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# Effect of hydrogen on the electrical resistance of NbSe<sub>2</sub> in a wide temperature range

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## ABSTRACT

The electrical resistivity of niobium diselenide (NbSe<sub>2</sub>) with hydrogen was investigated in the temperature range  $T_c - 300$  K. It was determined that hydrogen inhibits the formation of a charge density wave. It was shown that hydride phase with niobium is formed due to hydrogen in NbSe<sub>2</sub> layers at low temperatures, which decomposes with increasing temperature to form a solid solution. The temperature dependence of the resistivity is approximated by the Bloch–Grüneisen function. The approximation parameters vary depending on the amount of dissolved hydrogen.

## 1 Introduction

Anisotropic quasi-two-dimensional conducting compounds represent a large class of solids with unique physical properties [1–3]. These compounds include transition metal dichalcogenides (TMDs) [4, 5] and cuprate HTS (high-temperature superconductors) [6, 7], the best known representatives of which are layered single crystals of ReBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  (Re = Y or other rare earth ion) [8–10] and NbSe<sub>2</sub> [11, 12]. Interestingly, in NbSe<sub>2</sub> as the temperature drops below a certain critical value ( $T \sim 30$  K) [13], a periodic inhomogeneous distribution of the electron gas and lattice ions is spontaneously formed in the crystal. The displacement of lattice atoms in the superstructure leads to the appearance of a charge density wave (CDW) [14].

Layered crystals are in the spotlight mainly after the discovery of high-temperature superconductivity in 1986 [6]. In nonstoichiometric oxides with pronounced anisotropy of physical characteristics [15, 16], the main structural unit is Cu–O layers [17, 18], separated by atoms of rare earth and other elements, depending on the specific composition. Numerous studies point to possible parallels in the description of the state with CDW in the TMD and the pseudogap state in the HTS [12–14]. Revealing similar physical characteristics and distinctive features between low-temperature and high-temperature superconductors, associated with the crystal structure and the conduction mechanism, is an important issue in solid state physics. At the same time, in the absence of a microscopic theory of high-temperature superconductivity [19], experimental

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methods are of particular importance, allowing one to reveal those structural parameters of superconductors that most significantly affect their critical characteristics (critical temperature and field), since this allows the determination of possible ways to increase their electric transport characteristics (current density).

The intercalation of compounds of various atoms and molecules into the interlayer space opens up broad prospects for a designed tuning in their properties. Hydrogen as an impurity is of particular interest because it has a minimum mass and maximum mobility [20]. In layered compounds, hydrogen can be in two positions in the interlayer space and in the layer [21, 22]. The high mobility of hydrogen makes it possible for phase transitions to occur in metal–hydrogen systems at relatively low temperatures.

As a result of intercalation of the layered structure, regardless of the type of intercalant and its position in the lattice, a change in the lattice parameters is always observed [12], as well as a change in the carrier concentration due to charge transfer from the intercalant to the matrix and vice versa. Due to its small size and the simplicity of its electronic structure, hydrogen does not introduce significant distortions at low concentrations; therefore, all changes to lattice parameters can be associated with the concentration of carriers. Therefore, from the point of view of separation of the listed effects, intercalation with hydrogen seems to be very informative, since it makes it possible to neglect the change in the lattice parameter and the defectiveness of the crystal upon the introduction of impurities.

Hydride-forming layered systems are of interest from the point of view of their hydrogen content (either as a fuel or as a catalyst), and at the same time, NbSe<sub>2</sub> is a representative of a wide class of superconductors, the properties of which can be controlled by introducing hydrogen. The study of these processes is possible by analyzing the temperature dependences of the system resistance depending on the impurity concentration. This work is aimed at studying the effect of hydrogen on the physical properties of NbSe<sub>2</sub>, in particular, on the mechanisms of electron scattering in NbSe<sub>2</sub> in a wide temperature range and on the CDW transition.

## 2 Experiment

Niobium diselenide single crystals were grown by the method of chemical gas transport reaction. The technology is described in detail in previous studies [22]. As a result, a finely dispersed gray-green powder was obtained, the X-ray analysis of which showed that it is a 2H-modification of niobium diselenide with  $a \sim 3.45 \text{ \AA}$  and  $c = 12.54 \text{ \AA}$ , which agrees with the literature data [23]. Powdered NbSe<sub>2</sub> was placed in a quartz ampoule into which iodine was introduced. The ampoule was pumped out and sealed and then placed in a three-zone oven with a thermal control system. The growth process lasted for 240 hours, followed by slow cooling to room temperature for 24 hours. As a result, crystals grew in the form of thin plates up to  $10 \times 7 \times 0.2 \text{ mm}^3$  in size. The samples were saturated with hydrogen from the gas phase using an installation that made it possible to implement cyclic hydrogen saturation in the temperature range of  $20 < T < 500 \text{ }^\circ\text{C}$  and pressure  $10^5 < P < 10^7 \text{ Pa}$ . A sample with typical dimensions in the plane of  $6 \times 1 \text{ mm}^2$  was cut from the grown single crystals and, after saturation with hydrogen, was placed in a measuring cell, which makes it possible to measure electrical resistance and magnetoresistance in a wide temperature range. Resistance measurements were made in *ab*-plane at direct current using a standard four-probe method with a voltage sensitivity of  $2 \times 10^{-7} \text{ V}$ .

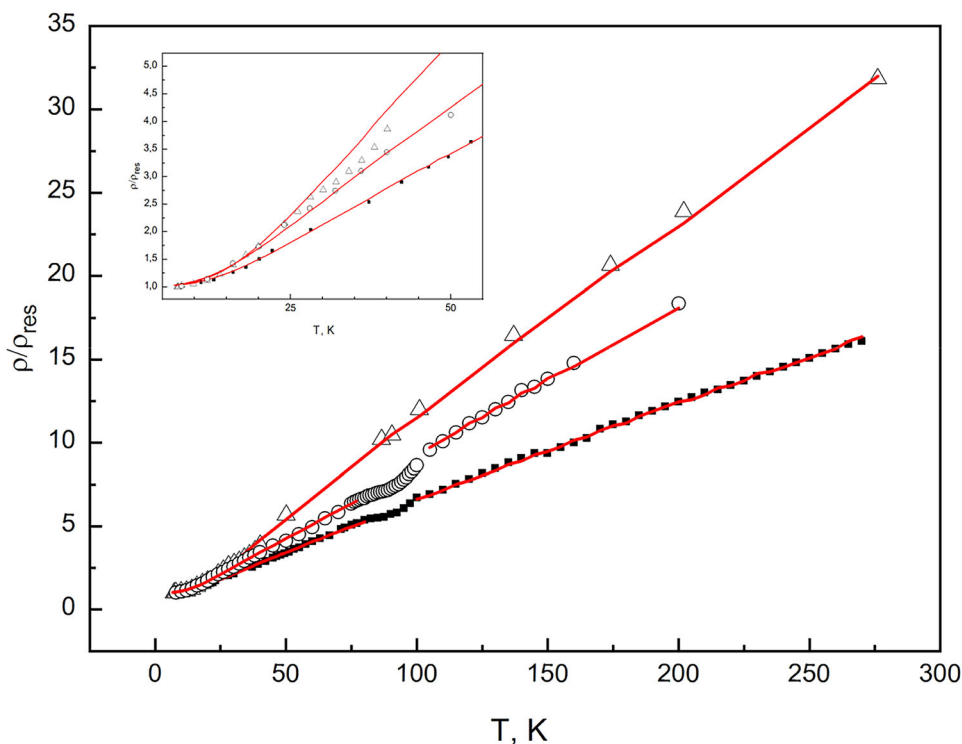
## 3 Results and discussion

Figure 1 shows the experimentally obtained temperature dependences of the electrical resistivity (normalized to the value of the residual resistance) of an NbSe<sub>2</sub> sample with different hydrogen contents. The following features are noteworthy:

- 1) The  $\rho(T)$  curve for the initial sample lies above the analogous curves obtained after the introduction of hydrogen, that is, the introduction of hydrogen decreases the resistance, probably due to the transfer of electrons from hydrogen to the conduction band. Note that the  $\rho(T)$  curves are not parallel, that is, the scattering of electrons by phonons and impurities (hydrogen) is not independent and the Matthiessen rule is not satisfied.

- 2) As the hydrogen concentration increases (notably the hydrogen concentration is proportional to

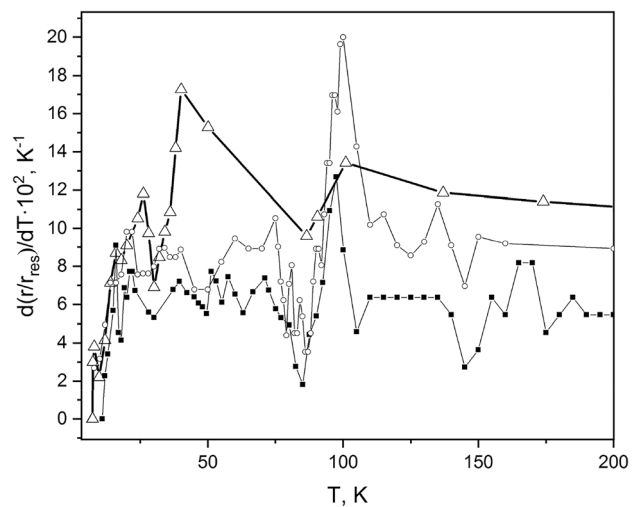
**Fig. 1** Temperature dependences of the electrical resistance of NbSe<sub>2</sub> with hydrogen:  $\Delta$ , initial state;  $\blacksquare$ , after saturation at a pressure of  $P = 2.3$  atm. (hydrogen content 0.13 at.%);  $\circ$ , after saturation at a pressure  $P = 10$  atm. (hydrogen content 0.66 at.%). Points are an experiment; solid lines—calculation according to (1). The inset shows an enlarged area of  $T_c^{\text{onset}} \sim 50$  K.  $\rho_{\text{res}}$ —residual resistance



the saturation pressure), the resistance changes non-monotonically—curve  $\rho(T)$  for 10 atm. lies between the curve for the pure sample and the curve for 2.3 atm. This is probably related to the two positions that are available for hydrogen (within the layer and in the interlayer space), and with an increase in the hydrogen concentration, one of these positions is filled first.

3) There are no signs of CDW formation in the hydrogenated state, which manifested themselves as a peak in the derivative in the region of 30 K on a pure sample, which is consistent with the literature data [22]. In this case, the presence of hydrogen leads to the appearance of a feature in the form of a blurred step near 100 K. This feature is especially clearly visible on the derivatives,  $d\rho(T)/dT$ , which are peaks in the curves in Fig. 2, and an increased concentration of hydrogen provides a higher peak temperature. This behavior of  $\rho(T)$  is due to the decomposition of the low-temperature hydride phase upon reaching the temperature with the formation of solid hydrogen in NbSe<sub>2</sub> [24].

Since NbSe<sub>2</sub> has a layered hexagonal structure with niobium atoms at the centers of trigonal selenium prisms [25], and Nb is a hydride-forming element, the hydride phase of which is formed inside the layers. The resistivity was measured along the *ab*-



**Fig. 2** The temperature dependence of the derivative of the reduced resistance  $d(\rho/\rho_{\text{res}})/dT$  for NbSe<sub>2</sub> with hydrogen. The designations are the same as in Fig. 1

plane; therefore, it is mostly affected by hydrogen inside the layer and having a concentration less than the total saturation concentration (0.09 and 0.23 at. % for 2.3 and 10 atm., respectively).

In metals,  $\rho(T)$  is due to the scattering of electrons by phonons and impurities and is usually described by the Bloch–Grüneisen function (see, for example, [26]):

$$\rho(T) = \rho_0 + C_3 \left(\frac{T}{\theta}\right)^3 J_3\left(\frac{\theta}{T}\right) + C_5 \left(\frac{T}{\theta}\right)^5 J_5\left(\frac{\theta}{T}\right), \quad (1)$$

where

$$C_3 = \frac{3h^3 \omega_d m_d P_{sd}}{8\pi(2m_s)^{1/2} e^2 E_F}$$

and

$$C_5 = \frac{3h^3 m_s^{1/2} P_{ss}}{8\pi 2^{1/2} e^2 E_F 2^{1/3} n^{2/3}}.$$

Here  $J_3(\frac{\theta}{T})$  and  $J_5(\frac{\theta}{T})$  are the Debye integrals ( $J_n(x) = \int_0^x e^x (e^z - 1)^{-2} z^n dz$ ),  $P$  is the transition matrix element,  $m$  is the effective mass,  $\omega$  is the degree of degeneracy of electronic states, and  $n$  is the concentration of electrons. Coefficient  $C_3$  describes the interband scattering of  $s$ -electrons into the  $d$ -band and coefficient  $C_5$  describes scattering inside the  $s$ -band.  $\rho_0$  characterizes the scattering of electrons by impurities.

We also approximated the  $\rho(T)$  dependence by relation (1); however, due to the presence of a singularity and a conducting transition at  $T_c \approx 7$  K, the resistance of the sample with hydrogen was approximated separately for the intervals  $T_c^{\text{onset}} - 80$  K and 100–300 K. The resistance of the initial sample was approximated in the interval  $T_c^{\text{onset}} - 300$  K.

The results of this approximation are shown in Fig. 1 with solid lines. The approximation parameters, determined by the least squares method and providing an accuracy of at least 5%, are given in Table 1.

Since the resistance was measured in the plane of the layers, all the parameters of the approximation characterize the scattering of electrons in the layers.

The Debye temperatures given in Table 1 are consistent with the results obtained for the low-temperature heat capacity of the 1-2-3 HTSC system [27]. This suggests that in the studied single crystal NbSe<sub>2</sub>,  $\rho_{ab}(T)$  is mainly determined by the scattering of electrons by transverse vibrations propagating along the  $c$  axis. In the region of existence of a hydride, the Debye temperature decreases with an increase in the hydrogen content. This means that the presence of hydride leads to an increase in the interatomic distance in the layer. On the contrary, in the region of a solid solution, the Debye temperature slightly increases with an increase in the hydrogen content, which may be associated with a change in the elastic constants. Some decrease in  $\rho_0$  with increasing

**Table 1** Influence of hydrogen on the parameters of approximations of the electrical resistance of NbSe<sub>2</sub>

	NbSe <sub>2</sub> T <sub>c</sub> <sup>onset</sup> – 300 K	NbSe <sub>2</sub> + H T <sub>c</sub> <sup>onset</sup> – 80 K	
		P = 2.3 atm	P = 10 atm
θ, K	110	100	95
ρ <sub>0</sub> , 10 <sup>-4</sup> , Ohm-cm	1.7	0.9	0.9
C <sub>3</sub> , 10 <sup>-4</sup> , Ohm-cm	22.0	8.4	8.9
C <sub>5</sub> , 10 <sup>-4</sup> , Ohm-cm	40.0	4.0	9.4
C <sub>3</sub> /C <sub>5</sub> ≈	0.5	2.0	1.0
Error, %	3.9	1.6	2.0
		100 – 300 K	
θ, K	–	90	94
ρ <sub>0</sub> , 10 <sup>-4</sup> , Ohm-cm	–	1.0	0.9
C <sub>3</sub> , 10 <sup>-4</sup> , Ohm-cm	–	8.8	10
C <sub>5</sub> , 10 <sup>-4</sup> , Ohm-cm	–	3.6	10
C <sub>3</sub> /C <sub>5</sub> ≈	–	2.5	1.0
Error, %	–	0.7	0.7

hydrogen content in the two-phase region is probably due to the transfer of “hydrogen” electrons to the conduction band. In the region of a solid solution, this effect can be compensated by an increase in scattering.

The parameters  $C_5$  and  $C_3$ , which characterize the scattering of electrons by phonons, increase with an increase in the hydrogen content, and this growth is more pronounced in the two-phase region. The latter may indicate that the electronic structure of the initial sample is closer to the electronic structure of the solid solution than to the electronic structure of the hydride. Specific mechanisms of quasiparticle scattering can play a certain role in this case [28–32].

### 4 Conclusion

From the above, the following conclusions can be drawn. Hydrogen in NbSe<sub>2</sub> is found both in the interlayer space and in the layers. The hydrogen in the layers gives up some of its electrons to the conduction band of NbSe<sub>2</sub>, which leads to a decrease in resistance. This effect dominates over impurity scattering. Hydrogen suppresses the formation of a charge density wave, the presence of which is evident from the peak of the derivative of the resistivity pure NbSe<sub>2</sub> in the region of 30 K [22]. At low temperatures, the hydrogen in the layers forms a hydride phase with niobium, which decomposes with an



increase in temperature to form a solid solution. At low temperatures, that is, in the region of existence of a hydride, the Debye temperature and electronic characteristics of the NbSe<sub>2</sub>-H system are more sensitive to the hydrogen content than in the region of a solid solution.

## Author contributions

V.I.B performed the experiments. All the authors analyzed and discussed the results and contributed to the writing of the paper.

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## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

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