An X-Ray Photoelectron and X-Ray Emission Study of the Electronic Structure of Nb Trichalcogenides and Their Lithium Intercalates

G. F. KHUDOROZHKO, I. P. ASANOV, A. V. MISCHENKO,
L. N. MAZALOV, S. B. ERENBURG, V. E. FEDOROV,
AND A. I. ROMANENKO

Institute of Inorganic Chemistry of the Siberian Branch of the Academy of Sciences of the USSR, 630090, Novosibirsk, USSR

The electronic structure of Nb trichalcogenides and their lithium intercalates was studied using X-ray photoelectron and X-ray emission spectroscopy. It was found that the metal $4d$ levels mainly contribute to the upper part of the $NbSe_3$ and NbS_3 valence zones whereas the deeper part of the valence zones is filled by the chalcogen levels. The intercalation was found to change the charge state of both Nb and chalcogen atoms. © 1988 Academic Press, Inc.

Trichalcogenides of niobium NbX_3 (X = S, Se) belong to the class of low-dimensional compounds whose structure and properties are now attracting increased interest. The intercalation reactions of niobium trichalcogenides with lithium were also found to be potential-forming ones and thus may provide the basis for chemical sources of current (*1*). Intercalation of these compounds with lithium makes it possible to change their physicochemical properties without appreciable modification of their structure.

There has been considerable progress in the studies of the spatial and electronic structure of NbS_3 and $NbSe_3$ in recent years. Their structure has been studied in detail (*2, 3*). The basic structural blocks of these compounds represent endless chains formed by triangular prisms of chalcogen atoms. The bases of the prisms have the form of an isosceles triangle. In $NbSe_3$ the metal atoms are equidistant (r_{Nb-Nb} = 3.48 Å) lying at the centers of the prisms whereas in NbS_3 they are displaced from the central positions by 0.16 Å to form Nb–Nb pairs (r_{Nb-Nb} = 3.04 Å). The density of states in the valence zone of NbS_3 and $NbSe_3$ has been calculated using a nonempirical method (*4–7*). X-ray photoelectron spectra of their valence zones have been reported (*8, 9*). The calculated density of states was in good agreement with the experimental data. All of the evidence indicated occurrence of an interchain interaction in niobium triselenide determining the semimetallic character of the conductivity. In niobium trisulfide such interaction is small and there is an intrachain metal–metal bonding resulting in pairing of the Nb atoms along the metal chains and the splitting of the half-filled d_{z^2}-zone into a filled and a free zone with an energy gap of 0.5 eV which renders the material semicon-
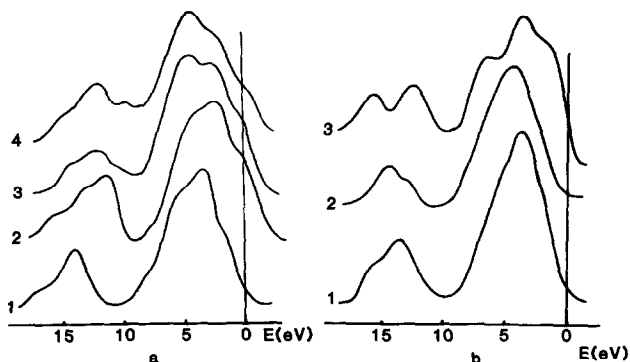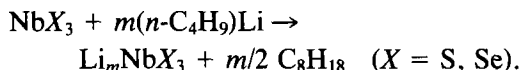
FIG. 1. X-ray photoelectron spectra of the valence bands of niobium trichalcogenides and their lithium intercalates. (a) 1, NbS_3; 2, $Li_{0.5}NbS_3$; 3, $Li_{0.9}NbS_3$; 4, $Li_{2.2}NbS_3$; (b) 1, $NbSe_3$; 2, $Li_{0.9}NbSe_3$; 3, $Li_{2.9}NbSe_3$.

ducting. The filled d_z2-zone shows up in the X-ray photoelectron spectra of the valence zone as a shoulder in the upper part of the valence zone.

The present work is an X-ray photoelectron and X-ray emission study of niobium trichalcogenide and their lithium intercalates. The starting phases were obtained by the ampoule method according to the procedures described in (*10*). Lithium intercalates of the overall composition Li_mNbX_3 ($0 < m < 3$; $X = $ S, Se) were prepared by interacting the solid chalcogenide phase with a hexane solution of butyllithium according to the reaction

$$NbX_3 + m(n\text{-}C_4H_9)Li \rightarrow$$
$$Li_mNbX_3 + m/2 \, C_8H_{18} \quad (X = \text{S, Se}).$$

The synthesis conditions and procedure of isolation of the intercalates from the reaction medium and their identification have been described in detail (*11*). The X-ray photoelectron spectroscopy spectra of the metal and chalcogen inner levels and of the valence zones of trichalcogenides and intercalated materials were obtained on the X-ray spectrometer described in (*12*). The energy scale calibration was performed according to the $C1_s$ level of the adsorbed hydrocarbon molecules. The contribution of

the adsorbed carbon- and oxygen-containing molecules to the valence zone spectrum did not exceed 10%. This contribution was estimated from the intensity ratio of the carbon and oxygen inner levels of the adsorbed molecules and the inner levels of the atoms of the compounds being studied taking account of the photoionization cross sections. The spectra were registered with the multichannel NTA-1024 analyzer and then processed on the EMG-666B computer integrated with the analyzer. The smoothing of the spectra was done using the Savitzky filter (*13*). The background due to the scattered electrons was subtracted using the procedure of Ref. (*14*). Our valence zone spectra for NbS_3 and $NbSe_3$ and their lithium intercalates are shown in Fig. 1. The valence zone spectra for niobium trichalcogenides coincide with those reported in (*8, 9*).

The SK_β and NbL_{β_2} emission spectra have been obtained on a "Stearat" spectrometer (Fig. 2) whose crystal-analyzer was focused according to the Johann scheme ($R = 500$ mm). The spectra were registered with a flow proportional counter. The spectral resolution of the instrument was 0.5 eV and better.

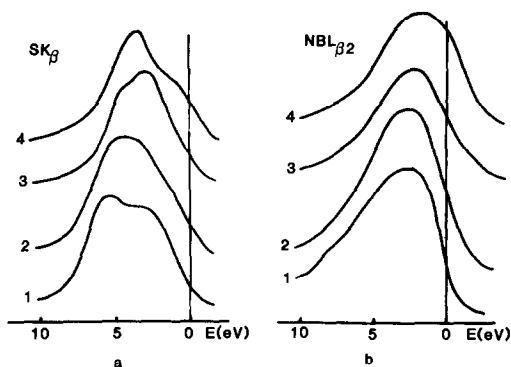Figure 3 shows X-ray photoelectron spectra of the $S2p$ and $Se3p$ levels of the

FIG. 2. X-ray emission spectra of NbX_3 (X = S, Se) and intercalates. (a) SK_β spectra: 1, NbS_3; 2, $Li_{0.9}$ NbS_3; 3, $Li_{2.2}NbS_3$; 4, $Li_{2.9}NbS_3$; (b) NbL_{β_2} spectra: 1, NbS_3; 2, $Li_{0.9}NbS_3$; 3, $NbSe_3$; 4, $Li_{0.9}NbSe_3$.

TABLE I

INNER LEVEL ENERGIES (eV) $Nb3d_{5/2}$, $S2p$, $Se3p_{3/2}$ IN NbS_3 AND $NbSe_3$

Compound	$Nb3d_{5/2}$	$S2p$	Compound	$Nb3d_{5/2}$	$Se3p_{3/2}$
NbS_3	204.3	162.2	$NbSe_3$	203.9	160.9
$Li_{0.5}NbS_3$	204.1	161.8	—	—	—
$Li_{0.9}NbS_3$	203.8	161.7	$Li_{1.1}NbSe_3$	203.4	160.0
$Li_{2.2}NbS_3$	203.9	161.4	—	—	—
$Li_{2.8}NbS_3$	203.5	161.4	$Li_{2.9}NbSe_3$	203.0	159.8

chalcogenide phases and their intercalates. The structure of the spectra indicates a nonequivalence of the charges on the chalcogen atoms in these compounds. This may be due to a nonequivalence of the chalcogen atoms at the vertex and in the base of the triangle (the triangle base is a dichalcogenide group X_2). The vertex chalcogen atom shows itself in the spectra as a shoulder at the low binding energy side whereas the main peak corresponds to the atoms of the dichalcogenide group X_2. The

charge nonequivalence of the vertex and dichalcogenide group atoms was also noted in (15) and is reflected in the crystallographic formula of the niobium trichalcogenides $Nb^{+4}X^{-2}(X_2)^{-2}$.

Table I lists the electron binding energies of the $Nb3d_{5/2}$, $S2p$, and $Se3p_{3/2}$ levels for all compounds. The binding energies of the metal and chalcogen inner levels decrease as the compounds become intercalated with lithium. It should be noted that in the spectra of the $S2p$ and $Se3p_{3/2}$ levels only the main peak is shifted with intercalation whereas the position of the low energy shoulder remains essentially unchanged. This indicates that the electronic density transfer from the lithium upon intercalation is both to the chalcogen atoms (mainly those of the X_2 group) and the metal atoms.
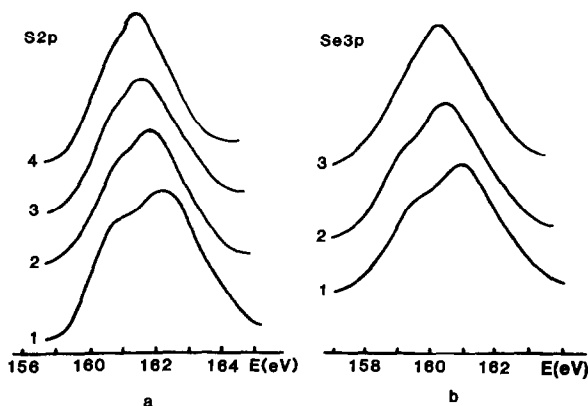

FIG. 3. X-ray photoelectron spectra of the $S2p$ and $Se3p_{3/2}$ levels of niobium trichalcogenides and intercalates. (a) The spectrum of the $S2p$ level: 1, NbS_3; 2, $Li_{0.9}NbS_3$; 3, $Li_{2.2}NbS_3$; 4, $Li_{2.9}NbS_3$; (b) the spectrum of the $Se3p_{3/2}$ level: 1, $NbSe_3$; 2, $Li_{0.9}NbSe_3$; 3, $Li_{2.9}NbSe_3$.
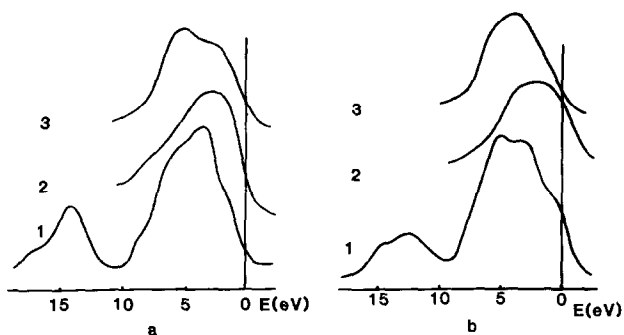
FIG. 4. X-ray photoelectron spectra of the valence band and X-ray emission NbL_{β_2} and SK_β spectra for (a) NbS_3: 1, valence band; 2, NbL_{β_2} spectrum; 3, SK_β spectrum; (b) $Li_{0.9}NbS_3$: 1, valence band; 2, NbL_{β_2} spectrum; 3, SK_β spectrum.

Figure 4 shows, on a common energy scale relative to the Fermi level, X-ray photoelectron spectra of the valence zones for NbS_3 and $Li_{0.9}NbS_3$ and X-ray emission NbL_{β_2} and SK_β spectra which reflect the contribution of these atoms to the valence zone spectrum. It can be seen that the metal $4d$-levels contribute mainly to the upper part of the valence zone while its deeper part is filled predominantly by the sulfur $3p$ levels. The part of the valence zone from 12 to 17 eV relative to the Fermi level is filled with the electrons of the sulfur $3s$ levels.

Comparison of the valence zone spectra of the pure and intercalated materials (Fig. 1) indicates that at low degrees of intercalation the changes in the density of states occur in both parts of the valence zone. At higher intercalation degrees such changes occur mainly in the chalcogen filled part of the valence zone.

As mentioned above, the semimetallic properties of $NbSe_3$ are due to the presence of an interchange interaction which results in incomplete splitting of the d_z2-zone, i.e., the formation of a conduction and valence zones which overlap each other. Intercalation of niobium triselenide with lithium may cause further splitting of the d_z2-zone. In this connection, it is of interest to follow the changes in conductivity depending on the degree of intercalation. For this purpose we have prepared single crystals of $NbSe_3$ in the form of thin needles of an average size of $10 \times 0.02 \times 0.05$ mm^3 using the vapor transport technique with the elementary selenium as a transport agent (16). The crystals grown by this method showed a $\rho_{298K}/\rho_{4.2K}$ ratio of 80 to 90. The electrical resistance was measured along the crystal growth axis (the b axis) by the four-contact potentiometric method. The procedure of the preparation of the electrical contacts which permit a relative electrical resistance measurement accuracy of $10^{-3}\%$ has been described in (17). It was found that with increasing degree of intercalation, a decrease in conductivity occurs and as the solid phase becomes saturated with lithium the conductivity changes to a semiconducting one with an energy gap of 0.1 eV. The resistance ratio is $\rho_{(m=3)}/\rho_{(m=0)} \sim 5 \times 10^4$. From this evidence it can be concluded that intercalation of niobium selenide leads to further splitting of the d_z2-zone and a reduction of the number of free carriers. With the saturation of the solid phase with lithium the d_z2-zone becomes completely split into a filled and a free zone with the formation of the energy gap.

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