Effect of injection of helium atoms on the superconducting properties of indium films

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We measured the characteristics (T_c, $H_{c\perp}$, $H_{c\parallel}$) of the superconducting transition of thin indium films exposed to various doses of helium ions. The injection of the helium particles leads to an appreciable increase of $H_{c\perp}$ and $H_{c\parallel}$, owing to the decrease in the mean free path of the electrons, and to an insignificant increase of T_c of the indium films. It is concluded from the results of the investigations and from a comparison with experimental and theoretical results by others that the method of injection of helium atoms into thin superconducting metals makes it possible to investigate in a wide range and in purer form the effect of the electron mean free path in the metal on the superconducting properties of thin films.

INTRODUCTION

It is known that one of the quantities that influence greatly the superconducting properties of a metal is the electron mean free path. A study of the influence of this parameter on the superconducting transition temperature and on the critical fields of thin metallic films has been the subject of many works. In these works, the electron mean free path was varied either by dissolving a small amount of another metal in the investigated metal, or by varying the film thickness, or else by depositing them on cold substrates with subsequent heating to various temperatures. The methods whereby the electron mean free path was varied in these studies possessed the feature that in addition to changing the considered quantity they produced some various additional effect, namely a change in the form of the phonon spectrum, of the Debye frequency, or of the electronic density of states, and these changes also affected the superconducting properties of the metal.

There is one more very effective method of changing the mean free path l in a metal, namely injection of inert-gas ions into the film. Preliminary experiments have shown that this method can be used to change l by more than one order of magnitude. At the same time, one can hope that introduction of inert-gas impurities into a film has little effect on the other characteristics of the metal, in which its superconducting properties depend. Consequently, it becomes possible to study in the purest form the influence of the electron mean free path in a metal on its superconducting characteristics. To ascertain the degree to which this possibility can be realized, we have investigated the influence of injection of helium ions on the superconducting properties of indium films.

APPARATUS AND PROCEDURE

The indium films were bombarded with a setup described in detail earlier (see[1,2]). The films were bombarded with He^+ ions whose energy was chosen to satisfy the condition $\bar{\lambda}/d \approx 1$ ($\bar{\lambda}$ is the mean free path of the He^+ ion of the given energy in indium, and d is the film thickness). Under this condition, an appreciable fraction of the bombarding-beam ions should penetrate into the film.

A helium-ion beam of current on the order of 1 μA and energy 7–10 kV passed through the electric field of the sweep capacitor and consequently executed oscillations about an axis perpendicular to the film surface. This resulted in uniform irradiation of the entire film surface. The radiation dose was defined as the product of the current of the helium ions incident on the film by the irradiation type. The films were irradiated at room temperature in a chamber with residual-gas pressure 5×10^{-7} Torr. During each bombardment session, we measured continuously the film resistance. Up to a dose 9×10^{17} ion/cm^2, a linear increase of the film resistance with increasing dose was observed. The film resistance attained at the end of the bombardment session remained unchanged after the bombardment was stopped. This meant that the helium particles that had penetrated into the film remained in it. The film-resistance increment due to the bombardment remained constant also during the subsequent handling of the film, i.e., its transfer to the device for the measurement of the parameters of the superconducting transition, following their measurement, and when the film was returned to the accelerator chamber where it was bombarded.

The investigations were performed with indium films of thickness 1100–1700 Å, condensed on mica substrates cooled to 223°K in a vacuum of 5×10^{-6} Torr. The deposition rate was 100 Å/sec. The film thickness was measured with a Linnik interferometer[1)]. The measurement was performed in the following manner. The prepared film was transported to the instrument for the measurement of the critical temperature T_c and the critical fields $H_{c\perp}$ and $H_{c\parallel}$. The film was then placed in the accelerator bombardment chamber and was bombarded with a definite dose of helium ions. After the first bombardment session, we measured the aforementioned superconducting-transition parameters of the film. This was followed by a second bombardment session and a new measurement of the investigated parameters, and so on up to a dose of 9×10^{17} ion/cm^2, corresponding to a film room-temperature resistance increment $\Delta R/R_0 \sim 60\%$.

In the measurement of the superconducting-transition parameters, the accuracy with which the orientation was maintained parallel was ~0.1°. The value of T_c was determined from the plots of the film resistance against the temperature, while $H_{c\perp}$ and $H_{c\parallel}$ were determined from the dependence of the resistance on the magnetic field at a fixed value of the current flowing through the film. The values of T_c and H_c were determined from those points of the R(T) and R(H) curves at which the resistance reached half the normal value. The measurement current was chosen to be in the range in which the transition curves were not shifted by variation of the current flowing through the film. The film resistance was measured by a four-probe method. At all bombardment doses the R(T) curves were characterized by a small transition width (the width of the transition did not exceed 0.01°K in the interval 0.1 Rn—0.99 Rn). This indicates that the distribution of the injected helium along the film is macroscopically homogeneous. The superconducting-transition temperature was determined also by extrapolating the temperature dependences of $H_{c\perp}$ and $H_{c\parallel}$. It should be noted that all three methods of determining E_c yield values that differ by not more than 0.005°K.

In addition to measurements of the superconducting-transition characteristics in indium films, we measured also their normal resistance during all the intermediate bombardment stages at 4.2°K. At this temperature, the resistance increases monotonically with increasing dose, without exhibiting a tendency to saturate in the investigated dose interval. The growth of the normal resistance indicates a change in the electron mean free path.

Bombardment of the film by an ion beam can decrease its thickness, because of the sputtering of the film material as a result of the ion bombardment material. The decrease of the film thickness increases the critical fields, and in the case of indium also the critical temperature. To ascertain whether this effect of film sputtering could noticeably change its thickness and by the same token influence the superconducting-transition parameters, special experiments were performed in which the films were bombarded with helium ions under the condition $\lambda/d \gg 1$. Under this condition, no injection of the helium particles into the film takes place. Since the bombardment of the film was carried out at room temperature, the radiation damage produced in the film becomes annealed during the course of the ion bombardment. Thus, the film-resistance increment observed under the indicated conditions is due entirely to a decrease of its thickness as a result of the sputtering of the film material by the ion beam. The decrease of the film thickness at a maximum bombardment dose 9×10^{17} ions/cm^2 did not exceed 30 Å. Such a small change in the thickness of the indium films in comparison with the initial thickness could not noticeably influence the superconducting transition parameters.

To determine the character of the distribution of the helium particles in the film material, we performed also preliminary electron-microscope and electron-diffraction investigations of the non-bombarded and bombarded films. According to the electron-microscope observations, the non-bombarded films are polycrystalline with very fine grain. Bombardment causes the grain of the film to increase appreciably, and gas bubbles with diameter on the order of 100 Å, located predominantly on the grain boundaries, are produced in the films. At an irradiation dose 5×10^{17} ions/cm^2, the average distance between bubbles on the grain boundaries is 250—300 Å.

Electron-diffraction measurements of the lattice parameter[2)] have shown that the dimensions of the unit cell of indium increase in comparison with the dimensions in the non-irradiated film. At a dose 5×10^{17} ions/cm^2 the change $\Delta a/a$ of the basal axis is 0.04 ± 0.02% and the $\Delta c/c$ increase of the tetragonal axis is 0.08 ± 0.02%. These results indicate that a fraction of the helium atoms becomes distributed in the form of point defects, and the helium atoms occupy interstitial positions.

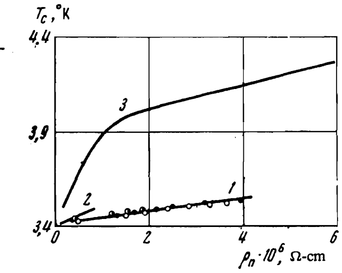

FIG. 1. Plots of the critical temperature T_c of the superconducting transition in thin indium films against the resistivity ρ_n of the film at 4.2°K. Curve 1—present results: ○—film thickness d = 1430Å, ●—1700Å, ◑—1150Å; curve 2—results of [4]; curve 3—results of [14].

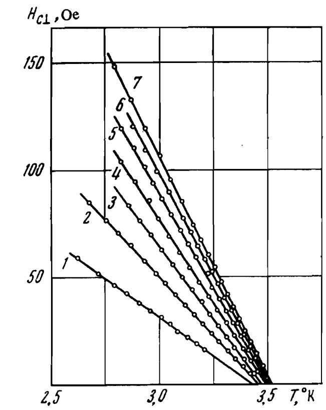

FIG. 2

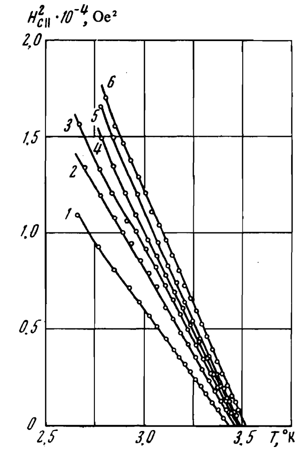

FIG. 3

FIG. 2. Temperature dependences of $H_{c\perp}$ for films bombarded by various doses of helium ions. Film thickness d = 1430Å. Curve 1—non-bombarded film. Bombardment doses for the others are: 2—$2 \cdot 10^{17}$, 3—$3 \cdot 10^{17}$, 4—$4.4 \cdot 10^{17}$, 5—$6 \cdot 10^{17}$, 6—$7.4 \cdot 10^{17}$, 7—$9 \cdot 10^{17}$ ions/cm^2.

FIG. 3. Temperature dependence of $H^2_{c\parallel}$ for films bombarded by different helium-doses. The film thickness and bombardment doses are the same as in Fig. 2.

RESULTS AND DISCUSSION

The measurements of the superconducting-transition temperatures of indium films during various bombardment stages have shown that this temperature is always higher for bombarded films than for non-bombarded ones, and increases monotonically with increasing bombardment dose, and consequently with increasing helium concentration in the film. As seen from Fig. 1, the increase of T_c correlates with the increase of the normal resistance at 4.2°K. A linear connection is observed between the quantities T_c and ρ_n, and extrapolation of this relation to the region of low resistances yields a value T_c = 3.410°K, which is quite close to the transition temperature 3.407°K of bulky indium[3]. The values of T_c for non-bombarded films are also close to the published ones (see[4]). The total increase of T_c is small—it amounts to 0.1°K at the maximum dose $N = 9 \times 10^{17}$ ions/cm^2.

A much stronger change than in T_c occurs in the critical fields of the films with changing helium concentration. Figure 2 shows the temperature dependences of $H_{c\perp}$ at different stages of bombardment of one of the films. At all helium concentrations, $H_{c\perp}$ varies near

T_c in proportion to $1 - t\,(t = T/T_c)$, in agreement with Tinkham's theory[5]. The derivative dH_c/dT at $T = T_c$ increases with increasing dose. Figure 3 shows the temperature dependences of $H_{c\parallel}^2$ for the same film and at the same bombardment doses. A proportionality of $H_{c\parallel}^2$ and $1 - t$ near T_c, in agreement with the Ginzburg theory[6], is observed for both the non-bombarded films with injected helium. The value of $H_{c\parallel}$ at the same relative temperature increases with increasing irradiation dose, just as $H_{c\perp}$.

Thus, the results of the experiment described above show that injection of helium particles into helium films leads not only to an increase of the normal resistance, but also to a noticeable change in the parameters of the superconducting transition in these films. It should be assumed that the observed effect is due to changes in the mean free path of the electrons in the film, both through the appearance of point defects and through the appearance of pores in the metal. On the basis of this assumption, we can compare the results of the study with the theory. We present below the results of such a comparison.

Measurements of $H_{c\perp}$ enable us to calculate the Ginzburg-Landau parameter κ with the aid of the relation

$$H_{c\perp}(T)=\sqrt{2}\,\varkappa H_s(T), \qquad (1)$$

where $H_s(T)$ is the critical field of the bulky superconductor. According to the Gor'kov theory[7], the dependence of κ on the electron mean free path l is given by

$$\varkappa=\varkappa_0+0.73\lambda_L(0)/l, \qquad (2)$$

where λ_L is the London depth of penetration at $t = 0$ and κ_0 is the Ginzburg-Landau parameter for a pure superconductor.

The values of κ calculated by formula (1) are shown as functions of $1/l$ in Fig. 4. In the calculation of κ, no account was taken of the possible change of $H_s(T)$ due to the increase of T_c in films with helium, since its relative change should not exceed the relative increase of T_c which is only 2% at the maximum helium concentration. The value of H_s for indium was taken from the paper of Gubser[3]. The value of l was determined from the relation ρl = const, the constant being chosen to be $1.35 \times 10^{-11}\ \Omega\text{-cm}^2$ [9].

It is seen from Fig. 4 that κ is a linear function of $1/l$, in agreement with (2). The values of κ_0 and $\lambda_L(0)$ estimated from the plot of κ against $1/l$ are 0.17 and 390 Å, respectively. For comparison, Fig. 4 shows in addition to the data obtained in the present paper also the results of investigations of indium films with bismuth and tin impurities[10,11]. The relation $\rho l = 1.35 \times 10^{-11}\ \Omega\text{-cm}^2$ was used also for the films with bismuth and tin impurities. The points plotted in accordance with Burton's data[10] (indium films with bismuth impurities) fall on the line for the indium films with injected helium particles. The results of Chang and Serin[11] (indium films with tin impurities), yield the same value of $\lambda_L(0)$ as our data, but somewhat smaller values of κ_0.

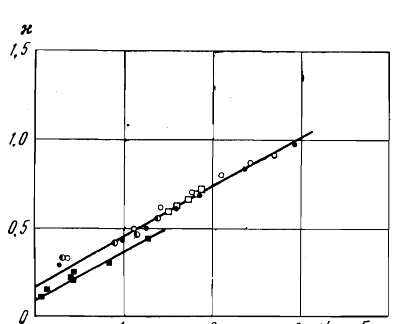

FIG. 4. Dependence of the Ginzburg-Landau parameter κ on the reciprocal electron mean free path in the metal. Results of present paper: ○–d = 1430Å, ●–d = 1700Å, ◐–d = 1150; □–results of [10], ■–results of [11].

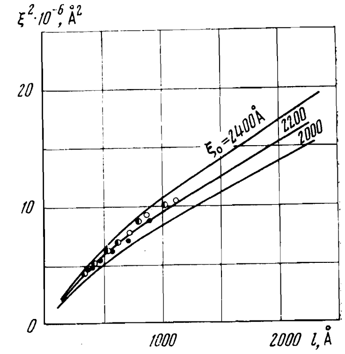

FIG. 5. Plot of ξ^2 ($t = 0.9$) against the electron mean free path in the metal. The solid curves were calculated by formula (4) for various ξ_0. The values of ξ_0 are shown on the figure. The experimental points represent our measurements. ○–d = 1430Å, ●–d = 1700Å, ◐–d = 1150Å.

Using the measured values of $H_{c\perp}$ we can calculate one more parameter of the superconductor, namely the coherence length $\xi(t)$, which depends significantly on l. At $l \ll \xi_0$ and as $t \to 1$, these quantities are connected by the relation

$$\xi(t)=0.85(\xi_0 l)^{1/2}(1-t)^{-1/2}. \qquad (3)$$

From a comparison of the experimental values of l and of the most reliable published data for ξ_0 of indium (ξ_0 = 2400–2600 Å [12]) it follows that only the condition $l < \xi_0$ is satisfied in the present experiments, but not the stronger condition $l \ll \xi_0$. At this ratio of l to ξ_0, an important role is played also by the next terms of the expansion of $\xi(t)$. According to Gor'kov[7] and Guyon et al.[12], the formula relating $\xi(t)$ with l should be

$$\xi^2(t)\,(1-t)=(0.85)^2\xi_0 l\left[1-\frac{l}{\xi_0}\left(0.527-0.46\ln\frac{l}{\xi_0}\right)-0.0984\left(\frac{l}{\xi_0}\right)^2+\dots\right]. \qquad (4)$$

Figure 5 shows curves plotted in accordance with this formula for several values of ξ_0. The experimental points lie near the curve corresponding to ξ_0 = 2200 Å. At the experimentally obtained $\lambda_L(0)$ = 390 Å and ξ_0 = 2200 Å, the theoretical value of $\kappa_0 = 0.96\,\lambda_L(0)/\xi_0$ [7] should be 0.17. This value also agrees with the κ_0 obtained by us. Thus, the change of $H_{c\perp}$ with increasing concentration of the helium particles injected into the indium film is well described within the framework of a theory that considers the influence of the electron mean free path on the value of $H_{c\perp}$.

The parallel critical field $H_{c\parallel}$ also increases with increasing helium concentration in the film. For films with injected helium particles the relation between d and $\xi(t)$ corresponds to neither of the limiting cases $\xi(t) \gg d$ or $\xi(t) \ll d$. The behavior of H_c for films, in the case of an arbitrary ratio of d and $\xi(t)$, was considered by Saint-James and de Gennes[13]. The experimental values of $H_{c\parallel}$ for films with various concentrations of the injected helium fit quite well a universal theoretical curve (see[13]). Thus, the change of $H_{c\parallel}$ with changing helium concentration in the indium films is also due to the variation of the electron mean free path with the helium concentration.

To gain an idea of the influence of different methods of varying the electron mean free path in indium films on the value of T_c of these films, Fig. 1 shows a comparison of the $T_c(\rho_n)$ plots obtained in the present study and by others[4,14]. In[4] the electron mean free path was varied by changing the film thickness. The same aim was accomplished in[14] by depositing the indium films on substrates cooled with liquid helium, and subsequently heating these films to different temperatures. At the same values of the residual resistance, the increase of T_c observed in[4,14] is much larger than that due to injection of helium particles in the indium film. A much higher T_c than observed by us is produced also by introducing into the indium a small amount of metal atoms with valence larger than that of indium (bismuth impurity in indium[10]).

It follows from our results that whereas the values of κ are very close at the same values of the electron mean free path but at different methods of varying this length, the values of T_c depend strongly on the method whereby l is varied. The largest increase of T_c is obtained for films deposited on a cold substrate. Indium films obtained by this method are characterized by a structure with very fine grain and by appreciable lattice distortions. Tunnel studies[15] have shown that the phonon spectrum in similar films of indium and of other methods becomes strongly distorted and shifts towards lower frequencies, and this appears to be the cause of the appreciable increase of T_c. When metal impurities with valence different than that of the matrix atoms are introduced, the electronic density of states is altered, and this in turn causes T_c to increase, although the increase is much smaller than when the lattice phonon spectrum is altered. The increase of T_c due to injection of helium particles is much smaller than obtained by other methods of varying l. From a comparison of all the presented data we can conclude that the appreciable increase of T_c observed when other methods are used to vary l is due mainly not to the decrease of the electron mean free path but to side effects that accompany the employed method of varying l and influence the value of T_c more strongly.

Structure investigations have shown that the helium particles injected into the indium films become partially coagulated and form gas bubbles, while others form interstitial point defects, and this leads to an increase in the dimensions of the indium unit cell (see above). According to rough estimates, the helium concentration in the interstitial solution, based on the measurements of the lattice parameters, does not exceed 0.1 at.%. The overwhelming part of the injected helium is concentrated in the bubbles.

Electron scattering by the helium bubbles should not change the value of T_c, since the bubbles change only the solidity of the film materials but cannot change the electron and phonon characteristics of the metal. The small increase of T_c observed in the present study can be due to two causes. One is the change of the effective atomic volume due to the dissolution of a small amount of helium in the indium lattice. This affect can lead to a small change of the Debye frequency ω_D and of the density of the electronic states, and consequently, can lead to a change of T_c[16].

Similar changes occur in metals subjected to hydrostatic compression. The change of T_c of a metal under pressure was considered by Bar'yakhtar and Makarov[17]. On the basis of their results of the measurements of $\partial T_c/\partial p$ and the published values of $\beta = -V^{-1}\partial V/\partial p$ and of the atomic volume, we can calculate the value of $\partial T_c/\partial V$ for indium. The sign of the value of $\partial T_c/\partial V$ calculated in this manner agrees with the sign obtained for this quantity from our results. However, the magnitude of the change of T_c is larger than the one expected to be produced by this mechanism alone.

Another mechanism of increasing T_c may be the appearance of local oscillation modes in the phonon spectrum. In the presence of small-mass impurity centers, modes of this kind occur at high frequencies, and this should cause a change in the lattice dynamics. A certain change in the lattice dynamics of indium following the injection of helium particles does indeed occur, since a deviation from the Mathiessen rule was observed in the films investigated by us. According to Maksimov's theory[18], $\Delta T_c/T_{c0}$ should be proportional to $\Delta\rho/\rho_0$, where $\Delta\rho$ is the change of the metal resistivity at high temperatures. Relations of this kind were observed in our study only at relatively small bombardment doses, whereas at larger doses ΔT_c increases more slowly than $\Delta\rho$.

We can conclude from our results that the method used by us to vary the electron mean free path in a metal makes it possible to vary this quantity within a wide range. As seen from the arguments presented above, the supplementary effects accompanying this method of varying l, which also influence the parameters of the superconducting transition in thin metallic films, are negligible. This uncovers a possibility of investigating in "pure" form the influence of the electron mean free path on the parameters of the superconducting transition in thin films.

In conclusion, the authors consider it their pleasant duty to thank A. L. Seryugin and I. S. Martynov for the structure investigations of the films and E. G. Maksimov for discussing some of the questions touched upon here.

1)The thickness d of the non-irradiated films could be determined also from the formula $d^2 = 6\Phi_0 H_{c\perp}/\pi H_{c\parallel}^2$ (Φ_0 is the magneticflux quantum, and $H_{c\perp}$ and $H_{c\parallel}$ are the critical fields of the film at perpendicular and parallel orientation of the magnetic field relative to the film plane). The values of d calculated from this formula agree within the limits of the measurement error with the film-thickness values measured by the optical method.

2)The lattice parameters were measured by comparing with TlCl films used as standard material.

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64