Temperature dependence of critical magnetic fields and electronic characteristics of Nb$_3$Ge films

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The temperature dependences of the parallel and perpendicular critical magnetic fields were measured for Nb$_3$Ge films produced by cathode sputtering. An algorithm based on measurement of the derivative of the critical field in the region of the linear temperature dependence, of the resistivity, and of the conduction-electron density was used to determine the electronic characteristics, viz., the state density near the Fermi energy, the electron velocity on the Fermi surface, the area of the Fermi surface, the mean free path, and others, as well as superconducting-state parameters such as the depth of penetration of the field into the superconductor, the coherence length, the Ginzburg-Landau parameter, and the values of the critical magnetic field at $T=0$. The observed dependence of the electronic characteristics on the electron mean free path is attributed to smearing of the abrupt singularities in the state density. The correlation between $T_c$ and the area of the Fermi surface is obtained for superconductors with A15 lattice.

INTRODUCTION

Despite intensive investigations of the properties of the superconducting compound Nb$_3$Ge, the possibilities of raising its critical temperature $T_c$ have not yet been fully exploited, and a number of its principal electronic characteristics remain undetermined. It is important to ascertain how these characteristics vary as the A15 structure becomes ordered, and which of them exert the decisive influence on $T_c$.

Nb$_3$Ge comes closest to being stoichiometric in films having a composition $C_0$ whose value depends on the production conditions. The phase that determines the $T_c$ of the film has in this case likewise a composition close to $C_0$. In this study we determine the electronic characteristic of Nb$_3$Ge films with different values of $C_0$ obtained in "soft" regimes, by measuring the temperature dependences of the critical magnetic field $H_c(T)$. We have succeeded in tracking the variation of the characteristics as the sample comes close to having an ideal structure.

1. EXPERIMENT

The samples were prepared by cathode sputtering with direct current in an argon atmosphere using an ultrahigh vacuum facility. The partial pressure of the oxygen ranged from 10$^{-8}$ to 3 x 10$^{-7}$ Torr. The sputtering procedure is described in detail in Ref. 3. The value of $T_c$ (which corresponds to the midpoint of the transition) was measured by a four-contact method accurate to 0.1 K. The temperature was measured with an Allen-Bradley thermometer. The resistivity measurement accuracy was 5-10% and was determined by the accuracy with which the film thickness $d$ was measured. The superconducting-transition curves of the films were plotted at different values of the magnetic field, perpendicular ($H_p$) and parallel ($H_l$) to the sample plane. The correction for the change of the thermometer readings in the magnetic field were obtained by using a standard capacitive thermometer made by the same firm. The beginning and end of the superconducting transitions were defined as the points at which the resistance deviated by 0.2%.

Figure 1 shows the temperature dependences of the perpendicular $H_{c2}$ and parallel ($H_{c1}$) critical magnetic fields for three samples with different $T_c$. Some deviation of $H_{c1}(T)$ from linearity, in excess of the measurement error, was observed only in weak fields near $T_c$. The slopes in the linearity region of $H_{c1}(T)$ were $H_{c1}^\prime = -dH_{c1}/dT = 30$ to 26 kOe/K. In strong fields $H_{c1}$ exceeds $H_{c2}$ noticeably. Near $T_c$ (in weak fields), besides the deviation of $H_{c1}(T)$ from linearity, the ratio $H_{c2}/H_{c1}$ decreases and apparently becomes less than unity in sample No. 119-21.

Figures 2 and 3 show the temperature dependences of $H_{c1}$ and $H_{c2}$ of sample 119-21 at the start, midpoint, and end of the superconducting transition. A slight broadening of the superconducting transition, more pronounced in the case of $H_{c2}$, is observed in strong fields. In weak fields, the transition is somewhat narrower than at $H=0$. The deviation of $H_{c1}$ from

![FIG. 1. Temperature dependences of perpendicular (circles) and parallel (triangles) critical magnetic fields for Nb$_3$Ge samples: 1) No. 119-21; 2) No. 116-31; 3) to 124-31. The inset shows the dependence of the change of the slope $H_{c1}$ on going from $H_{c2}$ to $H_{c1}$ on the sample resistivity $\rho$.](image-url)
FIG. 2. Temperature dependence of critical field $H_{c1}$ for sample 11b-11 at the start (dark circles), midpoint (triangles), and end (light circles), of the superconducting transition.

Non-linearity is more strongly pronounced near $T_c$. The $H_{c1}(T)$ curves plotted for the start of the transition are practically linear in the entire investigated field interval. The character of the plots in Figs. 2 and 3 indicates that they are determined by the main mass of the sample.

The higher critical fields obtained for films obtained by cathode sputtering in the case of $H_c$ are attributed to their columnar structure. A particularly distinct granular structure was observed by us in films produced in "hard" regimes. Improvement of the film structure (decrease of the resistivity) leads to a decrease in the difference between the slopes $H_{c1}$ and $H_{c2}$, as seen from Fig. 1. In the calculation of the electronic characteristics it is customary to use the quantity $H_{c2} - (dH_{c1}/dT)_{Tc}$ obtained in a perpendicular field. In samples with $H_{c1} > H_{c2}$, however, the closest to the upper critical field $H_c$ is $H_{c2}$. In addition, the presence near $T_c$ of effects due to the change of the relation between the roughness size, grain size, and film thickness, on the one hand, and the Ginzburg-Landau coherence length $\xi(T)$, on the other, the values of $H_{c2}$ for the linearity region of $H_{c1}(T)$ must be used in the calculation of the electronic characteristics.

In a real film having a columnar structure, a superconducting contact exists not between all neighboring columns. A somewhat idealized conception is that an intricate network of intersecting cylindrical superconducting regions, perpendicular to the substrate, is produced in the film. The characteristic thickness of these regions is determined by the diameter of the columns. The magnetic field, which is perpendicular to the plane of the sample, turns out to be parallel to the surfaces of these superconducting regions. It is this which causes the critical field $H_{c1}$ to be stronger than $H_{c2}$. Contributing to this effect, to one degree or another, is the increase of the upper critical field as a result of both surface conductivity ($H_{c2} = 1.69H_c$) for an ideal surface and the "total" penetration of the field (in this case the critical field is $2\pi H_s^2a_0/(L)$. The dimension $L$ is determined by the diameter of the column. The near-spherical form of the upper surfaces of the columns leads practically to absence of the effect of surface conductivity far from $T_c$ in the case of a field $H_c$. In this case there is likewise no size effect, because of the large film thickness.

As the sample temperature approaches $T_c$, the value of $H_{c2}$ increases and at $H_{c2} \gg L$ the surface superconductivity manifests itself in full strength in the case of $H_c$.

The experimental values of the parameters of the investigated films are given in the upper part of Table I, together with the parameters of the "amorphous" parameters of the sample of Ref. 6, obtained by evaporation in vacuum and bombarded by 2.5-MeV CY particles. In the table, $\rho$ is the resistivity at $T = 25$ K, $\rho(T)/\rho(0)$ is the ratio of the resistivities at room temperature and 25 K, $R_{So}$ and $R_{So,c}$ are respectively the values of $R_{So}$ for $H_c$ and $H_{c2}$. We note that $\rho$ still does not coincide with the residual resistivity, inasmuch as $\rho$ depends on $T$ at fields stronger than critical.

It must be constantly kept in mind that in the calculation of the electronic characteristics one must use the value of $\rho$ of precisely that part of the A15 phase which

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Characteristics</th>
<th>Experiment</th>
<th>Calculation</th>
</tr>
</thead>
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<tr>
<td>119-11</td>
<td>$H_{c1}$</td>
<td>0.17</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>$H_{c2}$</td>
<td>0.05</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>$\rho(0)$</td>
<td>0.11</td>
<td>0.11</td>
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<tr>
<td></td>
<td>$\rho(T)/\rho(0)$</td>
<td>0.06</td>
<td>0.60</td>
</tr>
<tr>
<td>116-A1</td>
<td>$H_{c1}$</td>
<td>0.17</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>$H_{c2}$</td>
<td>0.05</td>
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<td>0.60</td>
</tr>
</tbody>
</table>

*The experimental data for this sample were taken from Ref. 6.
is responsible for $T_c$. The actually measured $p$ can differ noticeably (is usually higher) in the case of inhomogeneously samples, particularly those with more than one phase. In our case, thus, the most homogeneous sample was No. 119-21.

The value of $p$ for the high-temperature phase of sample No. 116-1 is apparently somewhat lower than that actually measured, since the sample was prepared in a relatively harder regime. Nonetheless, the x-ray results and the small broadening of the superconducting transition of the sample in strong fields, compared with

$$ H=0, $$

(7)

The mean electron velocity on the Fermi surface is $v = v_F/(1 + \lambda)$, where $v_F$ is the band value of the velocity, and can be obtained from one of the equations

$$ v^2 = \left( \frac{3N}{2\pi^2} \right) \left( \frac{N}{N_0} \right) \left( \frac{N(0)}{N_0(0)} \right) \frac{1}{1 + \lambda}. $$

Here $v_F$ is the electron velocity for the Fermi sphere at a density $N_{val}$. The coherence length is

$$ \xi = \frac{\hbar v_F}{\sqrt{2\pi N_0}} = 1.38 \times 10^{-6} \xi_0^2. $$

(9)

The London penetration depth is

$$ \lambda_L = (\pi e^2/4\pi N(0) m)^{1/2} = 1.2 \times 10^{-6} \xi_0^2 S. $$

(10)

The diffusion coefficient is

$$ D = \frac{v_F^2}{4\pi N(0) m}. $$

(11)

Characteristics such as the mean free path $l$, the Ginzburg-Landau parameter $x$, and the quantity $H_c = -dH_c/2dT$ can be obtained from the values of $p$, $S$, $N_{val}$, and $\gamma$ by using the expressions of Ref. 7. The thermodynamic critical magnetic field near $T_c$ is

$$ H_c(T) = \frac{\Delta T}{T_c(T)} = \frac{c^2}{\Delta T} \left[ \frac{c^2}{\Delta T} + \frac{c^2}{\Delta T} \right]^{1/2}, $$

(12)

where the critical field at $T=0$ is

$$ H_c(0) = \frac{c^2}{\Delta T} \left[ \frac{c^2}{\Delta T} + \frac{c^2}{\Delta T} \right]^{1/2}. $$

(13)

The equation for the upper critical field in the $dirtty^*$ limit without allowance for the paramagnetic restriction on the spin-orbit scattering was obtained in Ref. 11. As $T \to T_c$, with allowance for the strong-coupling corrections,

$$ \text{Sov. Phys. JETP} 56, 3, 1982, \text{Golovashkin et al.}. $
Hence
\[ H_a(T) = \frac{\mu_a}{\mu} H_a(0) \left( 1 - \frac{T}{T_{c1}} \right) \]

(16)

The value of \( H_a(0) \) can be expressed in this case also in terms of other physical characteristics:
\[ H_a(0) = \frac{\mu_a}{\mu} T \frac{\psi}{\mu} \left( \frac{\mu_a}{\mu} T \right) - \frac{\psi}{\mu} \frac{\mu_a}{\mu} T \]

(18)

In the "pure" limit we have
\[ H_a(0) = 0 \]

(19)

The upper critical field at \( T = 0 \) which is bounded by the paramagnetic limit (without allowance for spin-orbit scattering), can be obtained from the equation
\[ H_a(T) = H_a(0) \left( 1 + \frac{T}{T_{c1}} \right) \]

(20)

where \( \alpha = \sqrt{2} \mu_a H_a(0) \) is the Maki parameter, and
\[ H_a(T) = \frac{\mu_a}{\mu} T \left( 1 + \frac{T}{T_{c1}} \right) \frac{\psi}{\mu} \left( \frac{\mu_a}{\mu} T \right) - \frac{\psi}{\mu} \frac{\mu_a}{\mu} T \]

(21)

is the limiting Pauli field.

Allowance for the spin-orbit interaction, which is characterized by the constant \( \lambda \), decreases the role of the paramagnetic restriction. At \( \lambda = 1 \) the effective limiting field is
\[ H_a = 1.2 \mu_a \alpha \frac{\mu_a}{\mu} T \]

(22)

so that in the limit of an infinite spin-orbit interaction the paramagnetic restriction on \( H_a(0) \) is completely lifted.

The strong-coupling correction for the energy gap \( \Delta \) is
\[ \eta_a(0) = \frac{\Delta}{\mu_a \alpha} \frac{\mu_a}{\mu} T \left( 1 + \frac{T}{T_{c1}} \right) \frac{\psi}{\mu} \frac{\mu_a}{\mu} T \]

(23)

where \( \omega_a \) is the characteristic frequency of the phonon spectrum, and \( \eta_a(0) \) is the value of \( \Delta \) from the value of \( \alpha \). This ratio permits calculation of the \( \eta_a \) correction for other quantities, such as, \( H_{c1} \), \( H_{c2} \), \( H_a \), and \( \lambda \), using the equations of Ref. 17.

3. ELECTRONIC CHARACTERISTICS

The algorithm described in the preceding section makes it possible in principle to determine a large number of electronic characteristics by measuring the temperature dependence of the critical magnetic field and the resistivity of the sample. Besides these quantities, one must know the area of the Fermi surface, the density of the conduction electrons. If the density \( N(0) \) of the electronic states on the Fermi surface is known from measurements of the heat capacity, the algorithm can be used also to determine \( N \) and \( S \).

It should be noted that the terms in the expressions for \( H_a \), that contain \( N \) and \( S \) are relatively large only when the pure limit is approached. Since the inter-

4. DISCUSSION

The described algorithm makes it possible, by measuring a few physical characteristics, to obtain a large number of the most important parameters of a strong-coupling superconductor, both for the normal and for the superconducting state of the material. To estimate
the accuracy of the algorithm and the validity the assumption made in it, it is very important to compare the results with data from other experiments. In Ref. 7 are analyzed data obtained for Nb$_3$Ge and V$_3$Si by using a similar algorithm based on a fit to the area of the Fermi surface. The authors of that reference have shown that it is possible to reconcile their results with the coefficient obtained for the linear heat-capacity term $\gamma$ obtained from the temperature dependence of the heat capacity.

A number of papers cite values of $\gamma$ determined experimentally by measuring the heat capacity. The value of $\gamma$ is approximately 0.3 (Refs. 6 and 24) or 0.37 $\times$ 0.01 mJ/cm$^3$K$^4$ (Ref. 25). These are close to the 0.28 mJ/cm$^3$K$^4$ obtained by us for a sample with $T_c = 19.7$ K and $\rho = 100$ $\mu$cm. Magnetic measurements yield $\gamma = 0.34$ mJ/cm$^3$K$^4$ for a sample with $T_c = 32$ K. According to heat-capacity measurements, the decrease of the state density $N(0)$ on going from an Nb$_3$Ge sample with $T_c = 21$ K to an amorphous sample with $T_c = 4$ K is $-50\%$. In good agreement with our data. We note there are no fit parameters in the algorithm used by us.

It is of interest to examine the changes of the obtained electronic characteristics when certain sample parameters are changed. The dependences of various characteristics of the investigated sample on the electron mean free path are shown in Fig. 4. The data of Table I and Fig. 4 show a significant change in the electronic characteristics with decreasing mean free path $l$. (Since the composition change in $A$Ge, $\gamma$ is negligibly small.) The "smearing" of the Fermi energy $E_F$ and of other characteristics should be observed when the energy uncertainty is

$$\Delta E = h\omega_l/l = h\omega_l/l_F.$$

i.e., at (for free electrons)

$$l = (h^2/3\pi m\omega_l)^{1/3}.$$  

Here $\tau$ is the electron relaxation time, $z$ is the valence, and $n_A$ is the number of atoms in the unit cell.

Even if we allow that actually $\gamma$ is much less than its value for free electrons, radical changes should be expected at $l \lesssim a$. The changes observed in experiment at larger values if $l$ are due to the effect of the relaxation time on the smearing of the abrupt singularities in the state density.

The observed dependence on $l$ (or, equivalently, on $\rho$) of such characteristics as $N(0)$, $T_c$, and $\lambda$ should cause them to be temperature-dependent. This dependence can be obtained on the basis of Fig. 4 if the dependence of $l$ (or $\rho$) on $T$ is known from experiment. It is seen, for example, that for sample No. 119-1 (Ref. 22) a change from 25 K to room temperature should increase $N$ by 40% and decrease $N(0)$ by 50%. Even more noticeable changes of the electronic characteristics should be expected with further increase in temperature should increase $N$ by 40% and decrease $N(0)$ by 50%. Even more noticeable changes of the electronic characteristics should be expected with further increase in temperature.

The strong dependence of the indicated characteristics on $T$ is due to the effect of the electron-phonon interaction on such superconductors. The smearing of the singularities of the electronic spectrum in these superconductors at sufficiently high temperature ($T \gg T_c$) is given by

$$\Delta E = 2\hbar l/T_c + \gamma l.$$  

The first term determines here the smearing due to scattering from impurities and defects (in case corre-

sponds to a temperature 25 K, and the contribution of the electron-phonon interaction to this quantity is neglected). At $T = T_c$, the smearing $\Delta E = 2\hbar l/T_c$ amounts to $-0.02$ eV even in a sample with $T_c = 22$ K.

The limiting value of the resistivity $\rho$ with decreasing $l$ can be estimated. Assuming that at the limit $l = l_{lim} = a/2 - a$, we obtain

$$\rho_{lim} = -\frac{3}{2^7} \times 10^{-6} \times \frac{1}{100} \rho_{lim} = 200 - 300 \mu\Omega \cdot \text{cm}.$$  

This estimate shows the limiting values of $\rho$ and of other characteristics have not yet been reached in the amorphous sample.

It is seen from Fig. 4 that many characteristics have not reached values corresponding to a fully ordered stoichiometric sample even in the best sample. For a sufficiently good approach to an "ideal" sample a value $l \sim 60 \AA$ must be reached (in the $\beta$ phase of a composition close to stoichiometric). It follows from the dependence of $N$ on $l$ (Fig. 4) that $N = 0.5 \times 10^{11}$ cm$^{-3}$ in ideal Nb$_3$Ge. A limiting value $T_c = 37$ to 30 K was previously estimated for stoichiometric Nb$_3$Ge with maximum order. Figure 5 shows the dependence of $T_c$ on $N$ for high-temperature superconductors with $A1_5$ lattice. The hypothetical ideal Nb$_3$Ge likewise agrees well with this dependence. It is seen from the figure that critical temperatures noticeably above 30 K are difficult to achieve, for this calls for the production of samples with very low conduction-electron
density (the semiconducting *break*). Figure 5 shows only the data for materials with A15 lattice that are closest to stoichiometric. The tendency shown (the lowering of $T_c$ with increasing $N$ or $N/N_{\text{opt}}$) is preserved if known data are added for all metals and alloys, including some with nonoptimal composition.10 This general dependence is confirmed also by the amorphous sample, the value of $N$ for which is estimated in the present article. It must be recognized that such samples begin to be influenced not only by the smearing of the abrupt state-density singularities, but to a considerable degree also by the loss of crystal symmetry. The inset of Fig. 5 shows the dependence of $T_c$ on the ratio of the area of the Fermi surface to the area $S$ of the free-electron sphere for three superconductors with A15 lattice. The values of $S$ for Nb$_3$Sn and Nb$_3$Ge were obtained in Ref. 1, and for Nb$_3$Ge$_x$Sn$_{1-x}$ in the present study. The observed dependence agrees with other correlations of $T_c$ and of the electronic characteristics.$^{17}$

The results attest to an increase of $H_{\text{c2}}(0)$ with $T_c$. If the linear character of this dependence is extrapolated, one can expect for samples with $T_c = 27$ to 30 K values $H_{\text{c2}}(0) = 400$ to 450 kOe (at the midpoint of the transition). It must be noted that we made no attempt to optimize the sample preparation conditions for the purpose of obtaining maximum values of $H_{\text{c2}}$. One can expect, in particular, samples having a specified $T_c$ and obtained in the hard regime (dilute) to have higher values of $H_{\text{c2}}$. A definite increase of $H_{\text{c2}}$ can be reached at a certain deviation from the C$_6$ composition, owing to the influence of the paramagnetic phases on the value of $\mu$ of the A15 phase.

The investigations of the properties of superconductors with A15 lattice indicate that they are highly interesting physical objects. We have in mind here not only their unusually high values of $T_c$ and tremendous $H_{\text{c2}}$. At sufficiently small values of $T$ these materials can be sufficiently pure superconductors in the sense that the ratio $t^* / I$ is small ($t^* / I < 0.8$ in the sample with the maximum $T_c$). They have in this case very high values of $\kappa$, reaching 30–50. At the same time, the smallness of the electron mean free path leads already to dependences of $N(0)$, $N_T$, and $A$ on $I$, which should naturally be reflected in their superconducting properties.

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12H. Maki, Physics 1, 124 (1964).

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