Preparation, Structures, and Properties of Niobium Chalcogenide Halides, NbX_2Y_2 (X = S, Se; Y = Cl, Br, I)

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The preparation of the compounds NbX_2Y_2 (X = S, Se; Y = Cl, Br, I). including that of large single crystals, by chemical transport techniques is reported. Most of these compounds exist in a triclinic low-temperature form and a monoclinic high-temperature form. The crystal structures of triclinic low-temperature NbSe$_2$Cl$_2$ and monoclinic NbS$_2$Cl$_2$ are reported; both structures consist of cage-shaped units of Nb$_2X_4$ which are linked together by the Cl atoms to form sheets parallel to the a, b planes. Both the Nb and the X atoms are present in pairs which indicates that the compounds can be formulated as Nb$_2^{4+}(X_2)_2^{2-}$$_2Y_4^-$, in agreement with XPS spectra. The presence of Nb^{4+} in pairs explains the observed diamagnetic and semiconducting properties of NbX_2Y_2. The preparation and some properties of MoS$_2$Cl$_2$ (orthorhombic) are also given.

Introduction

The preparation of the compounds NbX_2Y_2 with X = S, Se and Y = Cl,Br,I has been reported by Schäfer and Beckmann (*1*). The crystal structure of NbS$_2$Cl$_2$ (monoclinic) was determined (*2*) and from X-ray powder diffraction data it was concluded that NbS$_2$Br$_2$, NbSe$_2$Br$_2$, and NbSe$_2$I$_2$ (and probably also NbS$_2$I$_2$ and NbSe$_2$Cl$_2$) are isotypic with NbS$_2$Cl$_2$.

In connection with a study of the physical properties and spectra of the compounds NbX_2Y_2 we have reinvestigated their synthesis and crystal structures. In the present communication we report the preparation, thermal behavior, the structures of two modifications, and the magnetic and electrical properties of NbX_2Y_2. Some data on MoS$_2$Cl$_2$, which was (incorrectly) assumed to be isotypic with NbS$_2$Cl$_2$ (*3*), are

also included. XPS (*4*) and optical absorption spectra (*5*) of NbX_2Y_2 are reported elsewhere.

Preparation

The compounds NbX_2Y_2 with X = S, Se and Y = Cl, Br, I were prepared by heating mixtures of the elements or·mixtures of Nb, NbY_4, and X in evacuated glass or quartz tubes for 3 to 4 weeks; experimental conditions are listed in Table I. A small temperature gradient had to be maintained (within 0.5°C) between the two sides of the reaction tubes in order to separate the products NbX_2Y_2 from contaminating binary (NbX_3, Nb$_2$Se$_9$) and ternary products. Many new Nb–X–Y phases were found but only a few of them—including Nb$_3$Se$_5$Cl$_7$ (*6*) and compounds of compositions near NbX_3Y and Nb$_3X_{12}Y$ (*7*)—were fully characterized.

TABLE I

EXPERIMENTAL CONDITIONS FOR THE PREPARATION OF NbX_2Y_2 (X = S, Se; Y = Cl, Br, I) AND MoS_2Cl_2 CRYSTALS[a]

Compound	Color	Metal (g)	Mole ratio (Nb(Mo) : X : Y)	T_1, T_2[b] (°C)	$T_1 - T_2$ (°C)
NbS_2Cl_2	Red-brown	0.9	1 : 1.96 : 2.05	480 475	5
NbS_2Br_2	Red-brown	0.9	1 : 1.96 : 2.05	505 500	5
NbS_2I_2	Red	0.5	1 : 1.85 : 5.0	400 380	20
$NbSe_2Cl_2$	Brown-black	0.6	1 : 1.45 : 3.0	410 405	5
$NbSe_2Br_2$	Violet-black	1.7	1 : 1.96 : 2.05	480 475	5
$NbSe_2I_2$	Blue-black	0.4[c]	1 : 1.96 : 2.8	470 460	10
MoS_2Cl_2	Red-brown	1.4	1 : 1.98 : 2.05	515 510	5

[a] The syntheses were carried out in sealed tubes of 16-mm diameter and 200-mm length.

[b] Temperatures at the two sides of the reaction tube.

[c] Reaction tube of 16-mm diameter and 160-mm length.

The presence of such products explains the poor agreement of the powder pattern reported for NbS_2Cl_2 (1) with single-crystal data (2). The powder patterns and densities of NbS_2I_2 and $NbSe_2I_2$ reported by Schäfer and Beckmann (1) are also incorrect due to the presence of surface contaminants on their crystals (which are blackish-red and grey-black, respectively); we observed that the preparation of pure NbS_2I_2 (red) and $NbSe_2I_2$ (bluish-black with a metallic luster) requires considerable excess of iodine.

NbS_2Cl_2, NbS_2Br_2, and MoS_2Cl_2 were also prepared by heating the metal with stoichiometric amounts of S_2Cl_2 (S_2Br_2) at the same temperatures as given in Table I. This method is less satisfactory for the synthesis of $NbSe_2Br_2$, while from $Nb + Se_2Cl_2$ complex mixtures of ternary compounds were obtained in which no $NbSe_2Cl_2$ was detected.

Attempts to prepare solid solutions of $M_xNb_{1-x}X_2Y_2$ with M = Zr, Mo, W failed; obviously the solubility of M in NbX_2Y_2 is very small.

Thermal Behavior

The thermal behavior of the compounds NbX_2Y_2 above 77 K was investigated by

DTA, by DSC, and by low- and high-temperature X-ray powder diffraction techniques. It was found that most of the compounds occur in two different forms, a triclinic low-temperature form and a monoclinic high-temperature form; however, no evidence for the existence of triclinic NbS_2Cl_2 was found (down to 77 K), while NbS_2I_2 remains triclinic up to the decomposition temperature of 426°C (see below). The transitions between the high- and low-temperature forms are reversible, but the high-temperature forms of NbS_2Br_2 and $NbSe_2Br_2$ can easily be retained at room temperature by quenching; for $NbSe_2Cl_2$ and $NbSe_2I_2$ this is rather difficult.

The transition temperatures T_{tr} were determined by DSC (Fig. 1); the extrapolated onset temperatures of heating curves (8), taking the melting point of tin (231.9°C) as a reference (9), are listed in Table II. Table II also includes the decomposition temperatures of NbX_2Y_2, both when heating ca. 60 mg of the compounds in a sealed DTA ampoule with nearly zero dead volume ($T_d[max]$) and when heating the same amount in a sealed ampoule with a dead volume of 1.5 ml ($T_d[o.p.]$). Among the decomposition products are gaseous

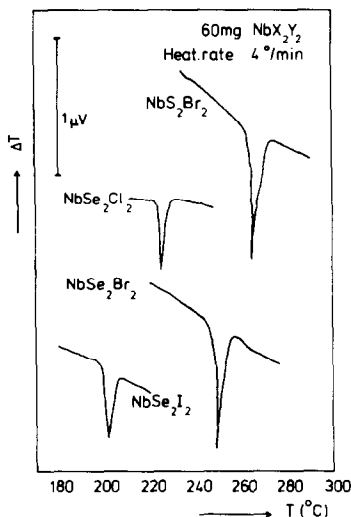FIG. 1. DSC heating curves of compounds NbX_2Y_2 (ca. 60 mg) showing the phase transition from triclinic to monoclinic; heating rate 4°C/min.

$NbXCl_3$ or $NbXBr_3$ ($X = S, Se$) for the chlorides and bromides, respectively, and NbI_4 in the case of NbX_2I_2.

NbX_2Cl_2 and NbX_2Br_2 are stable above 100°C only if they are kept under $NbXCl_3$ and $NbXBr_3$ pressure, respectively, while the iodides NbX_2I_2 have to be kept under NbI_4 even at room temperature (1). MoS_2Cl_2 is hygroscopic (3); above 100°C it is stable only if kept under its own decomposition vapor (probably $MoSCl_3$).

Crystallographic Data

Both the monoclinic and triclinic forms of NbX_2Y_2 ($X = S, Se$; $Y = Cl, Br, I$) have layer structures; for the settings adopted the layers are parallel to the a, b plane in both cases. The space groups are $C2/m$ and $P\bar{1}$, respectively. (For the monoclinic form we chose a C-centered cell, contrary to Ref. (2).) MoS_2Cl_2 is an orthorhombic layer compound with the layers parallel to the a, b plane; from the systematic absences (hkl for $h + k = 2n + 1$; $h0l$ for $l = 2n + 1$) the space group is derived as $Cmcm$, $Cmc2_1$, or $C2cm$.

When preparing the compounds NbX_2Y_2 under the conditions given in Table I, the compounds were obtained in the form of thin single-crystal plates (typically 0.8 × 0.8 to 3 × 3 mm^2) which showed a mosaic spread of only 0.5 to 0.8°. These crystals were well suited for studying the optical absorption spectra (5) and electrical conductivity of the compounds, but they were too large for X-ray diffraction. When cut or cleaved the crystals did not remain single. Smaller crystals grown by chemical transport usually showed strong disorder (except for MoS_2Cl_2); NbS_2I_2 and $NbSe_2Cl_2$, in particular, are inclined to disorder. Only a few single crystals of a size and quality suitable for X-ray diffraction could be found.

Accurate unit-cell dimensions were determined from Guiner and Weissenberg photographs taken with $CuK\alpha$ radiation, calibrated with NaCl as internal standard; calculation by least squares gave the values listed in Table III. The cell dimensions of the high-temperature modifications of NbX_2Y_2, i.e., triclinic NbS_2I_2 and the monoclinic forms of the other compounds, varied significantly from sample to sample; the values in Table III are averages from at least 12 samples. This variation is probably due to deviations from the ideal stoichiometry. A similar observation was made for ZrS_3 and isotypic compounds where it was tentatively ascribed to partial

TABLE II

TRANSITION TEMPERATURES, T_{tr}, AND DECOMPOSITION TEMPERATURES (°C) UNDER OWN VAPOUR PRESSURE (T_d[o.p.]) AND WITH ZERO DEAD VOLUME (T_d[max]) OF NbX_2Y_2 ($X = S, Se$; $Y = Cl, Br, I$) AND MoS_2Cl_2

Compound	T_{tr}	T_d[o.p.]	T_d[max]
NbS_2Cl_2		467	551
NbS_2Br_2	261 ± 5	543	629
NbS_2I_2		426	516
$NbSe_2Cl_2$	223 ± 2	414	534
$NbSe_2Br_2$	245 ± 5	521	571
$NbSe_2I_2$	199 ± 2	444	502
MoS_2Cl_2		630	656

TABLE III

A. AVERAGE UNIT-CELL DIMENSIONS OF MONO-
CLINIC NbX_2Y_2 (X = S, Se; Y = Cl, Br, I)[a]

Compound	a (Å)	b (Å)	c (Å)	β (°)
NbS_2Cl_2	6.27	11.09	6.69	111.07
NbS_2Br_2	6.54	11.32	6.91	110.54
$NbSe_2Cl_2$	6.64	11.23	6.96	108.93
$NbSe_2Br_2$	6.76	11.53	7.20	113.90
$NbSe_2I_2$	6.89	12.34–12.46	7.51	112.26

[b] Average values over at least 12 samples.

B. UNIT-CELL DIMENSIONS OF TRICLINIC NbX_2Y_2[a]

Compound	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
NbS_2Br_2	6.528(2)	6.589(2)	7.254(1)	67.72(2)	112.63(2)	120.05(2)
NbS_2I_2[b]	6.77	6.80	7.23	73.8	102.3	117.4
$NbSe_2Cl_2$	6.350(2)	6.538(3)	7.261(2)	66.93(3)	111.35(3)	119.01(3)
$NbSe_2Br_2$	6.667(2)	6.724(2)	7.084(2)	79.40(2)	111.83(2)	119.68(1)
$NbSe_2I_2$	7.060(1)	7.207(2)	7.757(2)	67.59(2)	113.20(3)	121.10(2)

[a] Space group $P\bar{1}$, Z = 2; standard deviations in units of the last decimal are given in paren-
theses.
[b] Average values over 12 samples.

C. UNIT-CELL DIMENSIONS OF MoS_2Cl_2,
ORTHORHOMBIC, Z = 64.

$$a = 11.979(5) \text{ Å}$$
$$b = 20.818(6) \text{ Å}$$
$$c = 30.310(6) \text{ Å}$$

substitution of $(S_2)^{2-}$ ions by S^{2-} ions (10). Such an explanation may also apply to the compounds NbX_2Y_2. A comparison of observed (by flotation) and calculated (from X-ray data) densities (Table IV) shows that the deviation from ideal stoichiometry cannot be large.

Structure Determinations

NbS_2Cl_2

The intensities of the $hk0$, $h0l$, and $0kl$ reflections of a NbS_2Cl_2 crystal with

TABLE IV

OBSERVED AND CALCULATED DENSITIES (g/cm^3)
OF NbX_2Y_2 (X = S, Se; Y = Cl, Br, I) AND MoS_2Cl_2

Compound	Form[a]	d_{obs}	d_{calc}	d_{lit}[b]
NbS_2Cl_2	m	3.47	3.49	3.45
NbS_2Br_2	m	4.30	4.34	4.30
NbS_2I_2	tr	4.49	4.53	4.72
$NbSe_2Cl_2$	tr	4.48	4.51	4.52
$NbSe_2Br_2$	m	5.28	5.32	5.26
$NbSe_2I_2$	tr	5.48	5.54	5.58
MoS_2Cl_2		3.40	3.445	

[a] m = monoclinic, tr = triclinic.
[b] Reference (1).

unit-cell dimensions $a = 6.278(2)$ Å, $b = 11.091(2)$ Å, $c = 6.693(2)$ Å, $\beta = 111.06(1)°$ were visually estimated from Weissenberg diagrams. The atomic positions were refined starting from the model given by von Schnering and Beckmann (2) which was transformed from a F-centered to a C-centered description. To each reflection a weight $W = (80/F_0)^2$ for $F_0 > 80$ or $W = (F_0/80)^2$ for $F_0 < 80$ was assigned. Atomic scattering factors were taken from Cromer and Mann (11) and corrected for anomalous dispersion (12).

At the end of the isotropic refinement the discrepancy factor $R_W \equiv [\sum W(F_0 - |F_c|)^2 / \sum WF_0^2]^{1/2}$ was 0.056. The final positional and thermal parameters with their standard deviations are given in Table V. The structure is essentially the same as that reported by von Schnering and Beckmann (2), except for the z parameter of S(1) which differs by 0.5 from their value. Probably, this is due to a mistake in the paper by von Schnering and Beckmann, since the figure in their paper (2) shows the correct structure.

Low-Temperature $NbSe_2Cl_2$

The intensities of the X-ray reflections of the low-temperature form of $NbSe_2Cl_2$ were measured with an Enraf–Nonius automatic three-circle diffractometer by the ω-scan method; Zr-filtered Mo$K\alpha$ radiation was used. The dimensions of the crystal were 0.12 × 0.15 × 0.03 mm³. Reliable intensities $[I > 3\sigma(I)]$ of 1377 independent reflections with $\sin\theta/\lambda < 0.71$ Å^{-1} were measured and corrected for Lorentz and polarization factors and for absorption $[\mu(Mo) = 199$ cm$^{-1}]$.

Atomic positions were derived from a Patterson synthesis, adopting space group $P1$, and refined by a full-matrix least-squares calculation. The atomic scattering factors were taken from Cromer and Mann (11) and corrected for anomalous dispersion (12). To each reflection a weight $W = (80/F_0)^2$ for $F_0 > 80$ or $W = (F_0/80)^2$ for $F_0 < 80$ was assigned. At the end of the anisotropic refinement the discrepancy factor $R_W = 0.086$. A list of observed and calculated structure factors is available from the authors on request. The final positional and thermal parameters with their standard deviations are given in Table VI. The structure was checked by a difference Fourier synthesis which showed no unusual features.

Other Phases

From the intensity sequences on Weissenberg photographs we conclude that the monoclinic high-temperature forms of the compounds NbX_2Y_2 are all isotypic with NbS_2Cl_2, while the triclinic low-temperature forms are isotypic with low-temperature $NbSe_2Cl_2$.

Physical Properties

The compounds NbX_2Y_2 ($X = $ S, Se; $Y = $ Cl, Br, I) and MoS_2Cl_2 show nearly temperature-independent diamagnetism. The observed molar susceptibilities (not corrected for core diamagnetism) in the range 100–300 K are given in Table VII; no differences were found between the low- and high-temperature forms of NbX_2Y_2.

The electrical conductivity, σ, of NbX_2Y_2 crystals above 4.2 K was measured by a four-point contact method. Above about 380 K ($X = $ Se) or 420 K ($X = $ S) decomposition of

TABLE V

POSITIONAL AND THERMAL (IN 10^{-2} Å^2) PARAMETERS OF $NbS_2Cl_2{}^a$

	Nb	S(1)	S(2)	Cl
x	0	0.6559(11)	0.8532(10)	0.2214(5)
y	0.1295(2)	0	0	0.2077(4)
z	0	0.8523(12)	0.6758(11)	0.7653(6)
U	0.52(5)	1.47(12)	1.06(11)	1.21(7)

^{a} Space group $c2/m$; standard deviations in units of the last decimal are given in parentheses.

TABLE VI

POSITIONAL AND THERMAL (IN 10^{-2}Å^2) PARAMETERS OF LOW-TEMPERATURE $NbSe_2Cl_2$[a]

	Nb	Se(1)	Se(2)	Cl(1)	Cl(2)
x	0.1290(5)	0.2673(6)	0.9165(6)	0.5747(14)	0.1603(14)
y	0.2601(5)	0.0465(6)	0.1049(6)	0.3522(14)	0.5113(15)
z	0.9997(4)	0.8542(5)	0.6679(4)	0.2157(10)	0.2164(10)
U_{11}	0.7(1)	1.6(2)	2.0(2)	1.5(3)	2.0(4)
U_{22}	0.6(2)	0.4(2)	0.4(2)	0.6(4)	1.1(4)
U_{33}	1.0(1)	1.9(2)	1.2(1)	1.2(3)	1.1(3)
U_{12}	0.2(1)	−0.1(1)	0.1(1)	0.0(3)	0.7(3)
U_{13}	0.2(1)	0.7(1)	0.4(1)	0.4(2)	0.4(3)
U_{23}	−0.3(1)	−0.6(1)	−0.3(1)	−0.0(3)	−0.4(3)

[a] Space group $P\bar{1}$; standard deviations in units of the last decimal are given in parentheses.

the crystal surface becomes noticeable; attempts to measure σ at higher temperatures in a closed system under an excess of $NbXCl_3$, $NbXBr_3$, or NbI_4 vapor results in reaction of this vapor with NbX_2Y_2. The resistivity of NbX_2Y_2 is so large that the crystals became short-circuited by the sample holder at low temperatures. Between 4.2 and about 200 K the log σ versus $10^3/T$ plots are not linear; a typical plot is shown in Fig. 2.

The room temperature conductivities and the activation energies, E_c, derived from the linear part of the log σ ($10^3/T$) plots are given in Table VIII. For comparison, the values of $E_i/2$ are also included, where E_i is the (indirect) optical band gap at room temperature (5). The closeness of E_c and $E_i/2$ indicates that the compounds NbX_2Y_2 are almost intrinsic semiconductors at room temperature.
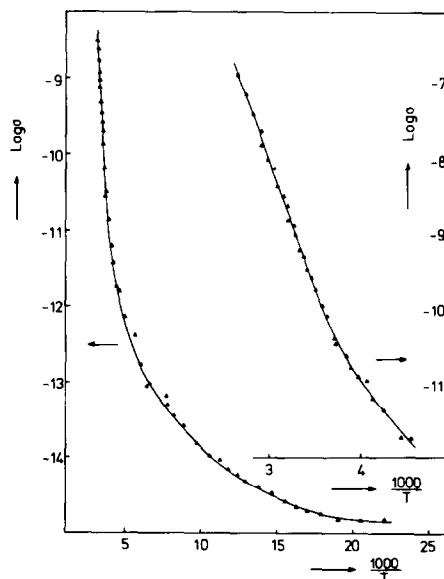
TABLE VII

MAGNETIC SUSCEPTIBILITIES, χ_m, OF NbX_2Y_2 (X = S, Se; Y = Cl, Br, I) AND MoS_2Cl_2[a]

Compound	χ_m ($\times 10^{-6}$ emu/mol)	Compound	χ_m ($\times 10^{-6}$ emu/mole)
NbS_2Cl_2	−28	$NbSe_2Cl_2$	−52
NbS_2Br_2	−62	$NbSe_2Br_2$	−75
NbS_2I_2	−91	$NbSe_2I_2$	−105
MoS_2Cl_2	−29		

[a] In the range 100–300 K; no correction for core diamagnetism is applied.

FIG. 2. Electrical conductivity σ of a single crystal of $NbSe_2Br_2$ (monoclinic); log σ is plotted versus $1000/T$ with σ expressed in (ohn · cm)$^{-1}$, T in K.

Compound	σ (ohm-cm)$^{-1}$	E_c (eV)	$E_i/2$ (eV)
NbS_2Cl_2	8×10^{-11}	0.84	0.96
NbS_2Br_2	8×10^{-11}	0.85	0.96
NbS_2I_2	2×10^{-10}	0.78	0.89
$NbSe_2Cl_2$	3×10^{-8}	0.68	0.75
$NbSe_2Br_2$	8×10^{-8}	0.73	0.77
$NbSe_2I_2$	1×10^{-7}	0.64	0.72

The conductivity observed for an uncleaved single crystal of $NbSe_2I_2$ (mosaic spread 0.7°) at low temperatures was considerably less than that reported by Weysenstein and Horák (13). Probably, high concentrations of crystal defects introduced during the preparation and cleavage of the crystals used by these authors are the cause of this discrepancy and also of the difference between our log σ versus $10^3/T$ plots and theirs (13).

Discussion

Two projections of the structures of monoclinic NbS_2Cl_2 and of triclinic low-temperature $NbSe_2Cl_2$ are shown in Figs. 3 and 4; bonding distances and their standard deviations are listed in Tables IX and X. It is evident that the two structures are closely related. Both structures contain cage-shaped units of Nb_2X_4 (X = S, Se) of approximately D_{2h} symmetry which consist of a pair of Nb atoms lying perpendicular to the plane of two X_2 groups. These cages are linked together by the Cl atoms to form sheets parallel to the a,b planes; in both forms the metal atoms are coordinated by four Cl atoms and two X_2 groups. Comparison of Figs. 3 and 4 shows that the two modifications of NbX_2Y_2 have somewhat different orientations of the Nb_2X_4 cages within the sheets and different stackings of the sheets. It may be remarked that similar Nb_2X_4 cages are also found in the structure of $Nb_3Se_5Cl_7$, where these cages are linked by Cl atoms to form chains (6).

The $X–X$ distances in NbS_2Cl_2 (Table IX) and $NbSe_2Cl_2$ (Table X) correspond to single bonds, indicating that the X_2 groups carry a (formal) ionic charge of -2. It follows that
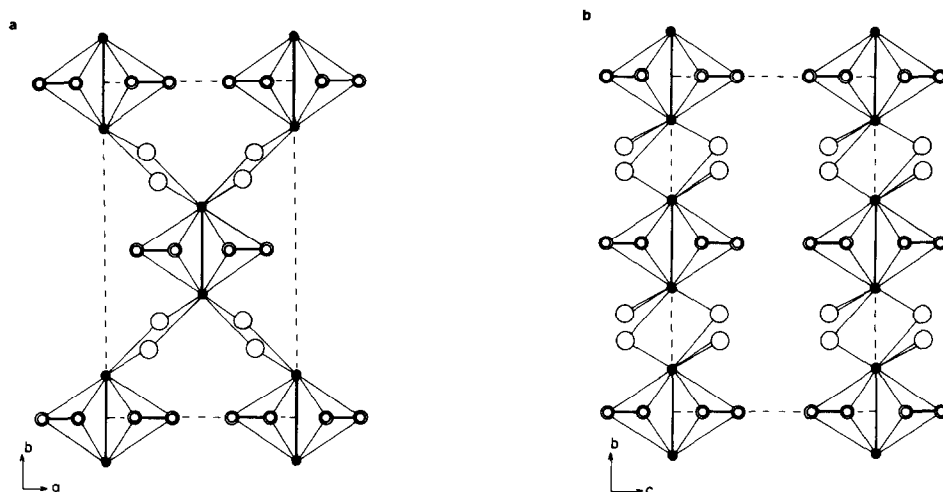

FIG. 3. The structure of monoclinic NbS_2Cl_2 projected along the c axis (a) and the a axis (b). Niobium atoms are shown as solid circles, sulfur as double circles and chlorine as open circles; Nb–Nb and S–S bonds are indicated by thick lines.
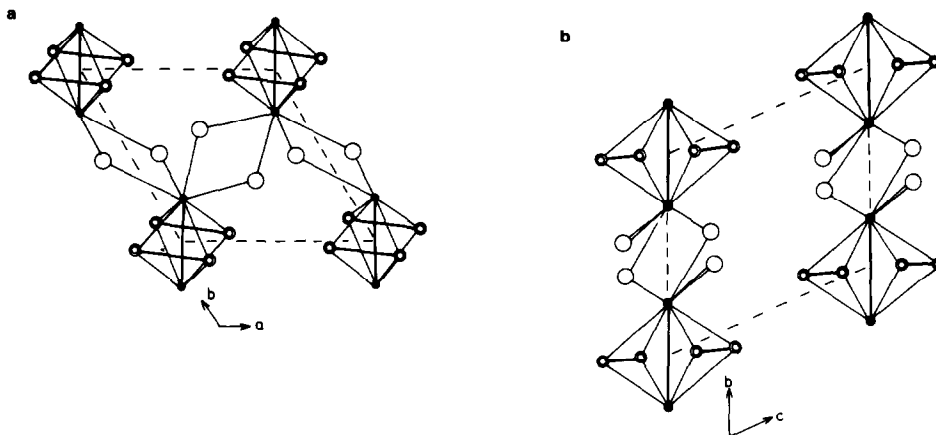
FIG. 4. The structure of low-temperature $NbSe_2Cl_2$ (triclinic) projected along the c axis (a) and the a axis (b). Niobium atoms are shown as solid circles, selenium as double circles, and chlorine as open circles; Nb–Nb and Se–Se bonds are indicated by thick lines.

TABLE IX

BOND DISTANCES (Å) IN $NbS_2Cl_2{}^a$

Nb–Nb	2.871(4)	S(1)–S(2)	1.996(12)
Nb–2S(1)	2.484(6)	Nb–2Cl	2.592(4)
Nb–2S(2)	2.486(6)	Nb–2Cl	2.612(4)

^{a} Standard deviations in units of the last decimal are given in parentheses.

the metal is in oxidation state +4 and that the compounds NbX_2Y_2 can be formulated as $Nb^{4+}(X_2)^{2-}Y^-{}_2$; this formulation is in agreement with the XPS spectra (4).

The occurrence of $Nb^{4+}(4d^1)$ in pairs with Nb–Nb distances comparable to those in Nb metal (2.858 Å) explains the diamagnetic

TABLE X

BOND DISTANCES (Å) IN LOW-TEMPERATURE $NbSe_2Cl_2{}^a$

Nb–Nb	2.973(4)	Se(1)–Se(2)	2.272(5)
Nb–Se(1)	2.619(4)	Nb–Cl(1)	2.586(7)
Nb–Se(1)	2.619(7)	Nb–Cl(1)	2.612(7)
Nb–Se(2)	2.622(5)	Nb–Cl(2)	2.587(12)
Nb–Se(2)	2.632(4)	Nb–Cl(2)	2.608(10)

^{a} Standard deviations in units of the last decimal are given in parentheses.

and semiconducting properties of NbX_2Y_2. Similar pairs of Nb^{4+} have been found, e.g., in NbS_3 (14), in niobium tetrahalides (15), and in the oxide halides $NbOY_2$ ($Y = $ Cl, Br, I) (15, 16), all of which are also diamagnetic semiconductors.

Acknowledgment

References

1. H. SCHÄFER AND W. BECKMANN, Z. Anorg. Allg. Chem. 347, 225 (1966).
2. H. G. VON SCHNERING AND W. BECKMANN, Z. Anorg. Allg. Chem. 347, 231 (1966).
3. J. P. RANNOU AND M. SERGENT, C.R. Acad. Sci. Paris Ser. C 265, 734 (1967).
4. J. RIJNSDORP, G. J. DE LANGE, C. HAAS, AND F. JELLINEK, to be published.
5. J. RIJNSDORP AND C. HAAS, to be published.
6. J. RIJNSDORP and F. JELLINEK, J. Solid State Chem. 28, 149 (1979).
7. J. RIJNSDORP, Thesis, Groningen (1978).
8. E. M. W. JANSSEN, F. POHLMANN, AND G. A. WIEGERS, J. Less Common Metals 45, 261 (1976).
9. Nat. Bur. Stand. (U.S.) Circ. 500, "Selected Values of Chemical Thermodynamic Properties" (1952).

10. F. JELLINEK, R. A. POLLAK, AND M. W. SHAFER, *Mater. res. Bull.* **9**, 845 (1974).

11. D. CROMER AND J. MANN, *Acta Crystallogr. Sect. A* **24**, 321 (1968).

12. "International Tables for X-Ray Crystallography," Vol. III, p. 215, Kynoch Press, Birmingham (1968).

13. J. WEYSENSTEIN AND J. HORAK, *Czech. J. Phys. B* **24**, 235 (1974).

14. J. RIJNSDORP AND F. JELLINEK, *J. Solid State Chem.* **25**, 325 (1978).

15. H. G. SCHNERING AND H. SCHAFER, *Angew. Chem.* **76**, 833 (1964).

16. J. RIJNSDORP AND F. JELLINEK, *J. Less Common Metals* **61**, 79 (1978).