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## *THE ANISOTROPY OF THE SUPERCONDUCTING PROPERTIES OF NIOBIUM DISELENIDE AND THE RELATIONSHIP BETWEEN THE PROPERTIES AND THE CRYSTAL STRUCTURE AND COMPOSITION*

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The effect of the anisotropy of the structure of a layer superconductor (niobium diselenide) on its superconducting properties is investigated. We have investigated in part I the magnetic properties and in part II the critical currents of niobium diselenide single crystals in connection with the structure of the crystal lattice and its controlled disordering due to its deviation from stoichiometry. Strong anisotropy of the magnetic properties as well as of the critical current depending on the direction of the magnetic field relative to the planes of the crystal is observed and ascribed to the anisotropy of the crystal structure of the compound. It is concluded that there exists in the given compound a most favorable direction for superconductivity which passes through the niobium planes. From the investigation of the effect of the controlled disordering of the crystal lattice on the magnetization and the behavior of the critical current it can be concluded that the state of the niobium sublattice, i.e., the degree of perfection of the niobium planes, has a decisive influence on the superconducting properties of niobium diselenide.

### I. THE MAGNETIC PROPERTIES OF NIOBIUM DISELENIDE WITH VARIOUS DEGREES OF DEVIATION FROM STOICHIOMETRY

ONE of the most important problems in the investigation of the superconductivity of solids is the relationship between the superconducting properties and the crystal structure of the substance. This problem takes on particular significance in studies of compounds containing transition metals whose d electrons can, as is assumed in [1,2] participate both in the superconductivity and in the lattice bonding. In a number of papers[3–6] investigating $A_3B$ compounds having the $\beta$-W structure, a correlation has been established between the magnitude of the critical temperature of transition to the superconducting state $T_c$ and the values of the various structure sensitive parameters (the melting point and the temperature of the martensitic transformation, and the rigidity of the lattice) which makes it possible to speak of a considerable influence of the state of the crystal lattice on the superconductivity.

However, none of the presently existing theories takes into account the relationship between the superconducting properties and the crystal structure of the material. The existing phenomenological theories (Anderson, Anderson, and Kim[7]) which investigate the behavior of the critical currents and of the related magnetic fields within the superconductor consider only the influence of structure defects on these properties; this reduces in essence to the production of pinning centers which inhibit the spontaneous motion of the magnetic flux.

The relationship between the crystallochemical properties of a material (its structure and composition) and its superconductivity should manifest itself most distinctly in the investigation of the superconducting properties of a compound with a clear anisotropy of the structure and with a sufficiently high superconducting transition temperature. These requirements of the object of investigation are satisfied by niobium diselenide which has, as is well known,[8,9] a sharply anisotropic layer structure consisting of elementary Se–Nb–Se layers where the niobium and selenium atoms are located on layers in accordance with the principal of hexagonal close packing, and a critical temperature of 7°K. By virtue of the fact that our proposed method of synthesis[10] made it possible to obtain only the double-layer modification of niobium diselenide without the admixture of other phases, all the investigations of the superconducting properties were carried out for this modification.

It was shown in previous papers[10, 11] that the superconductivity of niobium diselenide is determined by the state of the niobium sublattice, and chiefly by the degree of perfection of the niobium planes. These data can be readily explained starting from the nature of the distribution of niobium atoms in the lattice: the distance between niobium atoms lying on the plane is 3.44 Å, whereas the shortest distance between niobium atoms on neighboring planes is 6.28 Å.

The purpose of this part of the work is to explain how the anisotropy of the structure affects the magnetic properties of the compound. In addition, the rather broad range of existence of the double-layer phase of niobium diselenide (several atomic percent) makes it possible to follow the nature of the variation of the magnetic properties with the controlled disordering of the lattice.

## EXPERIMENTAL METHOD

Polycrystalline niobium diselenide of a composition close to stoichiometric (33.33 at.% Nb) was synthesized by the method of the "self-dissolving" crucible.[10] Polycrystalline niobium diselenide of controlled composition was obtained either by recrystallization of the synthesized product in a selenium melt or by annealing it in a furnace with a given temperature gradient. Samples with a niobium concentration of 31.7–34.3 at.% were thus obtained.

Single crystals of niobium diselenide with various degrees of deviation from stoichiometry were grown by the method of gas-transport reactions.[12] It has been established that in the transfer process the crystals grown were of the same composition and structure as the initial material.[10] The single crystals obtained by this method had the form of hexagonally bounded platelets with mirror surfaces between 10 and 200 μ thick and an average diameter of 5–10 mm.

The measurements of the magnetic moment were carried out by the usual ballistic method in a uniform field, the sample moving between two opposing coils each having 40 000 turns. The external magnetic field was produced by a superconducting solenoid and was current regulated in the 0–3100 Oe range; its uniformity was no worse than 0.1% over a 1 cm length along the axis of the coil. The investigated samples were in the form of cylinders 2.5 mm in diameter and 15 mm high, consisting of single-crystal platelets 80–150 μ thick with two different orientations of the planes of the platelets with respect to the cylinder axis: perpendicular and parallel to it. In the former case a sharp blade was used to prepare the single crystals in the form of small disks 2.5 mm in diameter; these were then stacked and glued together with BF-2 adhesive along the generatrix of the cylinder. In the latter case the single crystals were cut in the form of narrow strips ~10 mm long and 2.5 mm and less in width. These were stacked into small columns and also glued along the generatrix of the cylinder thus obtained. As a result of the close to ideal surface, the single-crystal platelets fitted very closely to one another in both cases and formed almost monolithic cylindrical samples. It should be noted that since the diameter and the height of the measuring coils between which the sample was placed were 3 and 8 mm respectively, one could for the chosen height of the samples neglect the effect of demagnetization.

As a result we carried out investigations of the magnetization curves for two mutually perpendicular directions of the external magnetic field: perpendicular and parallel to the basal plane of the single crystal.

## EXPERIMENTAL RESULTS AND DISCUSSION

### A. Niobium Diselenide of Stoichiometric Composition

Typical magnetization curves for samples of stoichiometric composition for the two investigated magnetic field directions are shown on Fig. 1. In recording the magnetization curves it was noted that the magnitude of the magnetic moment for fields larger than the value for which the full Meissner effect was observed varied, depending on the number of measurements carried out at a constant external field. A stable value of the magnetization was only obtained after numerous (five to ten) passages of the sample between the measuring coils. Such a change of the magnetization from the initial to the final value is particularly noticeable when the field is directed perpendicular to the surface of the crystal, and is very weak for parallel orientation of the field. This change of the magnitude of the magnetic moment due to the number of measurements can be partly explained by the fact that the investigated samples are not monolithic single crystals but consist of platelets anisotropic in their shape. However, this effect is apparently not decisive, since the magnitude of the difference between the initial and final values of the magnetization was the smaller the less defective the investigated single crystal.

A similar situation was also observed in sufficiently pure niobium samples by Finnemore, Stromberg, and Swenson[13] who concluded that the vibrations occurring in the course of the displacement of the sample assist the motion of the magnetic flux into the crystal (when the field is increased) or out of it (when the field is decreased). Our investigations confirm the correctness of this conclusion with aggregates of macroscopic defects apparently playing the main role in this phenomenon.

In view of the fact that the values of the magnetization determined from the first measurement are reproducible from measurement to measurement and characterize in our view the magnetic properties of the material, all magnetization curves presented here are plotted with values of the magnetic moment obtained in the first measurement.

It is seen from Fig. 1 that the magnetic properties of niobium diselenide are strongly anisotropic, a fact which manifested itself both in the shape of the magnetization curves and in the values of $H_{max}$ and $|M|_{max}$ [1)]

[1)] $H_{max}$ is the value of the external magnetic field at which the tangents to the ascending and descending branches of the magnetization curve near $|M|_{max}$ intersect. In considering irreversible magnetization curves the field $H_{c1}$ cannot be determined.

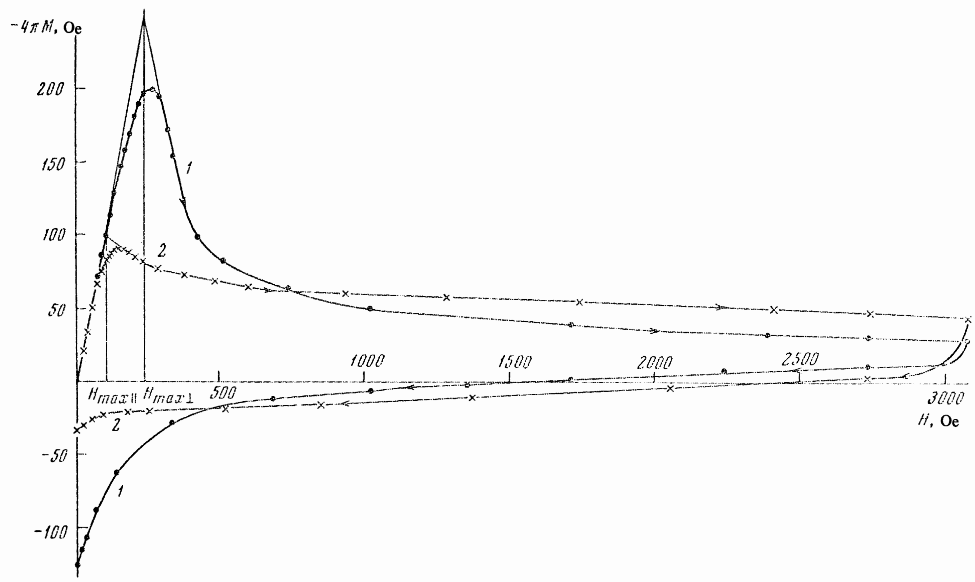



FIG. 1. Magnetization curves with the external magnetic field directed perpendicular (1) and parallel (2) for single crystals of stoichiometric composition of the double-layer phase of niobium diselenide.

The differences in the shape of the magnetization curves in perpendicular and parallel fields are clearly manifested in the dependence $-4\pi M/H_{max} = f(H/H_{max})$, and the degree of anisotropy of the magnetic moment is clearly manifested in the dependence $|M|_{\perp}/|M|_{\parallel} = f(H)$ which has a maximum near $H_{max}$.

The presence of large hysteresis of the magnetization curves for both orientations of the external magnetic field indicates the presence in the investigated single crystals of a number of extended defects capable of serving as pinning centers for Abrikosov vortices.[14] Taking into account the fact that single crystals grown under conditions close to equilibrium have practically no large region of strain, we see that the irreversibility of the magnetization curves is the result of the presence of structural defects (dislocations, packing defects, and aggregates of impurity atoms).

As is clear from general crystallochemical considerations (the weak binding forces between layers due mainly only to van der Waals forces), the presence of the above structural defects in layer structures is most probable in the double layers formed by the atoms of the metalloid. Thus the diffusion and elongation of the points on the Laue patterns of the investigated single crystals made it possible to establish that the elementary double layer formations are often misoriented with respect to one another by hundredths of a second of arc, this misorientation being the result of the shift of layers in planes parallel to the basal plane. It can thus be assumed that the pinning centers in these crystals should be preferentially located along the natural cleavage planes.

The preferential location of pinning centers along the basal planes is apparently the reason for the difference in the shape of the magnetization curves for perpendicular and parallel orientation of the magnetic field (see Fig. 1). In fact, if it is assumed that the structure of the vortex lattice is determined by the period of the distribution of defects which fulfill the role of pinning centers, then the resistance to the penetration of new magnetic vortices into the superconductor on increasing the field above $H_{max}$ will differ for different directions of the magnetic field: for a parallel field it is more difficult for the magnetic vortices to penetrate into the bulk of the sample than in a perpendicular field. This explains the lower slope of the $-4\pi M_{\parallel}(H)$ dependence compared with that of the $-4\pi M_{\perp}(H)$ dependence for fields greater than $H_{max}$. One can explain analogously the discrepancy in the difference between the initial and final values of the magnetic moment in perpendicular and parallel external magnetic fields, as was noted above.

The anisotropy in the value $H_{max}$ for two mutually perpendicular directions of the magnetic field (for stoichiometric samples $H_{max\perp} = 240$ Oe and $H_{max\parallel} = 100$ Oe) made it possible to arrive at the conclusion that the most convenient direction for superconductivity is the direction parallel to the basal plane of the single crystal. Indeed, for small values of the external magnetic field the surface superconducting currents induced by it prevent the penetration of the field into the crystal. The higher the limiting admissible magnitude of these currents, the higher the fields for which the full Meissner effect is still observed. From the fact that $H_{max\perp} > H_{max\parallel}$ it follows that the limiting magnitude of the admissible superconducting currents parallel to the surface is larger than that of currents perpendicular to it, and consequently the direction parallel to the basal plane is more favorable for superconductivity.

This conclusion in conjunction with that arrived at previously that the critical temperature of niobium diselenide is mainly determined by the degree of perfection of the niobium planes[11] allows one to assume that it is precisely the niobium planes which fulfill the main role in the superconductivity of niobium diselenide. Thus, niobium diselenide is a material with a predominantly plane character of the superconductivity.

Applying the concept of the "critical state" introduced by Bean and Kim[15, 16] and based on the presence of coupling between the local magnetic field and the critical current passing through this region to the data on the magnetization of niobium diselenide, one can conclude that the density of the critical current parallel to the basal plane should be larger for parallel orientation of the magnetic field than for perpendicular orientation of the field (compare the curves of Fig. 1). A check of this assumption by measuring the critical current for perpendicular and parallel orientations of the field showed that it is correct; this was a new confirmation of the existence of a coupling between the magnetization and the critical currents in the crystal (see Part II).

### B. Niobium Diselenide with Various Degrees of Deviation from Stoichiometry

In a previous paper on the investigation of the superconducting of niobium diselenide[11] it was shown that for a deviation from stoichiometry towards decreasing selenium concentration, as a result of the growth of selenium vacancies, beginning with a 33.7 at.% Nb concentration, a part of the niobium atoms shifts from its regular positions on the niobium planes and leaves these planes. Such a rearrangement of the niobium sublattice causes a sharp decrease of the critical temperature $T_c$ and the appearance of an additional point of inflection $T_{c2}$ on the curve of the transition from the superconducting to the normal state. The investigation of the effect of the deviation from stoichiometry on the magnetic properties of niobium diselenide was carried out on samples of three compositions: 33.33 at.% Nb (stoichiometric); 33.77 at.% Nb (the beginning of the disordering of the niobium sublattice); 33.92 at.% Nb (considerable change of the niobium sublattice).

Figures 2 and 3 show the concentration dependence of the magnetization curves for perpendicular and parallel external fields respectively. An analysis of the curves makes it possible to conclude that there is a relationship between the state of the niobium lattice and the magnetization. In fact, both $H_{max}$ and $|M|_{max}$ decrease as the degree of deviation from stoichiometry is increased. However, whereas on going from a sample of stoichiometric composition to one with a 33.77 at.% Nb concentration the decrease of $H_{max}$ is small (see the table), since the rearrangement of the niobium sub-

Dependence of the superconducting parameters on the sample composition

| Sample No. | Chemical composition, at. % Nb | $T_c$, °K | $H_{max\perp}$, Oe | $H_{max\parallel}$, Oe | $\frac{H_{max\perp}}{T_c}$, Oe/°K | $\frac{H_{max\parallel}}{T_c}$, Oe/°K | $\left(\frac{\lvert M\rvert_\perp}{\lvert M\rvert_\parallel}\right)_{max}$ |
|---|---|---|---|---|---|---|---|
| 1 | 33.33 | 7,0 | 240 | 100 | 34.3 | 14.3 | 2.5 |
| 2 | 33.77 | 6,75 | 170 | 90 | 25.20 | 13.30 | 2.12 |
| 3 | 33.92 | 6,1 | 55 | 23 | 9.02 | 3.77 | 2.42 |

lattice is not appreciable, for the sample with 33.92 at.% Nb the value of $H_{max}$ decreases considerably, a fact which can only be related to the change in the niobium sublattice.

The successive decrease of the value of $H_{max}/T_c$ on increasing the degree of deviation from stoichiometry (see the table) indicates that the observed decrease of $H_{max}$ is due not only to the decrease of $T_c$ but to a larger extent to the decrease of the magnetic moment connected with the rearrangement of the niobium sublattice.

The investigation of the magnetization curves obtained for samples of different composition has shown that the degree of anisotropy of the magnetic moment $(|M|_\perp/|M|_\parallel)_{max}$ does not change appreciably (see the table), and the position of the maximum on the $|M|_\perp/|M|_\parallel = f(H)$ curves shifts towards lower values of the external field corresponding to a decrease of $H_{max}$. In conjunction with the invariable nature of the magnetization curves this allows one to assert that the observed anisotropy of the magnetic properties is a consequence of the anisotropy of the structure.

The investigation of the course of the magnetization curves on increasing and decreasing the external magnetic field has shown that the degree of irreversibility of the magnetization curves decreases in accordance with the degree of deviation from stoichiometric composition. This attests to the fact that in the rearrangement of the niobium sublattice the defectiveness of the structure does not increase, i.e., the total number of extended defects fulfilling the role of pinning centers

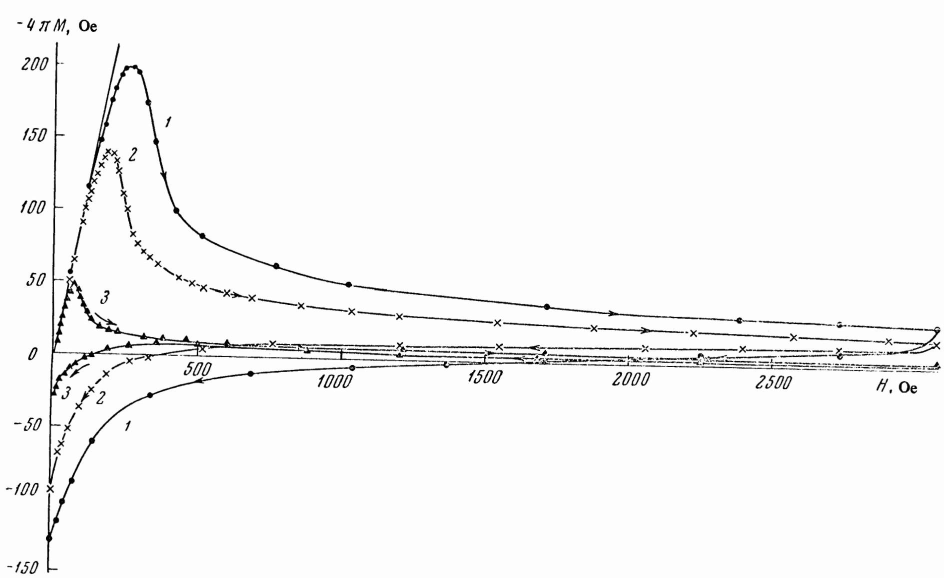



FIG. 2. Concentration dependence of the magnetization curves for a perpendicular external magnetic field. Chemical composition of the investigated samples: 1 – 33.33; 2 – 33.77; 3 – 33.92 at. percent Nb.

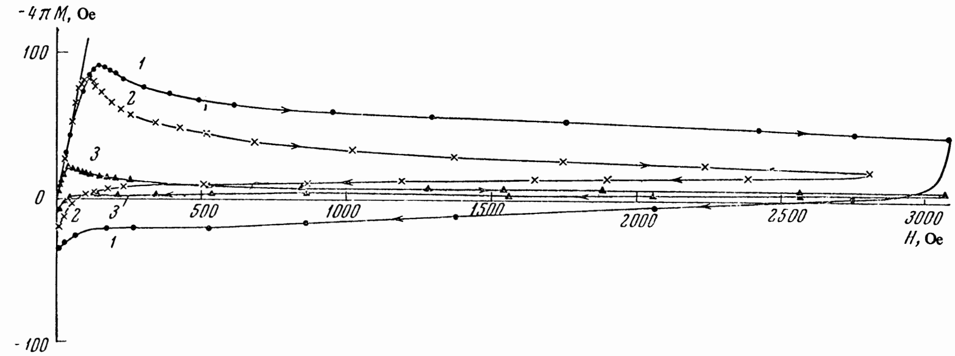



FIG. 3. Concentration dependence of the magnetization curves for a parallel external magnetic field. Chemical composition of the investigated samples: 1 – 33.33; 2 – 33.77; 3 – 33.92 at. percent Nb.

does not increase. It can consequently be assumed that the displacement of the niobium atoms from the regular positions on the niobium planes occurs in an orderly manner with the production of a superstructure. This is confirmed by the x-ray investigations of Debye–Scherrer photographs of compounds with various degrees of deviation from stoichiometry.[11]

## II. CRITICAL CURRENTS IN SINGLE CRYSTALS OF NIOBIUM DISELENIDE WITH VARIOUS DEGREES OF DEVIATION FROM STOICHIOMETRY[2)]

The orientational dependences of the critical current of single crystals of niobium diselenide have been previously obtained in the works of Beerntsen, Spiering, Armitage, and Revolinsky.[17, 18] The authors observed the dependence of the anisotropy of the current on the direction of the magnetic field, as well as the anomalies in the behavior of the critical current which they observed in certain samples. These anomalies manifested in an increase of $J_c$ with increasing field oriented perpendicular to the plane of the crystal were connected by the authors with the presence in the crystals of an excess of niobium due to the deviation from stoichiometry.

In view of the fact that the x-ray investigations of niobium diselenide have shown that a deviation from stoichiometry in the direction of increasing niobium concentration is realized by means of an increase in the number of vacancies in the selenium sublattice,[11] the anomalies of $J_c$ observed in [18] cannot be connected with an increase in the number of niobium atoms.

An anisotropy of the critical current on changing the orientation of the magnetic field similar to that observed in single crystals of niobium diselenide[17] was observed in [19, 20] in an investigation of film samples of Pb-Tl and Pb-Bi. In explaining this phenomenon Hart and Swartz,[19] having proposed a model of surface pinning, concluded that it is due to surface currents. Joiner and Kuhl,[20] on the other hand, assumed that the orientational dependence which they observed is determined by bulk currents and can be explained by the anisotropy of the pinning forces which have a maximum on the sample surface where the vortex lattice becomes denser. Thus, while differing in their opinion concerning the nature of the current (surface or bulk current), the authors of both papers considered the surface to be responsible for the anisotropy of the current.

It was, therefore, of interest to clarify whether the anisotropy of the critical current observed in single crystals of niobium diselenide is due to the anisotropy of its crystal structure or to the surface which plays an important role because of the plate-like geometry of the single crystals. To this end, we carried out investigations of the critical currents of the double-layer phase of niobium diselenide as a function of the magnitude and orientation of the magnetic field with respect to the crystallographic axes, and also as a function of the degree of controlled disordering of the selenium and niobium sublattices; these made it possible to show a relationship between the critical current and the crystallochemical parameters of this compound.

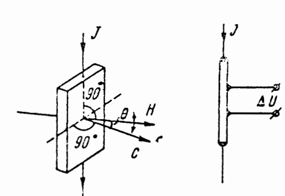
### Experimental Method

The investigations were carried out on single crystals of niobium diselenide with various degrees of deviation from stoichiometry. The crystals chosen for the experiment were cut into rectangular samples 1.5–2 mm wide; four copper probes—two current and two potential probes—were soldered to these with an indium solder. The use of stainless steel clamped contacts as potential probes did not change the results obtained.

The relative arrangement of the crystal, the current, and the magnetic field is shown in Fig. 4. The transport current J passed along the basal plane of the rigidly fixed single crystal, the magnetic field H rotated in the plane perpendicular to the direction of the current making an angle $\theta$ with the six-fold c axis. For $\theta = 0°$ the magnetic field was perpendicular to the surface of the single crystal, for $\theta = 90°$ the magnetic field was parallel to this surface.

The measurements of the critical current were carried out with a potentiometer circuit mainly at a temperature of 4.21°K. The critical current was taken to be a current which gave rise to a potential drop of $10^{-7}$ V on the potential contacts. The crystal was ori-

FIG. 4. The geometry of the position of the crystal relative to the current and to the magnetic field employed in the experiment.




2)The results presented in part II of the paper have been obtained by E. A. Antonova and S. A. Medvedev.

ented with respect to the magnetic field by finding the maximum critical current for a constant value of the field (not less than 1000 Oe). The direction of the magnetic field turned out to be strictly parallel to the surface of the superconductor; the accuracy in the determination of the position of the crystal amounted to 0.3°.

The absence of macroscopic defects in the single crystals of niobium diselenide, the good reproducibility of the composition as well as of all the investigated superconducting properties of these single crystals made it possible to discover the laws governing the variation of the critical current with the degree of deviation from stoichiometry and with the structure of this compound.

## EXPERIMENTAL RESULTS

### A. Niobium Diselenide of Stoichiometric Composition

The dependence of the critical current on the orientation for a single crystal of niobium diselenide of stoichiometric composition for different values of the magnetic field is shown in Fig. 5. The curves are symmetric with respect to the direction parallel to the crystal surface for which a sharp maximum of the critical current was observed; this is in agreement with [17]. The minimum current was observed for $\theta = 0°$ and the variation of the critical current with the magnetic field direction is small for low angles. As was shown by Beerntsen, Spiering, and Armitage,[17] such a form of the dependence cannot be due to the demagnetization effect due to the plate-like geometry of the samples. Thus, they measured the critical current densities of niobium diselenide crystals of rectangular shape with a width/thickness ratio of 14 and 7.7 with a cross-sectional area of $1.83 \times 10^{-3}$ cm$^2$ and found that the difference between these two pairs of curves is very small and becomes noticeable only for low fields ($J_{c\ max}/J_{c\ min}$ is somewhat higher for a broader crystal for fields up to 1000 Oe).

Analogous results were also observed in our experiments. One can thus conclude that the demagnetization effect which depends on the shape of the crystals appears mainly in low magnetic fields (H up to 1000 Oe).

It should be noted that all the critical currents considered here are in our opinion bulk currents; evidence for this are their rather large absolute values and the increase of the latter on increasing the crystal thickness. In this case one can determine the critical current density which for niobium diselenide of stoichiometric composition in zero magnetic field is close to $10^4$ A/cm$^2$.

In studying the family of curves $J_c(\theta)$ (Fig. 5), it was noted that the sharpness of the peak near the maximum of the critical current increases with increasing magnetic field so that the half-width of the peak Δ representing a change in the field direction in degrees for which there occurs a decrease of the current from $J_{c\ max}$ to $(J_{c\ max} - J_{c\ min})/2$ decreases with increasing field (see Fig. 6). Near a field of 2200 Oe one observes a sharp bend on the Δ(H) dependence (Fig. 6), after which the value of the half-width of the peak changes very weakly so that the slope of the $J_c(\theta)$ curve for fields above 2200 Oe remains practically unchanged.

We have also investigated the field dependence of the ratio $J_c(\theta)/J_{c\ min}$ which characterizes the degree of anisotropy of the critical current for various directions of the magnetic field (Fig. 7). A monotonic decrease of the value of $J_c(\theta)/J_{c\ min}$ with increasing field has been observed up to an angle of 89°. However, for a field direction parallel to the surface of the crystal a maximum is observed on the $J_{c\ max}/J_{c\ min} = f(H)$ curve for H = 2500 Oe. Such a nature of the $J_{c\ max}/J_{c\ min} = f(H)$ dependence is a result of the fact that a perpendicular field acts more strongly on the superconducting current than a parallel field, this resulting in an increase of the

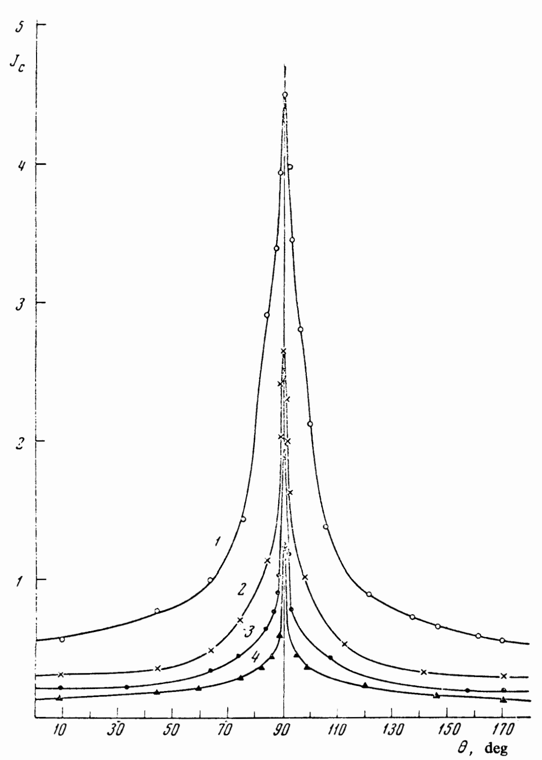



FIG. 5. Dependence of the critical current ($J_c$, A) on the orientation for various magnetic field intensities for a single crystal of niobium diselenide ($NbSe_2$) of stoichiometric composition: 1 – 783, 2 – 1758, 3 – 3691, 4 – 8500 Oe. T = 4.21°K.

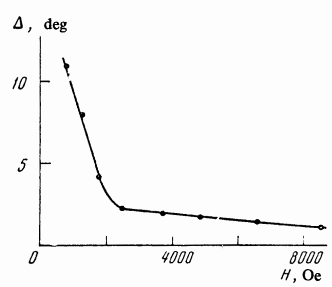



FIG. 6

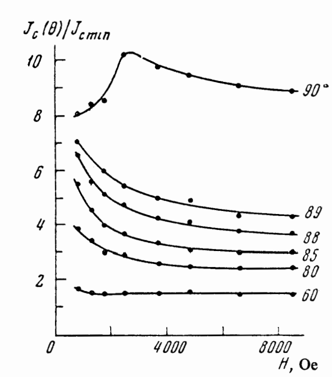



FIG. 7

FIG. 6. Field dependence of the half-width of the current Δ for a single crystal of stoichiometric composition; T = 4.21°K.

FIG. 7. Field dependence of the ratio $J_c(\theta)/J_{c\ min}$ for a single crystal of $NbSe_2$ of stoichiometric composition; T = 4.21°K.

difference $J_{c\,max} - J_{c\,min}$ for small field intensities.

The fact that the value of the magnetic field for which the anisotropy of the critical current reaches a maximum is close to the magnitude of the magnetic field at the turning point on the $\Delta(H)$ curve (Fig. 6) allows one to conclude that for fields of 2200–3000 Oe optimum conditions are established for the manifestation of the anisotropy of the critical current in stoichiometric niobium diselenide crystals.

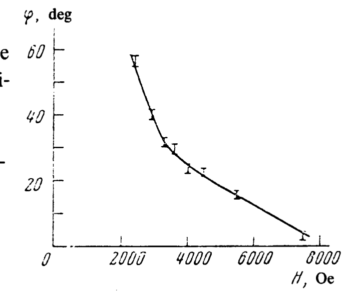



FIG. 9. Field dependence of the angular difference $\varphi$ between the directions of the magnetic field for which there exist fundamental and additional maxima for a single crystal of niobium diselenide with a concentration of 33.99 at. percent Nb; T = 4.21°K.

### B. Niobium Diselenide of Nonstoichiometric Composition

In the investigation of nonstoichiometric crystals of niobium diselenide it was observed that for samples of a composition below 33.7 at.% Nb, corresponding to the beginning of the rearrangement of the niobium sublattice,[11] the dependences of the critical current on the orientation and on the field are analogous to the corresponding dependences obtained for stoichiometric samples.

For samples with a niobium concentration above 33.7 at.%, beginning at a certain value of the magnetic field there appear on the $J_c(\theta)$ curves additional maxima which shifted with increasing field gathering closer to the main maximum (Fig. 8). Thus the difference between the directions of the magnetic fields, expressed in degrees, for which the main and additional maxima were observed decreased with increasing field (Fig. 9).

It should be noted that for sufficiently large magnetic fields the separation of the main and additional maxima on the $J_c(\theta)$ dependence becomes difficult. Consequently, the dependence of the critical current on the orientation takes on, as in the case of a stoichiometric crystal, the form of a curve with a single, but broader, peak. Thus,

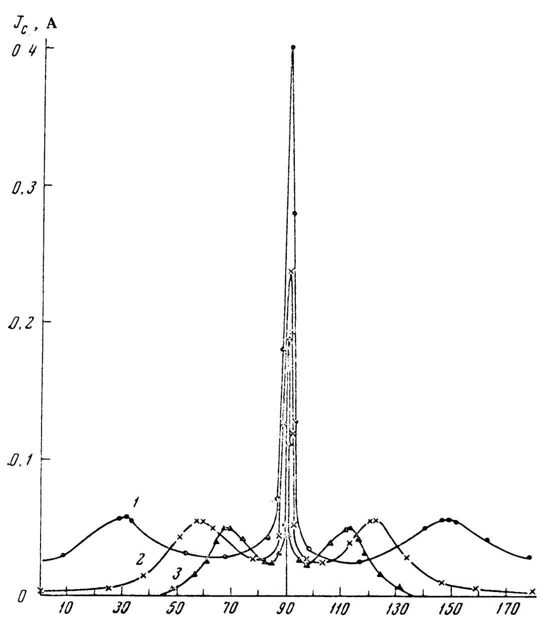



FIG. 8. Dependence of the critical current on the orientation for various magnetic field intensities for a single crystal of niobium diselenide with a niobium concentration of 33.99 at. percent: 1 – 2463, 2 – 3300, 3 – 3690 Oe. $T_c$ = 5.5°K; T = 4.21°K.

in the case of single crystal with a composition of 33.99 at.% Nb for H = 7400 Oe a change of the field direction by two degrees from a direction parallel to the basal plane decreases $J_c$ by a factor of two, whereas for lower fields an identical change of the magnetic field decreases $J_c$ by an order of magnitude.

The field dependence of the critical current for different orientations of the magnetic field for a nonstoichiometric crystal with a composition of 33.99 at.% Nb is shown in Fig. 10. A monotonic decrease of the critical current with increasing field occurs for the two basic magnetic field directions parallel ($\theta = 90°$) and perpendicular ($\theta = 0°$) to the basal plane. For intermediate directions of the magnetic field the variation of the critical current with the field is nonmonotonic, a fact which should have been expected from the existence of the additional maxima on the $J_c(\theta)$ curves. The presence of a critical current maximum at large angles $\theta$ on the $J_c(H)$ dependence confirms the existence for sufficiently high magnetic fields of additional current maxima not resolved on the $J_c(\theta)$ curves. Thus the anisotropy of the critical current of nonstoichiometric single crystals with a niobium concentration above the "critical" value is not determined only by the direction but also by the magnitude of the magnetic field.

An investigation of the field dependence of the critical current (Fig. 10) has shown that the curve of the $J_c(H)$ dependence for a particular orientation of the magnetic field has a sharp kink at the point H = 2600 Oe after which the magnitude of the critical current decreases rapidly. This value of the magnetic field can be taken to be the field $H_{c2}$ above which superconductivity is only retained in the layer adjoining the surface. With increasing $\theta$ the critical current begins to decrease steeply with increasing field directly after passing through the maximum, so that considering the transition from bulk to surface superconductivity, in analogy with the case $\theta = 0°$, we see that the value of $H_{c2}$ will be somewhere in the vicinity of the field corresponding to the maximum of the current. In this case the field $H_{c2}$ can only be determined with a certain degree of probability; it is, however, clear that $H_{c2}$ is anisotropic in the same way as the other superconducting properties and increases when the direction of the magnetic field is changed from being perpendicular to the crystal surface to being parallel to this surface.

A decrease of the temperature at which the measurements of the critical current were carried out led to a considerable increase of the threshold value of the magnetic field for which the additional maxima first appear, together with an increase of the absolute value of the critical currents. Thus, for a single crystal with a

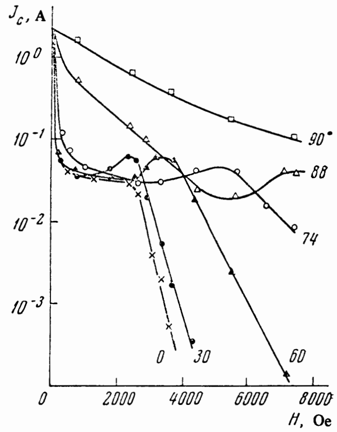



FIG. 10. Field dependence of the critical current for various orientations of the magnetic field for a single crystal of niobium diselenide with a composition of 33.99 at. percent Nb; T = 4.21°K.

composition of 33.99 at.% Nb for which the $J_c(\theta)$ dependence is plotted (Fig. 8) at a temperature of 2.59°K and a field of 6550 Oe the appearance of an additional maximum is just noticeable, and for a field of 8550 Oe the maximum is observed at $\theta = 33°$. Absolute values of the current at temperatures of 4.21 and 2.59°K for the same single crystal are respectively: for a field of 4800 Oe 0.20 and 1.83 A, and for a field of 6500 Oe 0.12 and 1.74 A.

The absolute values of the critical current for a constant magnitude and direction of the magnetic field decrease with increasing degree of deviation from stoichiometry leading to a decrease of the critical temperature of niobium diselenide.[11] This is also accompanied by a decrease of the threshold value of the magnetic field for which the appearance of additional maxima becomes noticeable. The picture is analogous to that observed on increasing the temperature of the measured single crystal.

## DISCUSSION OF RESULTS

It is well known that any conductor carrying a current in a magnetic field experiences a Lorentz force $\mathbf{F}_L = \mathbf{J} \times \mathbf{B}$. In a superconductor the Lorentz force acting on the magnetic vortices attempts to bring them into motion and thereby give rise to energy dissipation. The situation becomes critical when the Lorentz force reaches the magnitude of the retarding force $F_p$ which prevents the motion of magnetic fluxes.

In the case when the magnetic field is perpendicular to transport current parallel to the large faces of the platelet, using the model of surface pinning proposed by Hart and Swartz,[19] we obtain

$$J_c = mA(H, T, \theta) \,/\, B \sin(90° - \theta), \tag{1}$$

where m is the number of pinning centers per unit area of each force $A(H, T, \theta)$. If the retarding force of a single center does not depend on $\theta$, then one can write for constant temperature and field:

$$J_c(\theta) \,/\, J_{c\,min} \sim 1 \,/\, \sin(90° - \theta). \tag{2}$$

From a comparison of the dependence $J_c(\theta)/J_{c\ min} = f(\theta)$ with the curve $1/\sin(90° - \theta) = f(\theta)$ for a crystal of stoichiometric composition (Fig. 11) it is seen that angles $\theta$ close to 90° Eq. (2) is not valid and for smaller angles the deviation from Eq. (2) increases with increasing field. Consequently, the anisotropy in the behavior of the critical current in niobium diselenide cannot be explained solely by the presence of surface pinning.

As was shown in Part I of this paper, the anisotropy of the crystal structure of niobium diselenide results in an anisotropic distribution of structure defects: dislocations, packing defects, penetration impurity atoms, which fulfill in superconductors the role of pinning centers. It has also been shown (see [11], part I) that the most favorable direction for the superconductivity of this compound is the direction along the planes made up of niobium atoms which alternating with double planes consisting of selenium atoms run through the entire thickness of the crystal.

We assume therefore that the location of pinning centers mainly along natural cleavage planes together with the preferential plane nature of the superconductivity in niobium diselenide is the principal reason for the observed anisotropy of the critical current. In view of the parallelism of the niobium planes and the crystal surface, the dependence of the current on the magnetic field direction can be expressed by Eq. (1) in which the retarding force of a single center and the number of pinning centers depend on $\theta$. In this case the observed increase of the deviation of $J_c(\theta)$ from Eq. (2) (Fig. 11) and the decrease of the half-width of the peak $\Delta$ (Fig. 6) with increasing field can be explained by the increase of the magnetic field component perpendicular to the niobium planes which is responsible for the appearance of the Lorentz force that moves the flux lines across these planes.

The appearance of additional maxima on the $J_c(\theta)$ dependence in single crystals with a deviation from stoichiometry higher than 33.7 at.% Nb, when as a result of the increase of selenium vacancies the niobium sublattice begins to rearrange itself, shows that the critical current, as well as other superconducting properties ($T_c$, and the magnetization), are determined by the state of the niobium sublattice. The presence of these maxima confirms the previous conclusion ([11], Part I) that for a deviation from stoichiometry above 33.7 at.% Nb an ordered rearrangement of the niobium sublattice takes place.

No explanation was found for the existence of the additional maxima of the critical current depending on the direction of the magnetic field, and all the more not for their shifting when the field intensity is changed. However, as a first attempt one can assume that as a re-

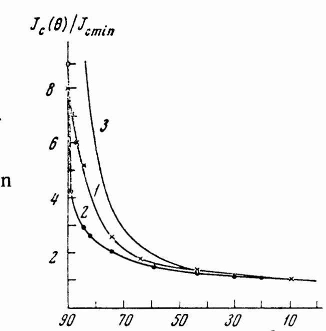



FIG. 11. Angular dependence of the ratio $J_c(\theta)/J_{c\ min}$ for a single crystal of stoichiometric composition for two values of the field: 1 – 780, 2 – 8500 Oe. For comparison we present curve 3: $1/\sin(90° - \theta) = f(\theta)$.

sult of the fact that part of the niobium atoms leave the planes due to a deviation from stoichiometry above the critical composition (33.7 at.% Nb) new planes tilted with respect to the fundamental planes, which operate in the same way as the fundamental planes, are produced. When the magnetic field is oriented parallel to these planes, additional maxima will appear.

## CONCLUSIONS

A combined consideration of the results obtained in an investigation of the magnetic properties and the critical current of single crystals of niobium diselenide which has a sharply anisotropic layer structure, as well as of the results of [11], made it possible to draw the following conclusions regarding the superconductivity of this compound and its relationship to the crystal structure.

1. The anisotropy of the magnetic properties and of the critical current is a direct consequence of the anisotropy of the structure.

2. As a result of the crystallochemical properties of layer structures the pinning centers are distributed in them anisotropically, predominantly along the natural cleavage planes; this affects both the magnetic properties and the behavior of the critical current as a function of the magnetic field direction.

3. The direction along planes consisting of niobium atoms is most favorable for the superconductivity of the double-layer modification of niobium diselenide.

4. The superconducting properties of niobium diselenide are determined by the state of the niobium sublattice, so that any rearrangement of the niobium sublattice gives rise, in the final analysis, to an impairment of the superconductivity.

5. The change in the niobium sublattice occurring for a deviation from stoichiometry above the "critical" composition (33.7 at.% Nb) takes place in an ordered manner right up to the production of a superstructure.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