

PACS: 64.60.My, 71.20.Be, 79.60.-i, 82.80.Pv

O.Yu. Khyzhun

# XPS STUDY OF THE ELECTRONIC STRUCTURE OF NbSe<sub>2</sub> SYNTHESIZED AT HIGH PRESSURE

Frantsevych Institute for Problems of Materials Science,  
National Academy of Sciences of Ukraine  
3 Krzhyzhanovsky st., 03142 Kyiv, Ukraine

Received January 31, 2000

*An X-ray photoelectron spectroscopy (XPS) method was used to investigate the electronic structure of niobium diselenide 4H(b)-NbSe<sub>2</sub> synthesized at high pressures (7.7–9.0 GPa). For comparison, the electronic structure of an initial polymorphous form of niobium diselenide, 2H-NbSe<sub>2</sub>, was also studied. The XPS core-level binding energies (BEs) and valence-band structures for the two NbSe<sub>2</sub> modifications have been determined. The XPS core-level BEs of pure niobium and selenium were also investigated. It is shown that, in the 2H-NbSe<sub>2</sub> and 4H(b)-NbSe<sub>2</sub> diselenides, a charge transfer occurs from Nb to Se atoms. The XPS core-level BEs of both niobium and selenium atoms remain constant (within the experimental errors) for the above NbSe<sub>2</sub> polytypes studied. In the sequence 2H-NbSe<sub>2</sub> → 4H(b)-NbSe<sub>2</sub> a small increase of the XPS valence-band half-width was observed. The present experimental results are compared with earlier theoretical studies of niobium diselenide.*

## 1. Introduction

The diselenides of transition metals of groups IVB to VIB of the Periodic Table are layer structures in which metal atoms have trigonal prismatic and/or octahedral selenium coordination [1,2]. According to Brown and Beerntsen [3], all the above compounds can be considered as two-dimensionally infinite «layer molecules». Within these «layer molecules» the chemical bonding is rather strong [1,3]. The mentioned «layer molecules» are stacked in a close-packed manner and the chemical bonding between them is rather weak [1–3].

The nearly stoichiometric niobium diselenide, NbSe<sub>2</sub>, is known to exist in several polytypes at atmospheric pressure as temperature varies; the atomic structures of the polytypes 1T-NbSe<sub>2</sub>, 2H[2H(a)]-NbSe<sub>2</sub>, 3R-NbSe<sub>2</sub>, 4H(a)-NbSe<sub>2</sub>, and 4H(d)-NbSe<sub>2</sub> have been established [3–7]. Both cell dimensions and space groups for the above polymorphous forms of niobium diselenide are listed in Table 1. Nevertheless, two niobium diselenide polytypes, 1T-NbSe<sub>2</sub> (octahedral coordination of niobium atoms) and 4H(d)-NbSe<sub>2</sub> (alternative octahedral and trigonal prismatic coordination of niobium atoms), exist only in high-temperature conditions ( $t > 950^{\circ}\text{C}$ ) [6]. These two polymorphous forms can not be stabilized at room temperatures. The both 1T-NbSe<sub>2</sub> and 4H(d)-NbSe<sub>2</sub> polytypes transform to 4H(a) or 2H[2H(a)] polymorphous forms of

niobium diselenide as temperature decreases. Thus, only polymorphous forms of NbSe<sub>2</sub> with trigonal prismatic coordination of niobium atoms can exist at atmospheric pressure [1,2]. Nevertheless, at high pressures (7.7–9.0 GPa) and high temperatures (1200–1400°C) a new niobium diselenide polymorphous form with alternative octahedral and trigonal prismatic coordination of the metal atoms, a 4H(b)-NbSe<sub>2</sub> polytype, can be synthesized [8–10]. This polytype of NbSe<sub>2</sub> exists at atmospheric pressure after the above high pressure–high temperature treatment, and only annealing under vacuum conditions at 900°C for 10–12 hours results in the transformation 4H(b)-NbSe<sub>2</sub> → 4H(a)-NbSe<sub>2</sub> [9,10].

Table 1  
Space groups and lattice parameters of some NbSe<sub>2</sub> polytypes

Polytype	Space group	Lattice parameters		Ratio <i>c/a</i>	Coordination type of the metal atoms	Reference
		<i>a</i> , nm	<i>c</i> , nm			
1T-NbSe <sub>2</sub> <sup>a)</sup>	$P\bar{3}m1$	0.353	0.629	1.781	octahedral	[6]
2H[2H(a)]-NbSe <sub>2</sub>	$P6_3/mmc$	0.344	1.255	2.1824	trigonal prismatic	[4]
		0.3440	1.2482	2.1814	trigonal prismatic	[7]
		0.3442	1.254	2.1821	trigonal prismatic	[6]
		0.345	1.272	2.1843	trigonal prismatic	[6] <sup>b)</sup>
		0.345	1.254	2.1817	trigonal prismatic	[3]
3R-NbSe <sub>2</sub>	$R3m$	0.346	1.877	3.1808	trigonal prismatic	[4]
4H(a)-NbSe <sub>2</sub>	$P\bar{6}m2$	0.345	1.888	3.1824	trigonal prismatic	[3]
		0.344	2.523	4.1833	trigonal prismatic	[5]
		0.3444	2.523	4.1832	trigonal prismatic	[6]
		0.344	2.524	4.1834	trigonal prismatic	[3]
4H(b)-NbSe <sub>2</sub> <sup>c)</sup>	$P6_3/mmc$	0.346	2.480	4.1791	alternative octahedral and trigonal prismatic	[8–10]
4H(d)-NbSe <sub>2</sub> <sup>d)</sup>	$P\bar{6}m2$ (or $P\bar{3}m1$ )	0.348	2.545	4.1828	alternative octahedral and trigonal prismatic	[6]

a) The polytype exists at temperatures above 980°C; cannot be stabilized at room temperatures [6];

b) Lattice parameters were determined at *t* = 850°C;

c) The polytype can be synthesized only at high pressure–high temperature treatment;

d) The polytype is stable in the temperature range of 910 to 980°C; cannot be stabilized at room temperatures [6].

The 4H(b)-NbSe<sub>2</sub> polymorphous form, which was synthesized under the mentioned high pressure–high temperature conditions, is the so-called metastable high-pressure phase (MHPP). The phases have long been studied (see e.g. Refs. [8–19]), and the study is very important because it clarifies mechanisms of irreversible phase transformations in solids due to high pressure–high temperature treatment.

While the electronic structure of 2H-NbSe<sub>2</sub> was investigated in a series of theoretical [20–25] and experimental [25–30] works, the MHPP modification, 4H(b)-NbSe<sub>2</sub>, has not been studied yet. So, the purpose of the present work is to apply an X-ray photoelectron spectroscopy (XPS) method to determine shapes as well as binding energies

(BEs) of both the XPS valence-band and core-level spectra for the above niobium diselenide polytypes. This study involves two NbSe<sub>2</sub> polytypes: the usual modification, 2H-NbSe<sub>2</sub>, and the 4H(b)-NbSe<sub>2</sub> polymorphous form synthesized at high pressure – high temperature conditions.

## 2. Experimental details

Two polymorphous forms of niobium diselenide, 2H-NbSe<sub>2</sub> and 4H(b)-NbSe<sub>2</sub>, studied in the present work, were synthesized as described in Refs. [8–10] by V.I. Larchev and S.V. Popova (Vereshchagin Institute of High Pressure Physics, Russian Academy of Sciences, Moscow–Troitsk, Russian Federation) who also performed the X-ray diffraction measurements. Parameters of unit cells of the niobium diselenides studied in the present work are listed in Table 1. Table 2 shows data of interatomic distances of the two niobium diselenides investigated. For comparison, interatomic distances for other polymorphous forms of NbSe<sub>2</sub>, the 3R-NbSe<sub>2</sub> and 4H(a)-NbSe<sub>2</sub> modifications, are also listed in Table 2.

Table 2

Interatomic distances (in nm) for some NbSe<sub>2</sub> polytypes

Polytype	Se–Se (between layers)	Se–Se (in the layer)	Nb–Se (trigonal pris- matic coordi- nation)	Nb–Se (octahedral coordi- nation)	Refer- ence
2H-NbSe <sub>2</sub>	0.352 <sub>5</sub> ±0.002	0.336±0.002	0.260±0.001	–	[3]
	0.352	0.334	0.259	–	[22] <sup>a)</sup>
3R-NbSe <sub>2</sub>	0.354±0.008	0.332±0.008	0.259 <sub>5</sub> ±0.006	–	[3]
4H(a)-NbSe <sub>2</sub>	0.360±0.013	0.334±0.015	0.259±0.008	–	[3]
	0.350±0.011	0.336±0.014	0.262±0.008	–	[3]
		0.344±0.010	0.258±0.008	–	[3]
4H(b)-NbSe <sub>2</sub>	0.356±0.002	0.346±0.002	0.258±0.001	0.257±0.001	[8,10]

<sup>a)</sup> Uncertainties were not reported.

The initial modification of niobium diselenide, 2H-NbSe<sub>2</sub>, was prepared by heating of mixtures of powdered niobium (99.9%) and selenium (99.997%) in an evacuated quartz ampoule at 1000°C for 12 h with subsequent homogeneous annealing at the same temperature conditions. In order to synthesize the MHPP modification, 4H(b)-NbSe<sub>2</sub>, the initial niobium diselenide, 2H-NbSe<sub>2</sub>, was placed in the high pressure chamber containing a capsule made from BN and a heater made from pure niobium. Experimental details for the specimen preparation have been reported elsewhere [9]. No traces of BN or another admixtures were found for the 4H(b)-NbSe<sub>2</sub> modification by conventional chemical analysis as well as by means of the XPS measurements. Fig. 1 shows the results of the XPS analysis of the both niobium diselenide modifications studied in the present work.

Measurements of the XPS valence-band and core-level spectra of the niobium diselenides were carried out in an ion-pumped chamber of an ES-2401 spectrometer. The chamber was evacuated to 5·10<sup>–8</sup> Pa. The Mg K<sub>α1,2</sub> (*E* = 1253.6 eV) excitation was used in the capacity of a source of X-ray radiation. The energy scale of the spec-

trometer was calibrated by setting the measured Au  $4f_{7/2}$  BE to 84.0 eV with respect to  $E_f$ . The surfaces of the investigated niobium diselenides were prepared by argon-ion bombardment (1700 V, 30 mA/cm<sup>2</sup>, 2 min) with subsequent mechanical cleaning in the spectrometer chamber as described in Refs. [31,32].

### 3. Results and discussion

Data of the present XPS core-level studies of the two polymorphous modifications of niobium diselenide,  $2H$ -NbSe<sub>2</sub> and  $4H(b)$ -NbSe<sub>2</sub>, are shown in Fig. 1. The XPS results indicate that, in the two studied polymorphous forms of NbSe<sub>2</sub> the niobium XPS core-level BEs increase while the selenium BEs decrease in comparison with BEs of pure metallic niobium and pure selenium, respectively. These facts indicate that when niobium atoms and selenium atoms combine to form the both  $2H$ -NbSe<sub>2</sub> and  $4H(b)$ -NbSe<sub>2</sub> compounds, the charge transfers from Nb to Se atoms. Our results are in good agreement with the theoretical band calculations of niobium diselenide [22–24]. As one can see from Fig. 1 and Table 3, transformation of the crystal structure from the  $2H$ -NbSe<sub>2</sub> modification to the  $4H(b)$ -NbSe<sub>2</sub> polymorphous form does not lead to any significant changes of the XPS core-level BEs. When going from  $2H$ -NbSe<sub>2</sub> to  $4H(b)$ -NbSe<sub>2</sub>, half-widths of the above spectra remain constant within the experimental errors (see Table 3). The above results are consistent with those derived previously for several transition metal MHPPs. As shown in works [17,19,33–36], irreversible polymorphous transitions induced by high pressure – high temperature treatment do not change considerably both half-widths and binding energies of the XPS core-level spectra of ReSe<sub>2</sub>, ReTe<sub>2</sub>, ReO<sub>3</sub> and TaN crystals.

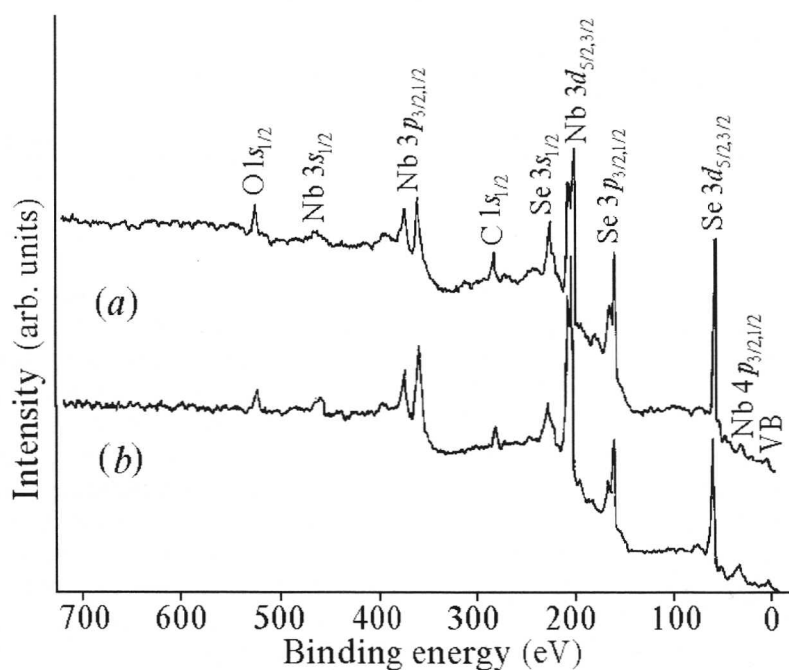


Fig. 1. XPS spectra recorded within the continuous energy range up to 700 eV with respect to  $E_f$  of the niobium diselenides studied: (a)  $2H$ -NbSe<sub>2</sub> and (b)  $4H(b)$ -NbSe<sub>2</sub>

Table 3

Half-widths and energy positions (in eV) of the XPS core-level spectra of the niobium diselenides studied

Core-level electrons	2H-NbSe <sub>2</sub>		4H(b)-NbSe <sub>2</sub>	
	Energy position of the maximum	Half-width	Energy position of the maximum	Half-width
Nb 4p <sub>3/2,1/2</sub>	32.90±0.08	7.3±0.3	32.74±0.08	6.9±0.3
Se 3d <sub>5/2,3/2</sub>	54.34±0.05	2.42±0.05	54.29±0.05	2.44±0.05
Se 3p <sub>3/2</sub>	160.36±0.06	3.28±0.08	160.44±0.06	3.37±0.08
Se 3p <sub>1/2</sub>	165.98±0.08	5.32±0.08	166.06±0.08	5.25±0.08
Nb 3d <sub>5/2</sub>	203.84±0.06	1.9±0.1	203.82±0.06	2.0±0.1
Nb 3d <sub>3/2</sub>	206.59±0.08	2.5±0.1	206.62±0.08	2.6±0.1
Se 3s <sub>1/2</sub>	229.0±0.2	5.0±0.2	229.1±0.2	4.8±0.2
Nb 3p <sub>3/2</sub>	362.23±0.08	3.8±0.1	362.28±0.08	3.7±0.1
Nb 3p <sub>1/2</sub>	377.7±0.1	6.4±0.3	377.8±0.1	6.1±0.3
Nb 3s <sub>1/2</sub>	468.1±0.2	7.1±0.3	468.3±0.2	7.5±0.3

Fig. 2 displays results of the XPS studies of valence-band structures of the both NbSe<sub>2</sub> modifications. The curves shown in Fig. 2 include also photoemission from the Nb 4p-like and Se 4s-like electrons. The spectra were normalized to one and the same peak intensity of the XPS Nb 3d<sub>5/2,3/2</sub> spin-doublets. Results of the above normalization indicate that integrated intensity of the XPS valence-band spectra remains constant (within the experimental errors) for the both 2H-NbSe<sub>2</sub> and 4H(b)-NbSe<sub>2</sub> modifications. When going from 2H-NbSe<sub>2</sub> to 4H(b)-NbSe<sub>2</sub> the XPS Nb 4p<sub>3/2,1/2</sub> core-level BEs as well as half-widths of the spectra remain constant (see Table 3).

Broad structures representing the valence band and the Se 4s-like subband have their maxima at BEs of about 3.7–3.9 eV and 13.6 eV, respectively. The mentioned broad structures do not allow to detect any tendency to shifts of the Se 4s-like subband maximum when going from 2H-NbSe<sub>2</sub> to 4H(b)-NbSe<sub>2</sub>. Nevertheless, as one can see from Fig. 2, maximum of the XPS valence-band spectrum of the 4H(b)-NbSe<sub>2</sub>

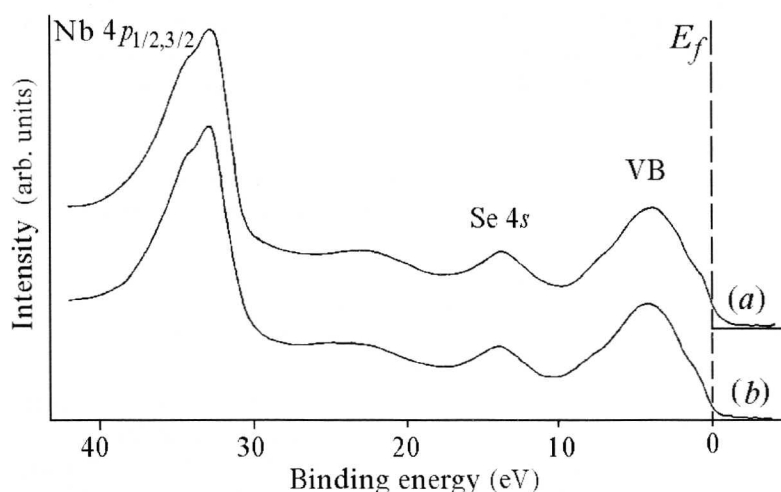


Fig. 2. XPS valence-band spectra (including photoemission from the Se 4s-like and Nb 4p-like electrons) of (a) 2H-NbSe<sub>2</sub> and (b) 4H(b)-NbSe<sub>2</sub>

compound shifted somewhat toward the higher BEs in comparison with its position in the initial  $2H\text{-NbSe}_2$  diselenide. The half-width of the XPS valence-band spectrum increases by 0.4 eV going from  $2H\text{-NbSe}_2$  to  $4H(b)\text{-NbSe}_2$ . Fig. 2 shows that, in the mentioned sequence of compounds the density of states (DOS) at the Fermi level,  $N(E_F)$ , slightly decreased. This fact may explain decreasing  $T_c$  in the sequence  $2H\text{-NbSe}_2$   $4H(b)\text{-NbSe}_2$ : from  $T_c = 7.0$  K for  $2H\text{-NbSe}_2$  to  $T_c = 3.5$  K for  $4H(b)\text{-NbSe}_2$  [8]. Our results for the above niobium diselenides appear to be consistent with the Mattheiss' results [22] obtained (using the nonrelativistic augmented-plane-wave method) for two polymorphous modifications of tantalum disulphide. When studying the electronic structure of two polymorphous forms of tantalum disulphide,  $1T\text{-TaS}_2$  (octahedral coordination of tantalum atoms) and  $2H\text{-TaS}_2$  (trigonal-prismatic coordination of tantalum atoms), Mattheiss [22] showed that DOS at the Fermi level considerably decreased going from  $2H\text{-TaS}_2$  to  $1T\text{-TaS}_2$ . Nevertheless, shapes of the XPS valence-band spectra of the two  $\text{NbSe}_2$  modifications studied in the present work are very much alike. This can be explained by the fact that the nearest NbSe distances in the both  $2H\text{-NbSe}_2$  and  $4H(b)\text{-NbSe}_2$  modifications are almost equal (see Table 2). Detailed discussion of changes of the XPS valence-band spectra as well as X-ray emission spectra during the irreversible polymorphous transition  $2H\text{-NbSe}_2 \rightarrow 4H(b)\text{-NbSe}_2$  will be reported elsewhere.

### Conclusion

Data of the present XPS studies indicate that, in the both diselenides studied,  $2H\text{-NbSe}_2$  and  $4H(b)\text{-NbSe}_2$ , a charge transfer occurs from the Nb to Se atoms. The XPS core-level BEs of both niobium and selenium atoms remain constant (within the experimental errors) for the above  $\text{NbSe}_2$  polymorphous modifications investigated. In the sequence  $2H\text{-NbSe}_2 \rightarrow 4H(b)\text{-NbSe}_2$  a small increase of the XPS valence-band half-width is observed. It is shown that, in the mentioned sequence of compounds, the density of states at the Fermi level slightly decreased.

### Acknowledgments

The author would like to express his thanks to Dr. V.I. Larchev and Prof. S.V. Popova (Vereshchagin Institute of High Pressure Physics, Russian Academy of Sciences, Moscow–Troitsk, Russia) for synthesis of the test specimens. He also thanks Mr. A.K. Sinelnichenko for his assistance in the present XPS studies.

1. J.-L. Calais, *Adv. Phys.* **26**, 847 (1977).
2. V.V. Sobolev and V.V. Nemoshkalenko, *Methods of computation physics in the theory of solids: Electronic structure of noble metal dichalcogenides*, Naukova Dumka, Kiev, 1990 (in Russian).
3. B.E. Brown and D.J. Beerntsen, *Acta Cryst.* **18**, 31 (1965).
4. K. Selte and A. Kjekshus, *Acta Chem. Scand.* **18**, 6971 (1964).
5. F. Kadijk, R. Huisman and F. Jellinek, *Rec. Trav. Chim.* **83**, 768 (1964).
6. F. Kadijk and F. Jellinek, *J. Less-Common Met.* **23**, 437 (1971).
7. M. Marezio, P.D. Dernier, A. Menth and G.W. Hull, *J. Solid State Chem.* **4**, 425 (1972).
8. V.I. Larchev and S.V. Popova, *High Temp. – High Pressure* **8**, 616 (1976).
9. V.I. Larchev and S.V. Popova, *Izv. AN SSSR: Neorgan. Mater.* **13**, 419 (1977) (in Russian).
10. V.I. Larchev, Ph.D. Thesis, M.V. Lomonosov Institute of High Chemical Technology, Moscow (1980) (in Russian).
11. S. Asano and J. Yamashita, *J. Phys. Soc. Jpn.* **35**, 767 (1973).

12. *E.S. Alekseev, R.G. Arkhipov and S.V. Popova*, Phys. Status Solidi (b) **90**, 133 (1978).
13. *A.V. Tsvyashchenko, S.V. Popova and E.S. Alekseev*, Phys. Status Solidi (b) **100**, 99 (1981).
14. *S.V. Popova*, DSc. Thesis, Institute of Crystallography, Academy of Sciences of the USSR, Moscow (1982) (in Russian).
15. *T.I. Dyuzheva, N.A. Bendeliani and S.S. Kabalkina*, J. Less-Common Met. **133**, 313 (1987).
16. *O.Yu. Khyzhun, Ya.V. Zaulychny and E.A. Zhurakovsky*, J. Alloys Comp. **244**, 107 (1996).
17. *O.Yu. Khyzhun, Ya.V. Zaulychny and V.D. Dobrovolsky*, Fiz. Tekhn. Vysok. Davl. **7**, № 4, 24 (1997).
18. *O.Yu. Khyzhun and Ya.V. Zaulychny*, Phys. Status Solidi (b) **207**, 191 (1998).
19. *O.Yu. Khyzhun*, Met. Phys. Adv. Tech. **17**, 625 (1998).
20. *R.A. Bromley*, Phys. Rev. Lett. **29**, 357 (1972).
21. *L.F. Mattheiss*, Phys. Rev. Lett. **30**, 784 (1973).
22. *L.F. Mattheiss*, Phys. Rev. **B8**, 3719 (1973).
23. *C.Y. Fong and M.L. Cohen*, Phys. Rev. Lett. **32**, 720 (1974).
24. *N.J. Doran, B. Ricco, D. Titterington and G. Wexler*, J. Phys. C: Solid State Phys. **11**, 685 (1978).
25. *F. Minami, M. Sekida, M. Aono and N. Tsuda*, Solid State Commun. **30**, 459 (1979); Ibid, **30**, 731 (1979).
26. *J.C. McMelamin and W.E. Spicer*, Phys. Rev. Lett. **29**, 1501 (1972).
27. *R.H. Williams*, J. Phys. C: Solid State Phys. **6**, L32 (1973).
28. *P.M. Williams and F.R. Shepherd*, J. Phys. C: Solid State Phys. **6**, L36 (1973).
29. *F.R. Shepherd and P.M. Williams*, J. Phys. C: Solid State Phys., **7**, 4427 (1974).
30. *V.V. Nemoshkalenko, M.A. Obolensky, L.V. Guseva, V.N. Uvarov, A.A. Yereshchenko and A.I. Senkevich*, Metallofizika **11**, № 1, 46 (1989) (in Russian).
31. *O.Yu. Khyzhun, E.A. Zhurakovsky, A.K. Sinelnichenko, V.A. Kolyagin*, J. Electron Spectroscopy Relat. Phenom. **82**, 179 (1996).
32. *O.Yu. Khyzhun*, J. Alloys Comp. **259**, 47 (1997).
33. *Ya.V. Zaulychny, O.Yu. Khyzhun, E.A. Zhurakovsky, V.D. Dobrovolsky and V.I. Larchev*, Fiz. Tekhn. Vysok. Davl. № 32, 12 (1989) (in Russian).
34. *O.Yu. Khyzhun, Ya.V. Zaulychny, T.I. Dyuzheva and E.A. Zhurakovsky*, Rep. NAS Ukr. № 2, 99 (1997) (in Russian).
35. *O.Yu. Khyzhun, Ya.V. Zaulychny and E.A. Zhurakovsky*, Poroshkovaya Metallurgiya, № 7/8, 93 (1998) (in Russian).
36. *O.Yu. Khyzhun*, Rep. NAS Ukr. № 8, 91 (1998).