoF₆ stoichiometric mixture was loaded into a 7/8-in. diameter × 1.5-in. long platinum tube which had been sealed on one end. The tube was collapsed around the sample and the open end was closed by folding tightly and crimping with pliers. The tube was removed from the drybox and immediately sealed with a small oxyacetylene torch. The platinum tube was then enclosed in a small heavy-walled silica tube filled with 1/3 atm of dry nitrogen. The silica served to contain any reagents which might leak out of the platinum had the platinum not been properly sealed. Any leakage would be immediately apparent due to the rapid corrosion of quartz by most fluoride salts at temperatures of 600–900°.

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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