East Eur. J. Phys. Vol.1 No.3 (2014) 85-89

PACS: 61.72.jd, 61.72.Dd

INTRINSIC POINT DEFECTS IN ANISOTROPIC CRYSTALLINE SYSTEMS (QUASI-TWO $NbSe_2$ AND QUASI-ONE $NbSe_3$)

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Received July 14, 2014

Established that the resulting of heat treatment of single crystals of $NbSe_2$ and $NbSe_3$ formed selenium vacancies. With the complex investigation of the temperature dependences of resistance $NbSe_3$ and $NbSe_2$ in different environments (air, vacuum, argon vapor selenium) in the field of 300 - 550 K, the investigations of the relative change of the linear dimensions $NbSe_2$, and the X-ray diffraction investigations have shown that during heat treatment $NbSe_3$ and $NbSe_2$ formation of selenium vacancies, which cause a deviation from the linear dependence of the resistance. The presence of selenium vacancies decreases the dimensions of the samples along $NbSe_2$ layers and increases the lattice parameters. Found that the effective energy of vacancy selenium in quasi-single crystals $NbSe_2$ decreases on the exposure time, that is, with increasing concentration of vacancies of selenium.
KEY WORDS: electrical resistivity, quasi two-dimensional monocrystals $NbSe_2$, quasi one-dimensional monocrystals $NbSe_3$, point defects, selenium vacancies

ВЛАСНІ ТОЧКОВІ ДЕФЕКТИ В АНІЗОТРОПНИХ КРИСТАЛІЧНИХ СИСТЕМАХ (КВАЗІДВОВИМІРНИХ $NbSe_2$ І КВАЗІОДНОВИМІРНИХ $NbSe_3$)

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Встановлено, що в результаті термообробки в монокристалах $NbSe_2$ і $NbSe_3$ утворюються вакансії селену. За допомогою комплексного дослідження температурних залежностей опору $NbSe_3$ і $NbSe_2$ в різних середовищах (повітря, вакуум, аргон з парами селену) в діапазоні температур 300-550 К, досліджень відносної зміни лінійних розмірів $NbSe_2$, а також рентгеноструктурних досліджень показано, що при термічній обробці $NbSe_3$ і $NbSe_2$ утворюються вакансії селену, які обумовлюють відхилення опору від лінійної залежності. Наявність вакансій селену призводить до зменшення розмірів зразків $NbSe_2$ уздовж шарів та до збільшення параметрів решітки. Встановлено, що ефективна енергія утворення вакансій селену в квазідвовимірних монокристалах $NbSe_2$ зменшується від часу витримки, тобто з ростом концентрації вакансій селену.
КЛЮЧОВІ СЛОВА: електричний опір, квазідвовимірні монокристали $NbSe_2$, квазіодномірні монокристали $NbSe_3$, точкові дефекти, вакансії селену

СОБСТВЕННЫЕ ТОЧЕЧНЫЕ ДЕФЕКТЫ В АНИЗОТРОПНЫХ КРИСТАЛЛИЧЕСКИХ СИСТЕМАХ (КВАЗИДВУМЕРНЫЕ $NbSe_2$ И КВАЗИОДНОМЕРНЫЕ $NbSe_3$)

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Установлено, что в результате термообработки в монокристаллах $NbSe_2$ и $NbSe_3$ образуются вакансии селена. С помощью комплексного исследования температурных зависимостей сопротивления $NbSe_3$ и $NbSe_2$ в различных средах (воздух, вакуум, аргон с парами селена) в интервале температур 300 –550 К, исследований относительного изменения линейных размеров $NbSe_2$, а также рентгеноструктурных исследований показано, что при термической обработке $NbSe_3$ и $NbSe_2$ образуются вакансии селена, которые обуславливают отклонение сопротивления от линейной зависимости. Наличие вакансий селена приводит к уменьшению размеров образцов $NbSe_2$ вдоль слоев и увеличению параметров решетки. Установлено, что эффективная энергия образования вакансий селена в квазидвумерных монокристаллах $NbSe_2$ уменьшается от времени выдержки, то есть с ростом концентрации вакансий селена.
КЛЮЧЕВЫЕ СЛОВА: электрическое сопротивление, квазидвумерные монокристаллы $NbSe_2$, квазиодномерные монокристаллы $NbSe_3$, точечные дефекты, вакансии селена

Intrinsic point defects in metal crystals have traditionally attracted a keen interest of researchers. By means of intrinsic point defects implemented process diffusion mobility in condensed matter Point defects (mainly vacancies) occur in the lattice of metals in the pre-melting temperatures and also in the presence of a variety of external influences (high-energy particle radiation, plastic deformation, rapid changes in temperature over a wide range), which are often subjected to materials in the implementation of service functions.

A unique experimental method of "small perturbations" (because of the small value of the equilibrium concentration at high temperatures $C_V \leq 10^{-2}$ at. % [1]) is an opportunity to experimentally modify the properties of metals due to the presence of intrinsic point defects, periodically returning to the main defect-free state as a result of rapid heating or cooling. This method can correctly identify changes in the properties of metals due to the presence of vacancies.

The formation of representations about the vacancies in metals is an opportunity to test the main outstanding ideas of modern solid state physics about the peculiarities of the phonon and electron spectra, the electron-phonon interaction in metals [2, 3]. This applies to the model of single vacancies in metals as an analogue of the substitutional impurity "zero" valence and weight [4, 5].

A special interest is the solution of such issues for a sharply anisotropic lattice - in the case of quasi-crystals of low-dimensional systems (2d and 1d). It is known that for the lattice high-temperature superconductors are characterized by low-dimensional structures (for example, $YBa_2Cu_3O_{7-x}$ – quasi one-dimensional chain CuO, quasi-two-plane CuO_2), containing a significant number of point defects (vacancies of oxygen) [6,7]. The complicated structure of high-temperature superconductors makes the interpretation of the results of investigation of the influence of defects in such systems on their properties. At the same time, the study of systems which possess or quasi one-dimensional or two-dimensional quasi structural elements can greatly simplify analysis of the experimental results.

Theoretically, the transition metal chalcogenides are model systems for the study of physical phenomena inherent in systems with reduced dimensionality. For example, a study of the kinetic and thermodynamic properties of low-dimensional crystals with point defects topical due with the problem of stability of the crystal lattice.

The typical representatives of transition metal chalcogenides are quasi two-dimensional monocrystals $NbSe_2$ and quasi one-dimensional monocrystals $NbSe_3$.

THE OBJECTS OF INVESTIGATION

A quasi two-dimensional monocrystals$NbSe_2$ have a layered structure in the form of sandwiches each of which consists of two layers of selenium atoms and niobium layer there between. The connection of atoms Nb and Se in the sandwich is relatively strong (predominantly covalent). The layers $NbSe_2$ are interconnected in a crystal by weak van der Waals forces. Monocrystals$NbSe_2$ are known in the three versions: type 2H - $NbSe_2$, 3R - $NbSe_2$ and 4H - $NbSe_2$ [8].

Of all known modifications $NbSe_2$ is the most studied 2H - $NbSe_2$. 2H - $NbSe_2$ is a metallic conductor type with a hole conductivity at temperatures above 26K. The hole concentration is 1.4×10^{22} sm^{-3} [8]. The temperature for $NbSe_2$, according to [8], is T_D = 222 K. At the temperature of 7.2 K niobium diselenide becomes superconducting. At the temperature of T_P = 35 K $NbSe_2$ undergoes a Peierls transition with the formation of a charge density wave (CDW).

The quasi one-dimensional crystals $NbSe_3$ made up of chains formed by trigonal prisms of selenium atoms. In the center of the prisms is niobium atom. Monocrystals$NbSe_3$ have a monoclinic lattice with a spatial group $P2_1/m$. he concentration of charge carriers at room temperature is n ~ 10^{21} sm^{-3}. On the temperature dependence of the electrical resistance observed two large anomalies at the T_{P1} = 145 K and T_{P2}= 52 K are caused by the two independent Peierls transition and the formation of a CDW [10].

POINT DEFECTS IN LOW-DIMENSIONAL STRUCTURES (LDS)

A significant effect on the properties of low-dimensional systems is the presence of point defects, in particular vacancies. The basic methods of creating relatively significant concentration of point defects are the radiation and high-temperature heating. These methods have substantial differences. Irradiating the crystals with high-energy particles are generated different types of defects - internodes, vacancies and their complexes.

Study the influence of irradiation on the properties of low-dimensional chalcogenides is dedicated to a considerable amount of articles [11 - 14]. In the article [11] theirradiation of $NbSe_2$ by electrons (2.5 MeV) leads to a decrease in the temperature of the superconducting and CDW transitions. In the article [11] irradiation of $NbSe_3$electrons (under 3 MeV) leads to an increase in residual resistance, which is associated with the disorder in the article lattice and electron localization, in the [12] is associated with the disorder in the lattice and the localization of the conduction electrons. The irradiation of $NbSe_3$ by protons (2.5 MeV) [13] has on the temperature dependence of the resistance is the same effect as the electric field, that is, leads to the suppression of the CDW.

In the article [14] found that irradiation of 2H - $NbSe_2$ by fast electrons leads to a redistribution of electron density, namely, to an increase in the planes with a high packing density - base and prismatic – {110}, {210}. The appearance of the diffuse scattering of X-rays and electrons at high doses is associated with an increase in the density of the electron Fermi liquid.

A small number of works is dedicated to the study of the influence of defects produced by heating and rapid cooling (quenching) on the physical characteristics of the studied LDS [15, 16]. In the article [15] monocrystals were heated to 620 C for about 4 minutes and then subsequent rapid (less than one second) cooling to ambient temperature. It was found that as a result of quenching of the CDW transitions are suppressed and the superconducting state is realized at 7.2 K. It is caused by the transformation of $NbSe_3$ in to $NbSe_2$ in the heat treatment.

In the article [16] established that at a deviation from the stoichiometric composition (31.7 – 34.3 at. % Nb) 2H - $NbSe_2$, the degree of the anisotropy the structure is not substantially altered. It is shown the correlation between the state of niobium sublattice and the critical temperature of the superconducting transition. Thus, almost no literature details on the influence of on the properties of low-dimensional positions systems. Therefore, this work is devoted to the experimental study of the effect of vacancies of Se on the structural and electrical properties $NbSe_2$ and $NbSe_3$.

HIGH-TEMPERATURE RESEARCHES OF THE ELECTRICAL RESISTIVITY AND THE THERMAL EXPANSION

In [17] the creation of vacancies in single crystals of NbSe3 and NbSe2 was carried out using degassing selenium atoms with isothermal samples in the region of high temperatures.

On the quasi two-dimensional monocrystals $NbSe_2$ and quasi one-dimensional monocrystals $NbSe_3$ explored quasi-temperature dependences of electrical resistivity in the temperature range 300 – 550 K along the layers and along the chains, respectively. Measurements of electric resistance were carried out with direct current by the compensation scheme. We used a standard four-probe method for measurement. Researches carried out in different environments (vacuum, air, argon selenium vapor). At T > 410 K there is a significant deviation from the linear dependence on all temperature dependences of the electrical resistivity.Fig. 1 shows a typical temperature dependence of the resistivity of single crystals of $NbSe_2$.

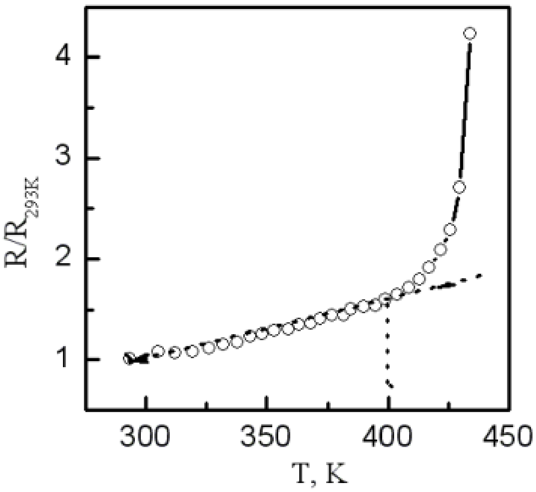


Fig. 1. Temperature dependence of the reduced the electrical resistivity quasi two-dimensional single crystal $NbSe_2$ in the 300 – 450 K (measured along the layers).

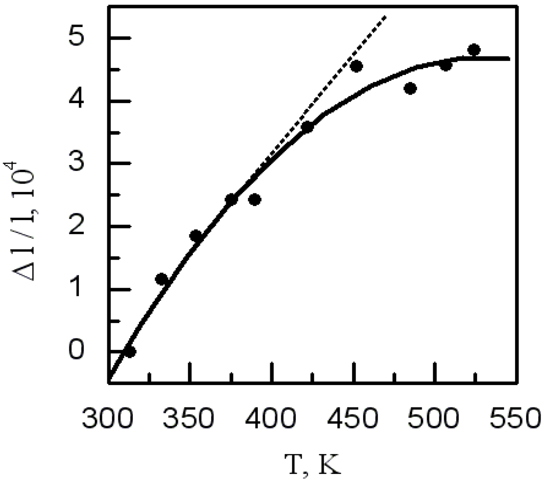


Fig. 2. The relative increase (Δl/l) length of the splice $NbSe_2$ of the temperature (T).

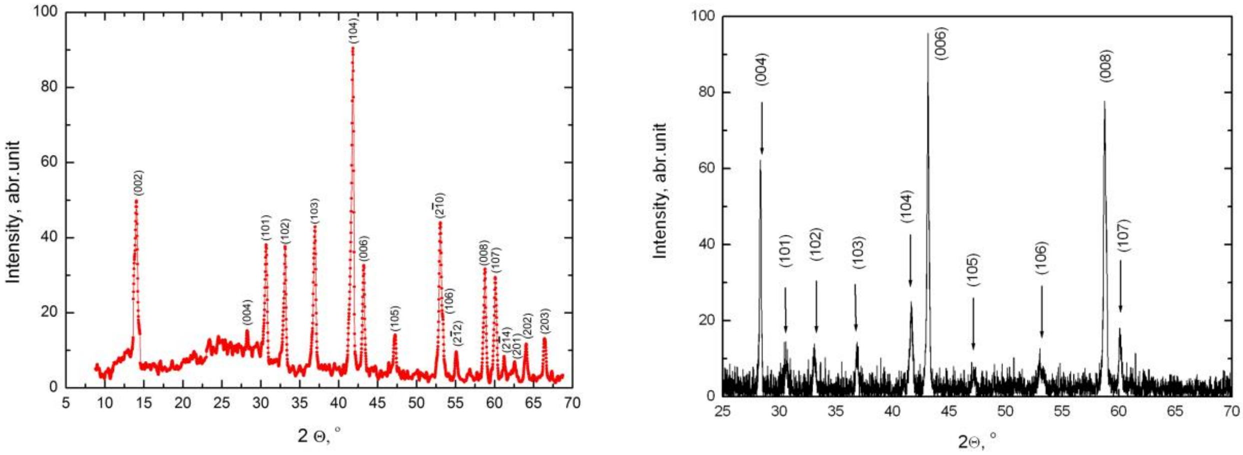
As the connection in $NbSe_2$ saturated and intercalation processes and oxidation processes in $NbSe_2$ begin only at T ≥ 620 K [18], we can assume that the observed changes in the electrical resistivity associated with the formation of its own equilibrium point defects (even when heated in air).

To investigate the formation of the lattice relaxation of point defects to splice $NbSe_2$ 6 mm in length was studied the thermal expansion parallel to the plane *(ab)* during the continuous heating from 300 to 550 K by the standard dilatometer Shevenara. Heating up to 550 K was carried out for 2.5 hours. The temperature dependence of the relative elongation Δl/l of the sample NbSe2 shown in Fig. 2. The figure shows that the temperature dependence of elongation deviates from linearity to lower values and saturates. The temperature of start deviations correlated with the data on the electrical resistivity.

The linear expansion coefficient $NbSe_2$ decreases by increasing the concentration the equilibrium point defects and its average value is 3·10–6 K–1, which is in agreement with the findings Gavarri J.R. and others[18]. The relative decrease of the length of the sample at the ambient temperature after high temperature exposure was Δl/l = – 0,4 %. The reducing Δl/l agrees well with the mechanism of vacancy selenium caused by discontinuity bonds Nb-Se and Se-Se, followed by degassing selenium atoms, i.e., is caused relaxation of the system due to the presence of selenium vacancies. In this sample was produced X-ray diffractometry analysis (Fig. 3).

It was found that after the heat treatment the sample is a single phase and has a hexagonal structure with lattice parameters a = 3,456 Å и c = 12,591 Å. Before heating the lattice parameters have values a = 3,44 Å иc = 12,54 Å. Thus, there is a slight increase in the lattice parameters of the formation of selenium vacancies. The relaxation of atoms surrounding the vacancy, should lead to a shift their in the direction of the vacancies, which is equivalent to the full stretch of the entire lattice in the case of an increase in the lattice parameters (unit cell volume). This process leads to a decrease of the crystal volume. According to [18] layered hexagonal phase is maintained with decreasing selenium up to 57% (at.). The period *a* varies weakly, and the period *c* assumes the values intermediates between 12.54 and 13.00 Å. Our values of the lattice periods suggest that in the research process after several exposures to high temperatures 490 K the samples of $NbSe_2$ retain a layered hexagonal structure and change their properties is caused by presence of selenium vacancies. According to the method described in [19], evaluated Se vacancy concentration, which for this sample was 2.6 % (at.).

For studying the process diffusion redistribution of vacancies selenium and care process selenium from the $NbSe_2$ measured the electrical resistivity of the samples along the layers during a series of isothermal exposures in the air environment as in the case of HTSC [17]. Fig. 4 shows typical results of measurements in one sample by consecutive isothermal exposures in the field of 353-453 K. The nonmonotonic character of the dependencies evidence of implementing complex (composite) processes that accompany the formation of vacancies selenium.



(a) (b)

Fig. 3. X-ray diffractometer spectrum of the splice $NbSe_2$ before (*a*) and after (*b*) the high temperature exposure.

The temporary cross section obtained isothermal dependence of the electrical resistivity, which in the rough assumption immutability of character defect, allowed us to estimate the dependence of vacancy formation energy of selenium on the exposure time [17]. Fig. 5 is a plot of the effective vacancy formation energy of selenium on the exposure time for the first series of isothermal exposures. The figure shows that the formation energy decreases with time and exposure energy value ranges 0,8 ÷ 0,3 eV.

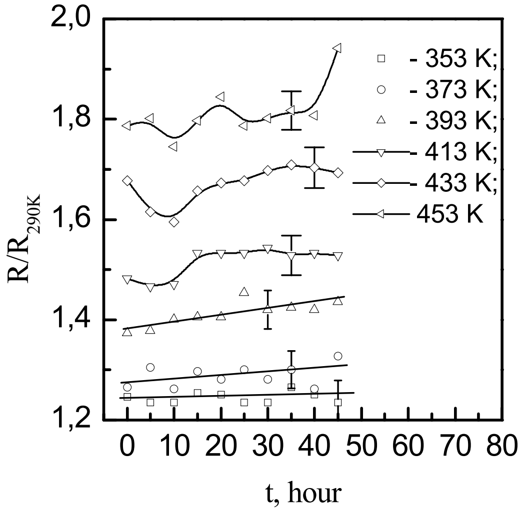


Fig. 4. Isothermal dependence of electrical resistivity $NbSe_2$.

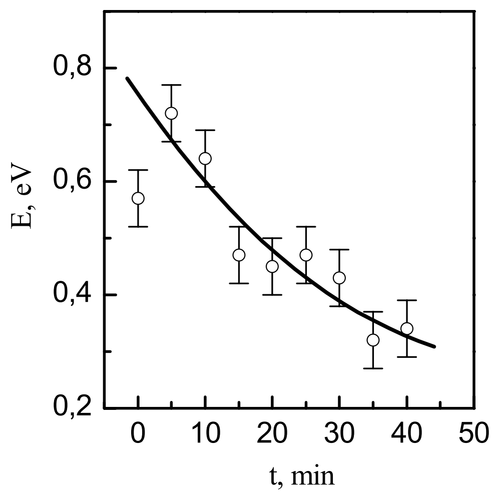


Fig. 5. The dependence of vacancy formation energy of selenium in $NbSe_2$ on the exposure time.

Decrease in the effective vacancy formation energy of selenium with increasing exposure time can be associated with the dependence of the energy of formation of the vacancy concentration.

The process of formation of a vacancy of selenium must be accompanied by an increase number of carriers in the conduction band due to the electrons, "liberated" from participating in covalent bonds Nb-Se. This injection of carriers in the conduction band should lead to a shift of the Fermi energy to higher values, i.e. to a change in the density of electronic states near the Fermi level, and as a consequence, to a change in the corresponding thermodynamic and kinetic properties. In addition, due to of this injection of carriers in the conduction band should be a redistribution the values of the binding energy due to changes in the electrostatic contribution. We can conclude that the experimentally observed decrease of the effective vacancy formation energy of selenium according to the time of exposure conditioned by weakening of bonds Nb-Se and strengthening links Nb-Nb as the concentration of selenium vacancies by increasing the carrier concentration in the layers of Nb.

Decrease in the effective energy, characterized by the formation of vacancies with increasing concentration can also be associated with the formation of vacancy clusters, or structural transformations, as in the area observed change in selenium content in the sample. According to the phase diagram in the sample can be some weakly different polymorphs [13].

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