The influence of point defects on the temperature dependence of quasi-two-dimensional 2H–$NbSe_2$ resistivity

A.A.Mamalui, T.N.Shelest, N.B.Fatyanova, V.A.Sirenko[*]

Kharkiv National Politechnical University,
21 Frunze St., 61002 Kharkiv, Ukraine
[*]B.Verkin Institute for Low Temperature Physics and Engineering,
National Academy of Sciences of Ukraine,
47 Lenin Ave., 61103 Kharkiv, Ukraine

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The processes of point defects forming in quasi-two-dimensional 2H–$NbSe_2$ crystals were studied experimentally by measuring the temperature-time resistivity dependencies in the temperature range 300–500 K. It is found out that the special property of (selenium vacancies) formation is the dependence of their formation energy on the time of isothermal exposure, i.e. concentration.

Экспериментально исследовались процессы образования точечных дефектов в квазидвумерных монокристаллах 2H–$NbSe_2$ посредством измерения температурно-временных зависимостей электросопротивления в области температур 300–550 К. Установлено, что характерной особенностью процесса образования точечных дефектов (вакансий селена) является зависимость их энергии образования от времени изотермической выдержки, т.е. от концентрации.

The quasi-low-dimensional systems (QLDS), among them the niobium chalcogenides $NbSe_2$ and $NbSe_3$, show a pronounced anisotropy of physical properties, for example, including those associated with the electrical transport. In particular, a Peierls type phase transition accompanied by a charge-density-wave caused by the electronic energetic spectrum anisotropy is observed in those materials [1, 2]. By today, a lot of experimental studies on the influence of substitutional (doping) impurities and high-energy particles irradiation on QLDS transport properties have been made [3–6]. At the same time, there are virtually no systematic studies of intrinsic point defects and their influence on QLDS physical characteristics, and the present works [7, 8] are fragmentary. At the same time, such studies are of much interest both from the viewpoint of the point defect influence on the transport properties of QLDS and also for investigation of the defects themselves.

Before, the influence of selenium vacancies on the temperature dependency of quasi-one-dimensional $NbSe_3$ single crystal resistivity has been studied [9]. $NbSe_3$ single crystals unit cell is of similar configuration to quasi-two-dimensional $NbSe_2$ single crystals unit cell [1, 2], but differ by the way of packing into, respectively, chains and layers. This work is aimed at the study of defect formation and evolution process and the influence thereof on some structure-sensitive 2H–$NbSe_2$ properties.

The quasi-two-dimensional niobium diselenide 2H–$NbSe_2$ monocrystals were obtained by chemical gas-transport reaction method. The electric contacts were made with conductive silver paste. Special attention was paid at the contacts stability. The resistivity was measured along the layers

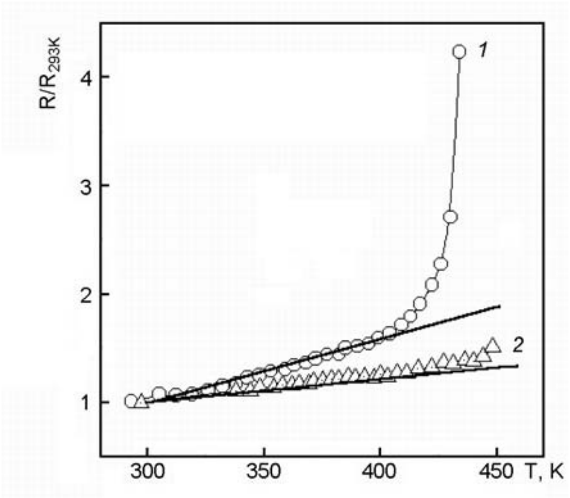

Fig. 1. Temperature dependences of the relative resistance for $NbSe_2$ heated in air (*1*) and in a medium containing Se vapor (*2*).

by four-probe method on direct current using compensation method.

The thermal expansion was studied on stationary Chevenar dilatometer in the direction of the (*ab*) plane. In this case, the sample under consideration was a set of $NbSe_2$ single crystals.

The study of temperature dependence of quasi-two-dimensional $NbSe_2$ single crystal resistivity at heating in air and in argon under excess pressure of selenium vapors in the temperature range 300–450 K, results in the picture presented in Fig. 1. The resistance deviation from linearity in the selenium vapor containing medium begins at temperatures about 20 K lower than in air and is considerably less. Similar results have been obtained for one-dimensional $NbSe_3$ single crystals [9]. In $NbSe_2$, the bonds are saturated, so the intercalation and oxidation processes start only at temperatures from 620 K and higher [10], so the resistivity changes observed under heating in air are connected with release of selenium atoms out of the sample. This is evidenced also by X-ray fluorescence analysis of the samples prior to and after thermocycling in air that has shown an excess selenium content in the initial samples (as compared to $NbSe_2$ stoichiometry) and a shortage thereof after thermocycling [11]. These data allow to suppose that the main contribution to the electrical resistance is due to the defect formation in the selenium sublattice.

The presence of an excess selenium amount in the initial samples, selenium existing possibly as subparticles (what is typical of sulfides and selenides) makes it possible to suppose that at the initial process stages, interstital selenium atoms may contribute considerably to the resistivity changes. As the $NbSe_2$ single crystals have a layered structure, the process of selenium release therefrom is facilitated due to high mobility of selenium atoms in the interlayer space. Getting into the interlayer regions, where Van der Waals forces dominate, selenium atoms can easily move along the planes, get onto the butt surface and leave the sample. Later, selenium may leave the lattice sites in a similar manner. Therefore, it is just the vacancies in the selenium sublattice that can to be considered as the most probable defects at the subsequent process stages. The resistivity may be changed also due to structure transforma-

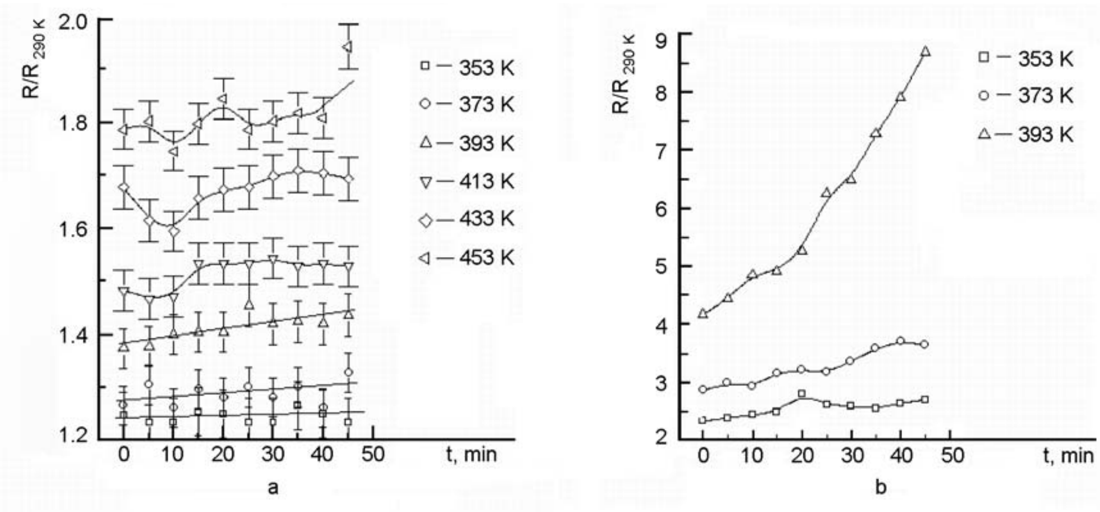

Fig. 2. The isothermal dependencies of $NbSe_2$ sample relative resistivities: the first series (a), the fourth one (b).

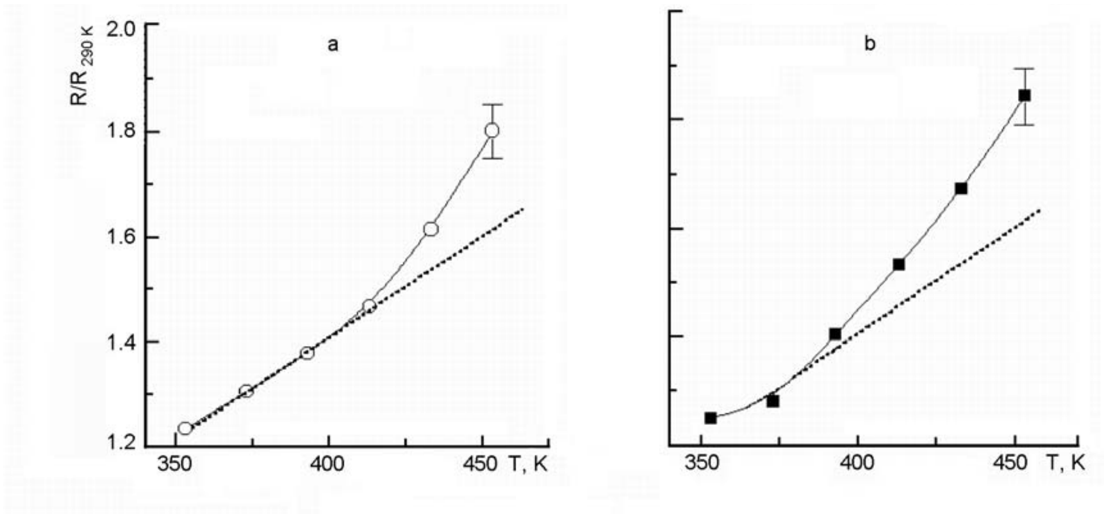

Fig. 3. The temperature dependence of relative resistivity at exposure time 5 min (a) and 20 min (b) for the first series.

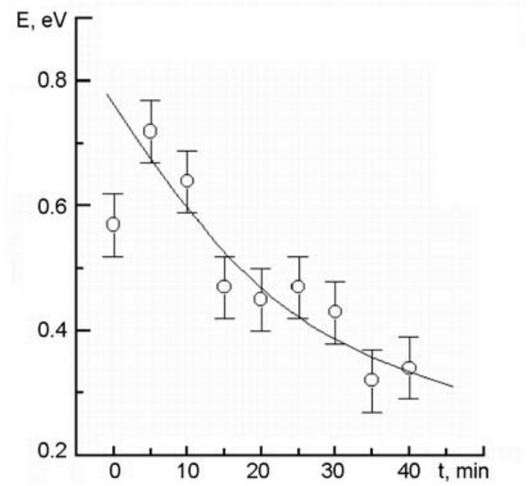

Fig. 4. Effective energy, characterizing selenium vacancies formation, dependence on exposure time at every temperature for the first isothermal series.

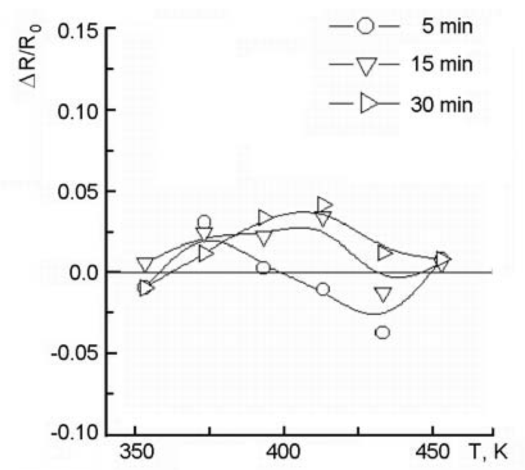

Fig. 5. The isothermal curves for the time-dependent part of $NbSe_2$ resistivity for the first series at exposure times 5, 15 and 30 min.

tions, since the phase diagram in the region of the observed selenium content range includes several polymorphs that are difficult to distinguish [10]. However, the temperatures of the corresponding transformations [7] exceed considerably those used in this work, so that these processes are unlikely.

At temperatures higher than 450 K in the $NbSe_2$ samples, the quantitative difference of resistivity value and activation energy of vacancies formation in different experimental series was observed, as well as in case of $NbSe_3$ [9]. This lets us suppose that the vacancies formation in these systems is a complicated process, and the effective activation energy can depend upon the concentration. In this connection, the $NbSe_2$ resistivity behavior was studied consistently at temperature and time parameters variation within wide ranges.

The sample under consideration underwent four identical series of isothermal exposures in air. This made it possible to study the effect of selenium loss from the sample accompanied by the diffusive redistribution of defects on the resistivity.

The resistivity measurements at a fixed given temperature (with the temperature step 20 K) in the interval 350–470 K lasted 45 min at every exposure temperature. The results obtained for several consecutive series of isothermal measurements of the relative electric resistance for a $NbSe_2$ sample are presented in Fig. 2. The experimental isotherms show that the defect formation process is a complex multistage one. It can be connected with selenium vacancies for-

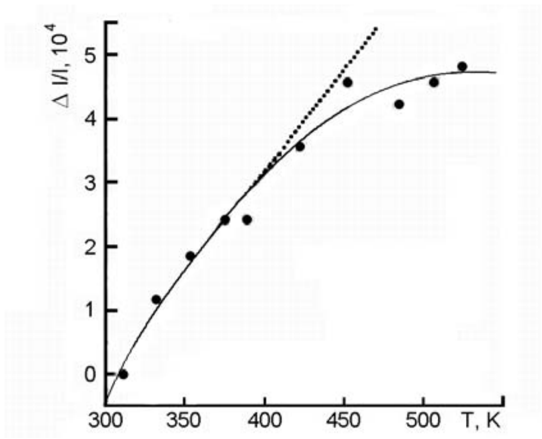

Fig. 6. Relative increase of the union $NbSe_2$ length $\Delta l/l$ depending on the temperature.

mation process caused by the bond breakdown and further migration of selenium atoms in the interlayer region followed by their loss. Along with this process, some other constituents are observed, perhaps connected with the coagulation of selenium vacancies.

In Fig. 3, the temperature dependences of relative resistance at 5 and 20 min exposures for the first isotherm series are presented (other series are similar in shape) that are isochronic sections of the isothermal dependences. These sections have made it possible to evaluate the effective energy of defect formation as a function of the exposure time. That dependence is plotted in Fig. 4. The energy value changes in the range 0.8 to 0.3 eV. The reducing of formation active energy with the exposure time is likely to be connected with the selenium vacancies formation energy dependence on their concentration. The energy value is low in the beginning because in the initial state $NbSe_2$ contained excess selenium.

The obtained vacancies formation energy dependence on the exposure time (Fig. 4) lets one evaluate the specific exposure time, necessary for high temperature studies. The time is obvious to be 15–20 min.

According to the isothermal measuring results, the temperature dependences of time-dependent (caused by diffusion processes in the defect subsystem) resistivity part for the sample under consideration are mapped. The value $\Delta R/R_0 = (R_t - R_0)/R_0$, (where R_t is the resistivity value of the sample at the time moment t; R_0 is the resistivity value of the sample at the time moment $t = 0$) is the time-dependent part of sample full resistivity. The time-dependent resistivity part reflects the diffusion processes, tending to the establishing the system equilibrium.

In Fig. 5 the dependences of $\Delta R/R_0$ on T, corresponding to the isochronal sections of the first isotherms series for exposures time $t = 5$, 15 and 30 min, are shown. All the dependences are of non-linear character and have singularities in the form of minima and maxima. These processes reflect the combined character of the vacancies formation processes and selenium atoms loss from the sample.

Dilatometric studies have been made in the temperature range 300–600 K. A 6 mm long set of $NbSe_2$ single crystals was used as the sample. The heating from 300 to 600 K lasted 2,5 h. Fig. 6 shows clearly that the temperature dependence of the elongation deviates from the linear towards smaller values $\Delta l/l$. The temperature of the deviation start correlates with the data on resistivity. The linear expansion factor of $NbSe_2$ decreases with the increase of vacancies concentration, and its average value is $3\cdot10^{-6}$ K^{-1}, which is in accord with the data from the paper [12]. The relative decrease of the sample length at room temperature after high-temperature exposure was $\Delta l/l = -0.4$ %. The decrease of $\Delta l/l$ is in good accord with the vacancies formation caused by the break of the Nb–Se and Se–Se connections followed by the selenium atoms loss, and so is caused by system relaxation. The Fig. 6 data with respect to a considerable concentration of vacancies ($C_v \geq 1$ at. %) show that the relaxation component $\Delta l/l$ is much smaller at selenium vacancies formation, than in case of 3D sysems.

In conclusion we can say that complicated, nonmonotonic behavior of resistivity isothermal dependencies (Fig. 2) reflects the complexity of diffusion processes, accompanying selenium vacancies formation, in particular, possible formation of vacancy clusters, as well as the complexity of vacancies influence on the properties of the quasi-two-dimensional systems under consideration.

The vacancies, which are additional centers of dispersion, formation should lead to the increase of resistance. Besides, the process of selenium vacancies formation appears to be accompanied with the increase of carriers in the conduction band due to the electrons, "free" from the connections Nb–Se. Injecting the carriers into the conduction band should lead to the displacement of Fermi energy to the greater values, i.e. to the density change of the electronic states, and so, to the change of corresponding thermodynamic and kinetic properties. Due to such injection, the energy of connections Nb–Nb and Nb–Se appears to be redistributed. One can suppose that the experimentally observed decrease of selenium vacancies formation active energy with the exposure time is caused by the weakening of Nb–Se connections in the course of selenium vacancies concentration growth and the strengthening of Nb–Nb bonds due to the increase of carriers concentration in Nb layers, which agrees well with the data obtained in [13]. This physical mechanism is of much interest and needs additional theoretic and experimental research for the final understanding.

The other mechanism, also able to decrease the active energy characterizing the vacancies formation with the growth of their concentration, can be the formation of vacancies clusters. But to establish the fact of clusters formation, the study of vacancies spatial distribution in quasi-two-dimensional objects is necessary.

References

1. Electronic Properties of Inorganic Quasi-One-Dimensional Materials, Monceau P. (ed.), part I. D.Reidel Publishing Company Dordreht, Boston, Lancaster (1985).
2. J.A.Wilson, A.D.Yoffe, *Adv.Phys.*, **18**, 193 (1969).
3. N.D.Ong, J.W.Brill, J.C.Eckert et al., *Phys. Rev.Lett.*, **42**, 811 (1979).
4. J.W.Brill, N.D.Ong, J.C.Eckert et al., *Phys. Rev.*, **B23**, 1517 (1981).
5. P.Monceau, J.Richard, R.Lagnier, *J.Phys. C.:Solid State Phys.*, **14**, 2995 (1981).
6. J.Fuller, *Phys.Rev.*, **B23**, 6259 (1981).
7. V.L.Kalikhman, A.G.Duksina, *Izv.AN SSSR Ser. Neorg.Mater.*, **7**, 1127 (1971).
8. K.Svoboda, A.Zettl, M.S.Sherwin, *Solid State Coommun.*, **70**, 859 (1989).
9. A.A.Mamalui, T.N.Shelest, H.B.Chashka, *Fiz.Nizk.Temper.*, **26**, 176 (2000).
10. V.A.Obolon'chik, Selenides, Metallurgia, Moscow (1972) [in Russian].
11. T.N.Shelest, A.A.Mamalui, H.B.Chashka, L.P.Fomina, in: Abstr. of the 18th Gen. Conf. of the Condensed Matter Division, Montreux, Switzerland (2000), p.43.
12. J.R.Gavarri, R.Mokrani, G.Vacquier, C.Boulesteix, *Phys.Stat.Sol.(a)*, **109**, 455 (1988).
13. O.Yu.Khyzhun, *Dop. NAN Ukraine*, No.8, 86 (2001).

Вплив точкових дефектів на температурну залежність електроопору квазідвовимірного 2H-$NbSe_2$

А.О. Мамалуй, Т.М. Шелест, Н.Б. Фат'янова, В.А. Сіренко

Процеси утворення точкових дефектів у квазідвовимірних монокристалах 2H–$NbSe_2$ досліджувалися експериментально вимірюванням температурно-часових залежностей електроопору в області температур 300–550 К. Встановлено, що характерною особливістю процесу утворення точкових дефектів (вакансій селену) є залежність їхньої енергії утворення від часу ізотермічної витримки, тобто концентрації.