

Influence of Se vacancies on the electron energy spectrum transformation of 2H-NbSe₂

A.A.Mamalui, O.N.Andreeva, A.V.Sinelnik

National Technical University "Kharkiv Polytechnic Institute",
21 Frunze Str., 61002 Kharkiv, Ukraine

Received December 3, 2015

The results of density functional calculations of 2H-NbSe₂ electron energy spectrum with Se vacancies at various concentrations are presented in the article. It is found that volume of the hole-like Fermi surface tends to decrease with increasing concentration of the vacancies. At vacancy concentrations corresponding to the beginning of the phase transition 2H-NbSe₂ → 4H-NbSe₂ the disappearance of carrier group occurs, that is an electronic topological transition of order 2.5 takes place.

Keywords: 2H-NbSe₂, single crystals, electron energy, vacancies concentrations.

Проведены расчеты электронного энергетического спектра 2H-NbSe₂ с вакансиями Se при различных концентрациях. Установлено, что объем дырочной зоны поверхности Ферми имеет тенденцию уменьшаться с увеличением концентрации вакансий. При концентрациях вакансий, соответствующих началу фазового перехода 2H-NbSe₂ → 4H-NbSe₂ наблюдается исчезновение группы носителей, то есть происходит электронный топологический переход 2.5 рода.

Вплив вакансій Se на трансформацію электронного енергетичного спектру 2H-NbSe₂. *А.О.Мамалуй, О.М.Андрєєва, О.В.Синельник.*

Проведено розрахунки электронного енергетичного спектра 2H-NbSe₂ з вакансіями Se при різних концентраціях. Встановлено, що об'єм діркової зони поверхні Фермі має тенденцію зменшуватися зі збільшенням концентрації вакансій. При концентраціях вакансій, які відповідають початку фазового переходу 2H-NbSe₂ → 4H-NbSe₂, спостерігається зникнення групи носіїв, тобто відбувається електронний топологічний перехід 2.5 роду.

1. Introduction

Lattice stability research of quasi-low-dimensional crystalline systems with nanostructured defects is of significant interest to a wide range of applications of condensed matter physics. In [1, 2], it was found that introduction of Se vacancies in perfect 2H-NbSe₂ crystals results in a phase transition to different structural polytype, namely 4H-NbSe₂.

Under formation of vacancies in three-dimensional lattice of monatomic metal the volume of the crystal changes as a whole ($\sim 0.5V_{at}$ by 1 vacancy) and the value

of the average electron density decreases [3]. In the case of metallic crystals with sharply anisotropic structure (2H-NbSe₂) formation of vacancies (Se) reduces the volume of the crystal as a whole due to the reduction of the number of Se atoms. At the same time the lattice parameters increase due to tension (lattice relaxation) in the absence of occupied site. Break of ionic-covalent Nb-Se bonds herewith increases the number of electrons in the conduction band.

In polyatomic metallic crystals deviation from stoichiometry (stoichiometric vacancies) can reach significant values

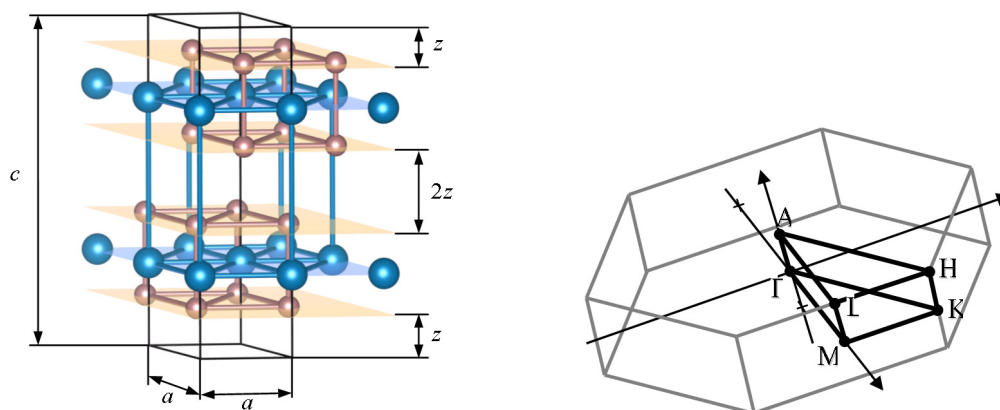


Fig. 1. a) 2H-NbSe₂ cell. Two Se-Nb-Se sandwiches are shown, consisting of Nb atoms (depicted as larger spheres) and Se atoms (depicted as smaller spheres). b) The Brillouin zone.

(≤ 10 at.%). In this case, as is known, lattice stability can be disturbed, which accompanied by the phase transitions [4]. When there is significant number of Se vacancies (≥ 1 at. %) in 2H-NbSe₂ crystal the phase transition is realized. The fact of the vacancies formation leads to changes in the cell volume and release of a certain number of electrons, of course, causes a change in the crystal energy spectrum.

For calculations of band structure of transition metal dichalcogenides, including 2H-NbSe₂, construction of wave functions within the augmented plane wave scheme (APW) was successfully used [5, 6]. Along with these techniques other research methods were applied: both theoretical [7, 8, 13, 15, 18] and experimental [9–11, 12, 14, 16–18]. Review of publications shows that investigation of pure (defect free) 2H-NbSe₂ crystals or ones intercalated with molecules were mainly performed. Despite the large number of publications there are no articles dedicated to the electron energy spectrum of 2H-NbSe₂ with vacancies. Since Se vacancies in 2H-NbSe₂ crystals lead to the structural transition 2H-NbSe₂ \rightarrow 4H-NbSe₂, it is of interest to study the electron energy spectrum of such crystals with vacancies.

In this paper, a number of density functional theory calculations of the electron spectrum in the presence of Se vacancies in 2H-NbSe₂ crystals near the structural phase transition 2H-NbSe₂ \rightarrow 4H-NbSe₂ were performed in order to study the electron energy spectrum transformation.

2. 2H-NbSe₂ structure

As known 2H-NbSe₂ structure represents the alternating layers consisting of hexagonal planes of Se and Nb atoms. Two atomic layers of Se and single Nb layer are combined with ion-covalent bonds, which form a "sandwich". 2H-NbSe₂ unit cell includes two Se-Nb-Se sandwiches, in which atomic planes of Se offset from each other, as shown in Fig. 1. 2H-NbSe₂ structure belongs to P6₃/mmc space group. The Bravais lattice is hexagonal. The atoms in the cell have the following positions [5]:

$$[[m, n, k]]_{\text{Nb}} = \pm \left[\left[0, 0, \frac{1}{4} \right] \right];$$

$$[[m, n, k]]_{\text{Se}} = \pm \left[\left[\frac{1}{3}, \frac{2}{3}, z \right] \right];$$

$$[[m, n, k]]_{\text{Se}} = \pm \left[\left[\frac{1}{3}, \frac{2}{3}, \frac{1}{2} - z \right] \right].$$

Here the parameter $z \approx 1/8c$ defines the position of Se atomic layer, which essentially (for fixed c) defines the height of Se-Nb-Se sandwich.

3. The main results of NbSe₂ X-ray structure studies after annealing

To investigate the stability of NbSe₂ crystal lattice to their own point defects, which are the selenium vacancies corresponding to [1], X-ray studies were carried out after the heat treatment at different temperatures.

Table 1. Lattice constants obtained from X-ray data, change of cell volume, estimated vacancy concentration and corresponding structural modification.

Annealing temperature T_a , K	Lattice constants		Change of the cell volume ΔV , \AA^3	Vacancy concentration C , %	Structural modification
	a , \AA	c , \AA			
443	3.78	13.57	39	1	2H
453	3.05	22.04	48	5	2H \rightarrow 4H

To study the stability of the crystal lattice of niobium diselenide to the intrinsic point defects, which according to [1] are Se vacancies, NbSe₂ X-ray diffraction studies were carried out after the heat treatment at different temperatures, i.e. at different vacancy concentrations C . From [19] it is known that the object under study exists in three basic models: 2H-NbSe₂ (hexagonal unit cell, consisting of two layers), 3R-NbSe₂ (three-layered rhombohedral unit cell) and 4H-NbSe₂ (four-layer hexagonal unit cell). A comparison of the lattice parameters calculated for each temperature based on the data from X-ray analysis, with parameters for different polytypes showed that at $T = 443$ K the sample has structure with the unit cell 2H-NbSe₂. The subsequent high temperature treatment leads to increase in the lattice parameter c , thereby bringing the structure of the object under test closer to 4H-NbSe₂. The lattice parameters calculated for NbSe₂ annealed at 453 K for its value corresponds to the intermediate structural state 2H \rightarrow 4H (see Table 1) [24]. In [24] it is shown that as a result of the high-temperature heat treatment at $T = 453$ K, the crystal lattice stretches along the layers. This agrees with the data of [2] in which on the basis of dilatometric studies it was found that after the heat treatment, there is a relative decrease in the sample length along the plane (ab). Also in [24] the concentration of vacancies C was estimated. It is seen that, as expected, the vacancy concentration changes (increases) with increasing the heat treatment temperature. For more detailed investigation of the influence of intrinsic point defects in the crystal lattice of single crystals NbSe₂, analyzing changes in the cell volume (ΔV) for all states of the crystal under study (see Table 1), we can establish that increase of the vacancy concentration of selenium leads to non-monotonic increase in the unit cell volume. Intensive growth ΔV after the isothermal annealing at $T = 463$ K is due, most likely, to the re-

structuring of the crystal lattice, that is, the change of the crystal polytype.

Thus, the introduction of vacancies in an amount of ≈ 5 % leads to the polytype transformation of 2H-NbSe₂ into 4H-NbSe_{2-x}.

4. Calculations of the band structure of 2H-NbSe₂ defect-free crystal

We performed our electronic energy structure calculations using the linearized augmented plane wave scheme with the full potential (FP-LAPW+local orbitals) [20], which represent a set of basis functions used to solve the Kohn-Sham equation in the density functional theory (DFT). The exchange-correlation potential was modeled using the generalized gradient approximation GGA-PBE [21].

For matching with other results we carried out our electron band structure and the Fermi surface calculations for the ideal (defect free), 2H-NbSe₂ crystal. The lattice constants that were used in our calculations were taken from experimental data [22], namely, $a = 3.44 \text{ \AA}$, $c = 12.48 \text{ \AA}$, $z = 0.12 \text{ \AA}$. The results of the electron band structure calculations shown in Fig. 2, and the Fermi surfaces are shown in Fig. 3. Our results are generally consistent with the results obtained in the studies performed by others researchers [10, 12, 13, 16–18]. As seen from the graphs obtained by us, the Fermi energy level ($E_F = 0$) is intersected by three bands. Accordingly, these three bands form three Fermi surfaces. All three surfaces are hole-like as filled states are outside of each of them. Bands 1 and 2 near Γ point (see Fig. 1b) are close to the degeneration. Bands 2 and 3 between points ALHA are degenerated. These points correspond to the ALH plane of the Brillouin zone (see Fig. 1b). Our calculations indicate the presence of a small pancake shaped band centered on Γ point. Although this region is not observed in the earlier studies [5–7], in the later studies, in particular ARPES [10, 12, 16–18], it is pre-

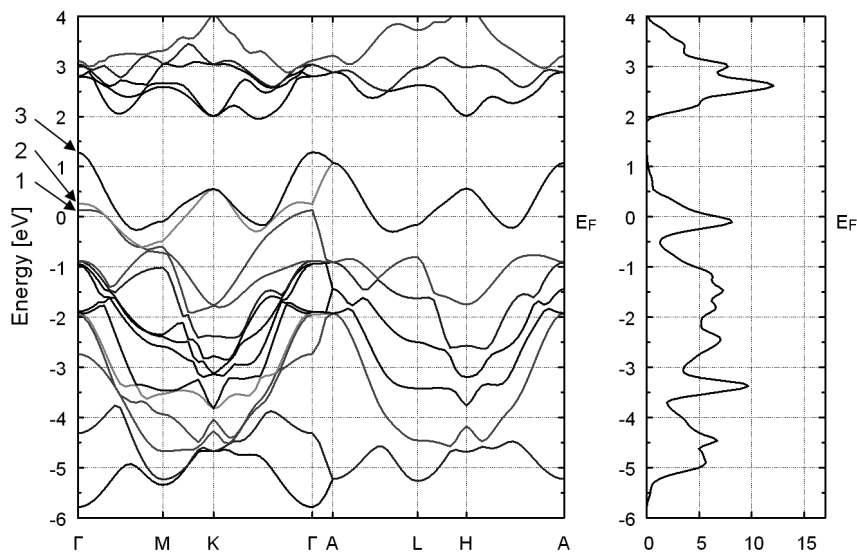


Fig. 2. Band structure of defect free 2H-NbSe₂. The Fermi energy set to 0 ($E_F = 0$). Bands intersecting the Fermi level, labeled as 1, 2 and 3.

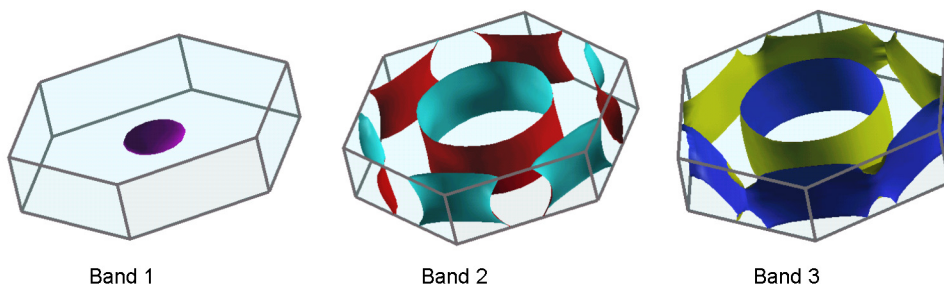


Fig. 3. Fermi surface of defect free 2H-NbSe₂ Band structure is depicted on Fig. 2.

sent, which confirms the sensitivity of the method used.

5. Band structure calculations of 2H-NbSe₂ with Se vacancies

As it was mentioned above, the Se vacancy formation leads to the abandonment of Se atoms. This results in lattice relaxation due to the tension. The rupture of ionic-covalent bonds between Nb and Se leads to the growth in the number of free electrons. In this paper we consider the impact of these two effects on the energy spectrum of electrons independently of each other.

5.1. Account of lattice strain due to the vacancies formation

To account of the lattice strain, we used the experimental results (see Table 1) in the region prior the phase transition. Intermediate values of a and c were obtained by the linear interpolation. The parameter z adjusted so that the height of the sandwich Nb-Se-Nb remained constant. The assumption that the distance between the planes of

Nb and Se remains constant during the vacancy formation based on the fact that Nb-Se bonds are ionic-covalent, and they are stronger than the van der Waals forces acting between the adjacent Se atomic layers.

We carried out a series of calculations of the electron band structure of 2H-NbSe₂ crystal with the lattice parameters corresponding to annealing temperatures of 400 K to 450 K, i.e. before and in the region of 2H → 4H structural phase transition. This annealing temperature range corresponds to the vacancy concentration in the range from 1 to 5 % (see Table 1). The results of such calculations of the electronic band structure are shown in Fig. 4, and the Fermi surface in Fig. 5. These diagrams correspond to the structure obtained after annealing at 440 K, which results in the vacancies formation with the concentration of 1 %. The lattice parameters are $a = 3.77 \text{ \AA}$, $c = 13.55 \text{ \AA}$, $z = 0.13$.

Analysis of our calculation results shows that as concentration of Se vacancies in the 2H-NbSe₂ crystal increases due to anneal-

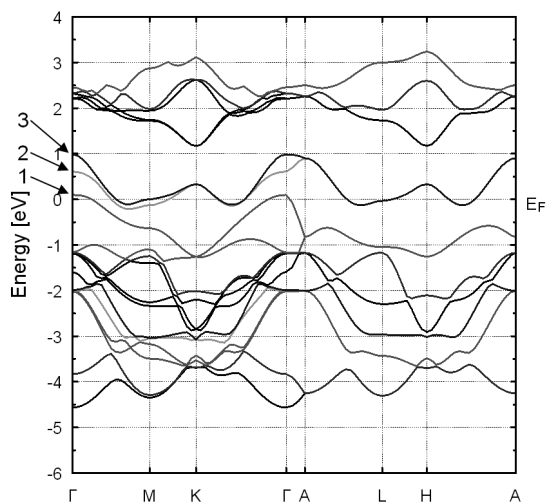


Fig. 4. 2H-NbSe₂ band structure taking into account the lattice stretching due to the vacancies formation. It is shown the position of the same bands 1, 2, 3, as in Fig. 2.

ing at different temperatures, the band structure is changing. Changes are in the gradual degeneration of the upper two bands (2 and 3) as well as a gradual reduction in the volume of the band 1, and then its complete filling. Filling of band 1 occurs in a region where there is a rearrangement of the crystal lattice during the 2H → 4H phase transition.

5.2. Account of carriers concentration increase due to the vacancies formation

In this paper, based on the assumption that under formation of a small number of vacancies the band structure does not change or changes only slightly. Then, if the formation of the vacancies leads to the release of electrons, the Fermi level increases, that is, changing the filling of certain bands.

In the free-electron approximation an expression for the Fermi energy is given by:

Table 2. Calculated change of Fermi energy at different vacancy concentrations.

C	ΔE_F , eV
1 %	0.025
2 %	0.050

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}, \quad (1)$$

where N is the total number of free electrons, and V is the crystal volume.

If as a result of vacancy formation the total number of free electrons increases by ΔN , then

$$E_{F'} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 (N + \Delta N)}{V} \right)^{2/3}. \quad (2)$$

Then

$$\frac{\Delta N}{V} = \frac{1}{3\pi^2} \left(\left(\frac{2mE_{F'}}{\hbar^2} \right)^{3/2} - \left(\frac{2mE_F}{\hbar^2} \right)^{3/2} \right). \quad (3)$$

Considering that the vacancies concentration is $C = N_v/N_{at}$, where $N_v = \Delta N/N_{el/v}$ is the number of vacancies in the crystal, N_{at} is the number of atoms, and $N_{el/v}$ is the number of electrons, which is released during the formation of the vacancy. Expressing the number of atoms as $N_{at} = N_c \cdot N_{at/cell}$, where $N_c = V/V_c$ is the total number of cells, and $N_{at/cell}$ is the number of atoms per cell, and V_c is the cell volume, we obtain the following expression:

$$\frac{\Delta N}{V} = \frac{CN_{el/v}N_{at/cell}}{V_c}. \quad (4)$$

Expressions (3) and (4) allows to relate the concentration of vacancies C , which leads to the growth of number of free electrons ΔN and the corresponding increase of

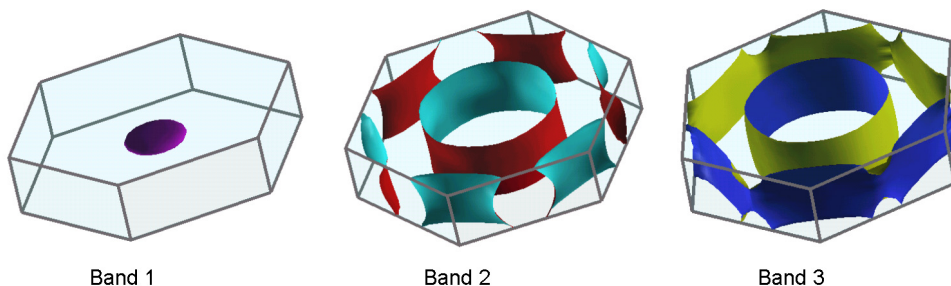


Fig. 5. The Fermi surface of 2H-NbSe₂ taking into account the lattice stretching due to the formation of vacancies with $C = 1\%$. Band structure is depicted in Fig. 4.

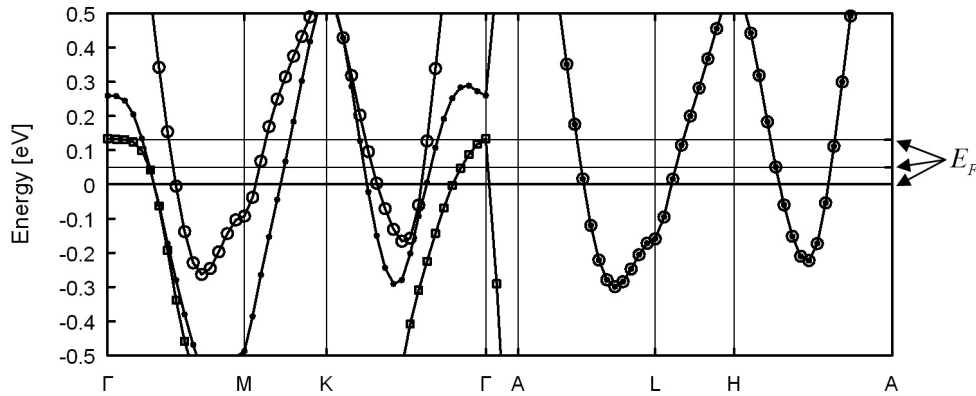


Fig. 6. Band structure of defect free 2H-NbSe₂ and the Fermi level offset with increasing concentration of the conduction-band electrons introduced by Se vacancies at various concentrations. Position of the Fermi level E_F indicated by horizontal lines: the lower line corresponds to an ideal crystal; line above it corresponds to the crystal with concentration of vacancies $C = 2\%$; the top line corresponds to the crystal with $C = 5\%$.

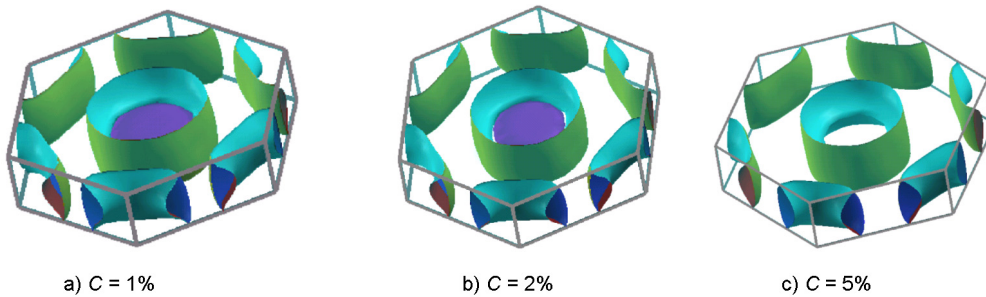


Fig. 7. 2H-NbSe₂ Fermi surface transformation due to the Fermi level shift at several vacancy concentrations. Each figure shows all three bands.

the Fermi energy $\Delta E_F = E_{F'} - E_F$. Table 2 shows the calculated values of ΔE_F corresponding to the different vacancy concentrations observed in the experiment [24]. Fig. 6 shows a fragment of the electronic band structure of the defect free crystal 2H-NbSe₂ near the Fermi energy. The Fermi level of the defect free crystal, and the Fermi levels, corresponding to different concentrations of selenium vacancies are also marked on the same figure. Our calculated Fermi surfaces at the indicated vacancy concentrations are shown in Fig. 7. As can be seen, with increasing concentration of selenium vacancies the filling of band 1 increases and its size reduces (Fig. 7). At $C \approx 5\%$ this band is completely filled, and the corresponding Fermi surface disappears, that is implemented the topological phase transition of order 2.5 [23].

6. Conclusions

The lattice strain effects and increase of the electrons concentration due to forma-

tion of the vacancies in 2H-NbSe₂, discussed above, lead to change in the electron energy spectrum. In the both cases the band 1 filling (see Fig. 2 and 4) increases, and the size of the band's Fermi surface decreases (see Fig. 3, 5 and 7). As can be seen, the impact of these effects by increasing the vacancies concentration occurs in the same direction. In this regard, under combined action of the above effects we expect more dramatic change in the electron energy spectrum of the 2H-NbSe₂ crystal with the growth in it the concentration of Se vacancies. In the end, all the states of band 1 are filled, which will leads to the disappearance of the corresponding Fermi surface, i.e. the topological phase transition of order 2.5. The electron phase transition occurs at about the same concentrations of selenium vacancies as the structural phase transition 2H \rightarrow 4H-NbSe₂. Apparently, the electronic topological transition may contribute to the lattice instability and subsequent structural phase transition.

References

1. O.N.Andreeva, I.S.Braude, A.A.Mamalui, *Phys.Met.Metallography*, **113**, 9 (2012).
2. A.A.Mamalui, T.N.Shelest, N.B.Fatyanova et al., *Functional Materials*, **12**, 521 (2005).
3. A.C.Damask, G.J.Dienes, Point Defects in Metals, Gordon and Breach, New York (1963).
4. N.F.Mott, Metal-insulator Transitions, Taylor & Francis Ltd., London (1974).
5. L.F.Mattheiss, *Phys.Rev.Lett.*, **30**, 784 (1973).
6. L.F.Mattheiss, *Phys.Rev.B*, **8**, 3719 (1973).
7. C.Y.Fong, Marvin L.Cohen, *Phys.Rev.Lett.*, **32**, 720 (1974).
8. G.Wexler, A.M.Woolley, *J.Phys.C: Solid State Phys.*, **9**, 1185 (1976).
9. J.Brandt, J.Kanzow, K.Roßnagel et al., HASYLAB Annual Report (2000).
10. T.Yokoya, T.Kiss, A.Chainani et al., *Science*, **294**, 2518 (2001).
11. E.E.Krasovskii, W.Schattke, V.N.Strocov, R.Claessen, *Phys.Rev.B*, **66**, 235403 (2002).
12. T.Kiss, T.Yokoya, A.Chainani et al., *Physica B*, **312**, 666 (2002).
13. M.D.Johannes, I.I.Mazin, C.A.Howells, *Phys.Rev.B*, **73**, 205102 (2006).
14. D.S.Inosov, V.B.Zabolotnyy, D.V.Evtushinsky et al., *New J.Phys.*, **10**, 125027 (2008).
15. S.Lebegue, O.Eriksson, *Phys.Rev.B*, **79**, 115409 (2009).
16. V.Sirenko, A.Gasparini, A.de Visser et al., *J.Phys.:Conf.Ser.*, **150**, 042185 (2009).
17. S.V.Borisenko, A.A.Kordyuk, V.B.Zabolotnyy et al., *Phys.Rev.Lett.*, **102**, 166402 (2009).
18. S.V.Borisenko, A.A.Kordyuk, V.B.Zabolotnyy et al., *J.Phys.Chem.Solids*, **72**, 562 (2011).
19. V.L.Kalikhman, Y.S.Umanskiy, *Usp.Fiz.Nauk*, **108**, 503 (1972).
20. A.Gulans, S.Kontur, C.Meisenbichler et al., *J.Phys.:Condens.Matter*, **26**, 363202 (2014).
21. J.P.Perdew, A.Ruzsinszky, G.I.Csonka et al., *Phys.Rev.Lett.*, **100**, 136406 (2008); Erratum *Phys.Rev.Lett.*, **102**, 039902 (2009).
22. M.Marezio, P.D.Dernier, A.Menth, G.W.Hull Jr., *J.Solid State Chemistry*, **4**, 425 (1972).
23. I.M.Lifshitz, M.Y.Azbel, M.I.Kaganov, *Elektronnaya Teoriya Metallov*, Nauka, Moscow (1971) [in Russian].
24. O.N.Andreeva, *Tochechnye Defekty v Kristallicheskikh Sistemakh Razlichnoy Razmernosti (3D — Pbln; 2D — NbSe₂)*, Diss. Kandidata Fiz.-mat. Nauk, Kharkiv (2014).