SUPERCONDUCTIVITY OF LAYERED STRUCTURES. INVESTIGATION OF SOLID SOLUTIONS IN THE NbSe₂–NbTe₂ SYSTEM

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An investigation was made of the crystal structure and superconducting properties of layered single crystals of solid solutions in the $NbSe_2$–$NbTe_2$ system. The results obtained were used to draw the conclusion that the superconducting properties of layered transition-metal dichalcogenides are governed not only by the state of the niobium planes but also by the degree of correlation between them.

THE two-layer modification of niobium diselenide $NbSe_2$, which has the highest superconducting transition temperature ($T_c = 7°K$) among transition-metal dichalcogenides, was investigated earlier[1, 2] and it was found that there was a definite correlation between the superconductivity and the crystal chemistry of this compound. It was shown that the superconductivity of $NbSe_2$ is governed primarily by the state of the niobium sublattice and, above all, by the degree of perfection of the niobium planes.

It is known that niobium ditelluride $NbTe_2$, which also belongs to transition-metal dichalcogenides and crystallizes in a layered structure, has a transition temperature $T_c = 0.74°K$,[3] i.e., a temperature which is almost an order of magnitude lower than that of $NbSe_2$. Bearing in mind that the superconductivity of both compounds is due to the Nb atoms and that the relative concentration of these atoms is the same in both compounds, we may conclude that the cause of this large difference between the transition temperatures is the difference between the structure of the two crystal lattices.

It is known that the metal atoms in the layered structures of transition-metal dichalcogenides may be surrounded by the metalloid atoms in two ways: the configuration may be trigonal-prismatic or octahedral.[4] $NbSe_2$ belongs to compounds with the trigonal-prismatic configuration of the metalloid atoms. The two-layer modification of this compound has a packing in which Nb atoms in neighboring layers are located one above another; they are separated by distances of 6.28 Å, forming chains perpendicular to the basal plane (packing of the aa type), as shown in Fig. 1a.[5] In the $NbTe_2$ structure, the atoms of Te surrounding the niobium atoms have the octahedral configuration and the Nb sublattice consists of closely packed planes whose relative positions obey the abc law. Thus, in contrast to the $NbSe_2$ lattice, the interacting Nb atoms in niobium tel-

luride are separated by three layers along the c axis, i.e., by distances of 19.87 Å (Fig. 1).

A gradual replacement of selenium with tellurium in the $Nb(Se_{1-x}Te_x)_2$ solid-solution system should result in a distortion of the crystal lattice of niobium diselenide and, finally, it should produce a change in the structure type from $NbSe_2$ to $NbTe_2$. Therefore, the purpose of our investigation was to determine the dynamics of changes in the crystal lattices and critical temperatures of solid solutions in this system in order to find the correlation between structural and superconducting properties of layered compounds.

INVESTIGATION METHOD

All the investigations were carried out on single crystals of $Nb(Se_{1-x}Te_x)_2$ solid solutions ranging in concentration from pure $SbSe_2$ to pure $NbTe_2$. These single crystals were grown by the gas-transport reaction method.[6] The crystal structure was investigated by applying the standard techniques to obtain the rocking diffraction patterns of single crystals and the patterns of powders prepared by grinding such crystals. The critical temperature of the transition to the superconducting state was measured by an induction method: we recorded the unbalance of a system due to a change in the inductance of a coil resulting from the transition to the superconducting state of a sample enclosed by this coil. The lowest temperature which could be measured by this method was 1.8°K.

The chemical composition of the investigated single crystals was determined from the relative concentrations of Se and Te. The similarity of the chemical properties of Se and Te made it practically impossible to identify chemically small amounts of these elements with a sufficient degree of accuracy. Therefore, the compositions of the investigated single crystals were determined by the method of x-ray fluorescence analysis, based on a calculation of the ratio of the intensities of the lines representing Se and Te and a comparison of the results obtained with the corresponding data for standard samples consisting of $NbSe_2$ and $NbTe_2$ mixtures of known proportions.

EXPERIMENTAL RESULTS

It has been reported earlier that the stoichiometric $NbSe_2$ prepared by us consists of the two-layer modifi-
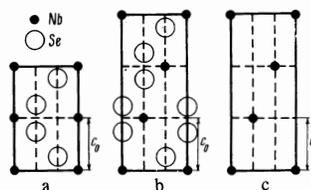

FIG. 1. Distribution of atoms in the (11$\bar{2}$0) plane of the two-layer (a) and three-layer (b) modifications of niobium diselenide, and the distribution of Nb atoms in niobium ditelluride (c).

cation, belongs to the structure class $P6_3/mmc$, and has the following unit-cell parameters: a = 3.46 Å, c = 12.563 Å;[1] NbTe₂ has the three-layer structure of the C3m class and the following unit-cell parameters: a = 10.99 Å, c = 19.87 Å.

Our investigations of the chemical composition and the structure of the $Nb(Se_{1-x}Te_x)_2$ solid-solution system for x = 0−1 demonstrated that:

1) solid solutions based on the NbSe₂ lattice are formed in the range of concentrations from NbSe₂ to $Nb(Se_{0.82}Te_{0.18})_2$, which we shall call region I;

2) solid solutions based on the NbTe₂ lattice are formed in the range of concentrations from $Nb(Se_{0.69}Te_{0.31})_2$ to NbTe₂, which we shall call region II;

3) single crystals cannot be obtained between the compositions $Nb(Se_{0.82}Te_{0.18})$ and $Nb(Se_{0.69}Te_{0.31})_2$ because of the multiphase nature of the system.

Figure 2 shows the dependences, on the composition, of the shortest distances between the Nb atoms in their planes (a_0) and between the Nb planes (c_0) in regions I and II (for the NbSe₂ structure we have a_0 = a and c_0 = c/2; for the NbTe₂ structure we have a_0 = a/3 and c_0 = c/3; see Figs. 1a and 1c). The curves in Fig. 2 indicate that the process of solution of Te atoms in the NbSe₂ lattice (region I) results in the elongation of the unit cell along the c axis. The distribution of the Nb atoms in their planes is initially practically unaffected (the parameter a remains constant) and only in the final stage, just before the destruction of the diselenide lattice, does the parameter a increase strongly. The process of solution of Se atoms in the NbTe₂ lattice (region II) results in a monotonic fall in the parameters c and a; at the limit of existence of this structure, the parameter a reaches a value corresponding to the lattice of stoichiometric NbSe₂ (3.447 Å).

Figure 3 shows the dependence of the critical temperatures on the $Nb(Se_{1-x}Te_x)_2$ solid solutions on their concentrations in regions I and II. It is evident from this figure that the temperature T_C of the NbSe₂ lattice (region I) begins to fall appreciably at tellurium concentrations as low as x ≈ 1%. The rate of fall of T_C is greatest at low concentrations of Te (x < 6%) and this rate decreases appreciably at higher tellurium concentrations. It is worth noting the small maximum (T_C = 7.18°K) at which the critical temperature exceeds the

FIG. 3. Dependence, on the tellurium concentration, of the critical temperature of the transition to the superconducting state T_C for regions I and II corresponding to the NbSe₂ and NbTe₂ lattices, respectively. The value of T_C for pure NbTe₂ was taken from [3].

value of T_C of the stoichiometric NbSe₂; this maximum occurs at a low concentration of Te (x ≈ 0.3%).

The critical temperature T_C of the samples with the NbTe₂ lattice (region II) increases monotonically with increasing concentration of Se atoms.

DISCUSSION OF RESULTS

An analysis of the experimental curves discussed in the preceding section shows a strong correlation between the superconductivity and structural properties in regions I and II.

Within the range of existence of the NbSe₂ lattice (region I), the dependence of T_C and of the lattice parameter c on the composition are well correlated: the fall of T_C and the rise of the parameter c begin at the same concentration of tellurium x ≳ 1% (Figs. 2 and 3). This demonstrates that the deterioration of the superconductivity in the $Nb(Se_{1-x}Te_x)_2$ solid-solution system, observed within the range of existence of the NbSe₂ lattice, is due to the "loosening" of the lattice along the c axis. Obviously, this is the consequence of the weakening of the correlation between the niobium planes because these planes govern the superconducting parameters of the layered dichalcogenides.[1,2] The dependence of the critical temperature on the shortest distance between the niobium planes (c_0) within the range of the existence of the NbSe₂ lattice (Fig. 4) confirms this conclusion.

The rise of T_C with increasing concentration of the Se atoms dissolved in the NbTe₂ lattice (region II) is also accompanied by structural changes: the parameters a and c decrease (Figs. 2 and 3). Consequently, this change in T_C can be explained in two ways: 1) by the reduction in the distance between the Nb atoms in their own planes; or 2) by reduction in the distance between the niobium planes, i.e., by an increase in the correlation between atoms in the Nb sublattices. However, since the shortest distance between the niobium
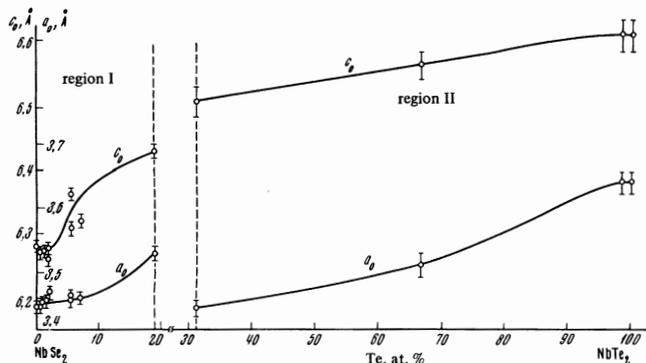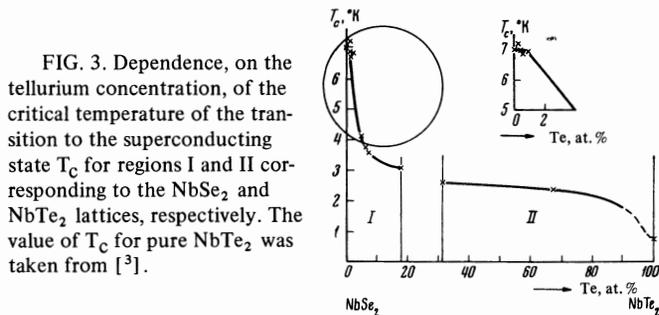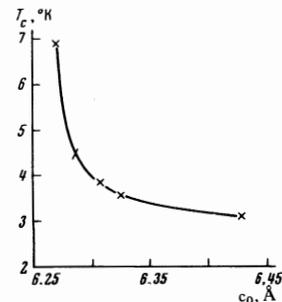

FIG. 2. Dependences, on the tellurium concentration, of the shortest distances between Nb atoms in their own planes (a_0) and between the Nb planes (c_0) for regions I and II corresponding to the NbSe₂ and NbTe₂ lattices, respectively.

FIG. 4. Dependence of the critical temperature T_C on the shortest distance c_0 between the niobium planes in the NbSe₂ lattice.

planes (c_0) in the $NbTe_2$ lattice is considerably greater than that in the $NbSe_2$ lattice (Fig. 2) and the distance between the Nb atoms in the chains perpendicular to the basal plane is of the order of 20 Å, the change in c_0 does not affect T_C as strongly as it does in the $NbSe_2$ lattice.

The small rise of the critical temperature at a Te concentration $x \approx 0.3\%$ (where this temperature increases above the value $T_C = 7°K$ for the stoichiometric $NbSe_2$) can be explained as follows. At low concentrations of tellurium, the replacement of selenium does not distort the crystal lattice of $NbSe_2$ but it should weaken the covalent component (and strengthen the metallic component) of the chemical binding within a layer. Consequently, the density of states at the Fermi surface, and therefore the value of T_C, should increase slightly.

It follows from our analysis that the superconducting properties of layered transition-metal dichalcogenides are governed not only by the state of the niobium planes but also by the degree of correlation between them. This is confirmed by the absence of superconductivity in the three-layer modification of $NbSe_2$,[7] which differs from the superconducting two-layer phase only by the absence of a direct interaction between the niobium planes because of their screening by selenium layers (Fig. 1b). It follows that a single layer of niobium atoms does not exhibit superconducting properties.

The results obtained can be regarded as an experimental confirmation of the theoretical calculations of Ferrell,[8] who has questioned the possibility of the existence of superconductivity in purely two-dimensional systems.

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