Superconductivity of amorphous vanadium

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The superconducting properties of amorphous vanadium films obtained by low-temperature condensation are investigated for the first time. In contrast to other amorphous metals, the superconductivity temperature (T_c) of amorphous vanadium is much lower than that of the stable crystalline phase. The critical magnetic field is $H_c \approx (2\text{–}3) \times 10^4 T_c$ in the 300–50 Å-thickness range.

Only several papers have been devoted so far to the superconducting properties of films of vanadium in its usual stable modification[1-4]. The main reason is that the superconducting properties of vanadium are very sensitive to impurities, so that to obtain films having the superconducting characteristics of the bulk metal it is necessary to have perfect vacuum conditions. Thus, for example, vanadium films obtained by condensation in a vacuum of $\sim 10^{-6}$ mm Hg and worse revealed no superconductivity whatsoever down to 2°K[1]. Improvement of the vacuum to $\sim 5 \times 10^{-7}$ mm Hg led to an increase of the superconducting temperature1) to 3.95°K[2]. It is shown in Ivanovskaya's dissertation[4] that the ratio of the fluxes of the residual gas and of the metal on the substrate, when superconducting vanadium films are produced, should range from 0.0014 to 0.01, in order for T_c of the film to be 5–4.5°K respectively. The thickest ($\sim$2000 Å) and the purest vanadium films obtained in[4] were superconducting at ~5.4°K, i.e., at the value of T_c of the initial bulk vanadium.

It is known that when condensed on substrates cooled with liquid helium, hydrogen, or nitrogen, a number of metals—bismuth, beryllium, iron, chromium, nickel, etc[5]—form amorphous allotropic modifications with short-range order, similar to the short-range order of the corresponding liquid metals. Suits[6] has shown that when vanadium vapor is condensed in high vacuum ($\sim 6 \times 10^{-12}$ Torr during the evaporation time) on a liquid-helium-cooled substrate, a new allotropic modification of this metal is produced, with a high resistivity. This modification was preserved only in films thinner than 200 Å. When this thickness was exceeded, a phase transition took place with formation of a stable modification of vanadium. A similar behavior was observed by us in bismuth, gallium, ytterbium, and iron films obtained by low-temperature condensation[7], namely, when the critical thickness d_{cr} is exceeded during the course of their condensation, a jumplike transition to the crystalline state takes place.

It should be noted that although no direct structural investigations of the low-temperature modification of vanadium were made, this modification seems to constitute amorphous vanadium. This is confirmed by electron-diffraction observation of the amorphous modification of vanadium in films obtained at room temperature in vacuum $\sim 10^{-5}$ mm Hg, i.e., in the presence of stabilizing gaseous impurities[8]. Indeed, the stabilization of amorphous modifications of metals obtained by low-temperature condensation in relatively poor vacuum ($\sim 10^{-6}$ mm Hg), up to room temperature and above, was demonstrated by Fujime[9]. Suits[6] obtained for the superconducting temperature of vanadium films that have gone over into the stable crystalline state the estimate 4.6°K[6]. No superconductivity of the low-temperature metastable modification of vanadium was observed down to 3.5°K.

We present here the first investigation of the superconducting characteristics (the critical temperature T_c and the critical magnetic field H_c) of amorphous vanadium films. We investigated films in the thickness range from ~20Å to the critical thickness ($d_{cr} \approx$ 300–350 Å for the films investigated by us). The initial material for the preparation of the films was vanadium with $R_{300}-R_6 \approx 550$ (R_{300} and R_6 are the resistances of the sample at 300 and 6°K, respectively). The vanadium layers were condensed in ultrahigh vacuum ($\sim 10^{-12}$ mm Hg) on a liquid-helium-cooled glass substrate, using a previously described procedure[7]. The rate of condensation ranged from 4 to 500 Å/min. No dependence of the results on the condensation rate was noted.

The superconducting characteristics as functions of the layer thickness were measured for films obtained by successive building-up of the thickness in the same regime during identical time intervals (without heating the films). The final layer thickness was determined by an electric method[10-11]. Additional control was exercised by means of an interferometer. The intermediate thicknesses were determined from the condensation time. The vanadium was evaporated from tungsten evaporators. Although the evaporation temperature of vanadium is high (1700–1900°C), no noticeable tungsten contamination was apparently observed in the films[12], since the evaporation was effected for the most part by sublimation. The purity of the films investigated by us was confirmed by the good agreement between their superconducting characteristics in the annealed state and the earlier data[4, 6], where minimum contamination of the films was ensured. The purity of the investigated films is also evidenced by the rather high ratio, for thin films, of the resistivity at room temperature to the resistivity at 6°K, amounting to 3–4 for the thickest films.

As already mentioned, the critical thickness of the amorphous vanadium films investigated by us was approximately 300–350 Å. The resistivity of the amorphous vanadium layers of below-critical thickness was ~200 μΩ-cm, and according to our estimates remained practically constant in the thickness interval 100–300 Å. When freshly condensed layers thinner than d_{cr} are heated to a definite temperature T_{tr}, they go over to the crystalline state. This transition corresponds to a characteristic irreversible jump of the resistance on the R(T) curve (Fig. 1). In analogy with other amorphous metals[13, 14], the temperature of the transition from the amorphous state to the crystalline one for vanadium films depends on their thickness in accordance with a hyperbolic law (Fig. 2): $T_{tr} - C = C^*/d$. The constant

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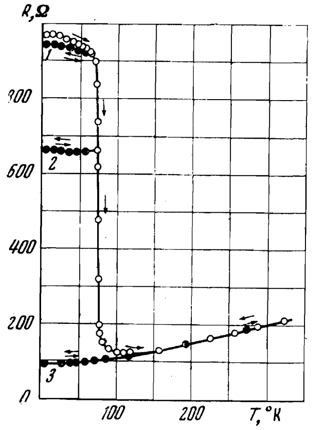

FIG. 1

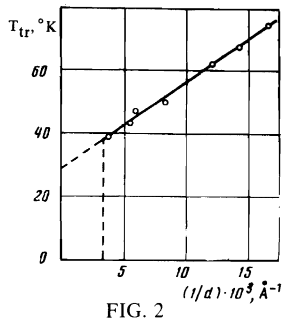

FIG. 2

FIG. 1. Temperature dependence of the resistance of a film of vanadium ~60 Å thick. The numbers 1, 2, and 3 denote the sections of the reversible course of the resistance (dark circles) after heating the film to respective temperatures 65, 73, and 150°K (and 320°K).

FIG. 2. Dependence of the temperature of the transition from the amorphous to the crystalline state for vanadium films on their thickness. The vertical dashed line corresponds to the critical thickness.

C has the meaning of the phase-transition temperature for a layer of infinite thickness; C* is the slope of the straight line $T_{tr}(1/d)$. The vertical dashed line in Fig. 2 corresponds to the critical thickness.

It was found by us in this study that the amorphous modification of the vanadium is superconducting, and its superconductivity temperature is much lower than T_c of the stable phase. Figure 3 shows the superconducting transitions of the film whose temperature dependence of the resistance is shown in Fig. 1, during different stages of annealing. The numbers on the curves correspond to the numbers of the sections of the reversible plot of the resistance in Fig. 1. Thus, curve 1 characterizes the transition to the superconducting state of a freshly condensed film having an amorphous structure. This curve is practically fully reproduced after the layer is heated to the temperature of the start of the phase transition (~65°K for the film in question). Curve 2 was plotted after annealing the film to T - 73°K, when a partial transition to the crystalline state has already occurred. The steplike shape of this curve signifies that the layer contains a mixture of two phases, amorphous and crystalline with different superconducting temperatures. After the complete transformation of the amorphous vanadium into the crystalline form, the superconducting temperature of the film is characterized by curve 3.

Just as in films of other superconducting metals[15], including amorphous films[16], the superconducting temperature of the amorphous vanadium depends on the film thickness. This dependence is represented in Fig. 4 by curve 1. The temperature spread of the superconducting transitions of amorphous-vanadium films amounts to 0.3–0.4°K (taking into account the average 90% drop of the resistance during the transition). In films close to critical thickness, the spread increases to 0.6–0.8°K. The possible reason may lie in pre-crystallization processes that take place in the amorphous modification of the vanadium when the critical thickness is approached. As shown earlier, in amorphous layers of bismuth of thickness close to critical, a change takes place in the coordination number[14] and in the Hall constant[7].

Curve 2 of Fig. 4 shows the $T_c(d)$ dependence of crystalline vanadium films. Each point on curve 2 (with the exception of $d > d_{cr}$) was obtained after annealing an amorphous film of suitable thickness. For a layer approximately 400 Å thick, T_c is 4.5°K, which is still much lower than the T_c of the initial vanadium (5.4°K). This fact seems to be due to the thickness of the film. In Ivanovskaya's work[4] the superconductivity temperature of the stable vanadium films obtained under very pure conditions came close to T_c of the bulk metal only at film thicknesses ~2000 Å; a film of thickness ~800 Å had T_c = 4.88°K. The ratio R_{300}/R_6 of these films was, as in the present investigation, 3.5–3.7.

In the literature, the lowering of the critical temperature with decreasing thickness of thin films is most frequently attributed to the influence of the surface of the substrate and of the fluctuations[15, 17, 18]. However, the large discrepancies between the experimental data[15, 19], due to the different conditions under which the films were produced, make it very difficult to explain the nature of the $T_c(d)$ dependence. It is appropriate to emphasize that there exists a large thickness interval in which the variation of T_c is observed for both amorphous and crystalline vanadium films.

In our opinion, it is also of interest that, unlike the amorphous modifications of bismuth, gallium[20], and beryllium[21], amorphous vanadium has a lower superconductivity temperature than its stable phase. So far, this is the only encountered case of such a behavior. To explain its causes it is necessary to carry out additional investigations of the amorphous modification of vanadium and, in particular, to determine experimentally its phonon spectrum. Experiments of this kind, performed on bismuch and gallium films[22, 23], have made it possible to relate the appreciable increase of T_c of the amorphous modifications of these metals to the decrease in the average phonon frequency upon "amorphization."

In addition to the critical temperatures, we investigated also the critical magnetic fields H_c of the amorphous vanadium films. A magnetic field perpendicular to the film plane was produced with the aid of a superconducting solenoid rated 40 kOe. Figure 5 shows the dependence of H_c on the reduced temperature for amorphous

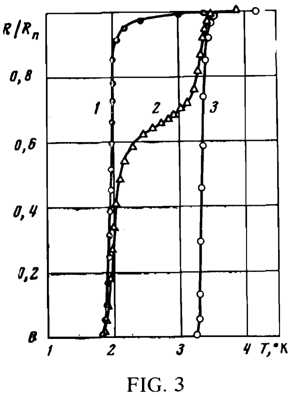

FIG. 3

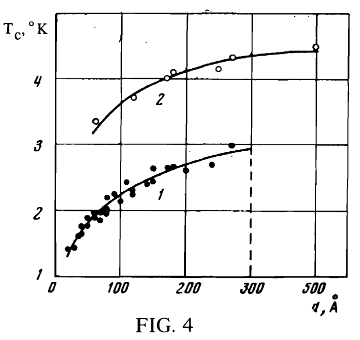

FIG. 4

FIG. 3. Superconducting transitions of vanadium film of thickness ~60 Å in different stages of annealing (the annealing curve of this film is shown in Fig. 1): 1—after heating to ~65°K (amorphous modification); 2—after heating to 73°K (mixture of amorphous and crystalline phases); 3—after heating to 150°K (stable crystalline phase).

FIG. 4. Dependence of the critical temperature on vanadium film thickness: 1—amorphous films; 2—crystalline films.

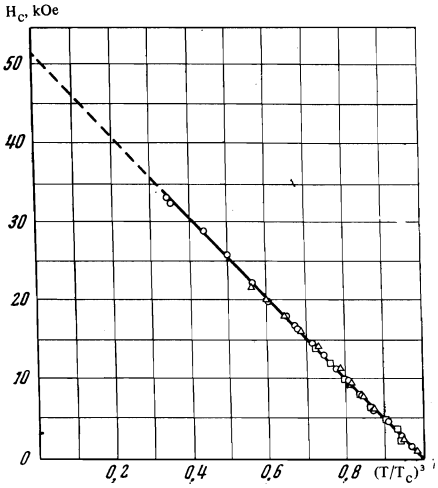

FIG. 5. Dependence of the critical magnetic field on the reduced temperature for amorphous vanadium films of different thicknesses: ○—$0.91d_{cr}$; △—$0.62d_{cr}$; □—$0.4d_{cr}$ (here $d_{cr} \approx 350$ Å).

vanadium films of various thicknesses. It follows from the figure that in the considered thickness interval this dependence is satisfactorily described by the expression

$$H_c = H_{c0}[1-(T/T_c)^3], \qquad (1)$$

where H_{c0} is the value of H_c at T = 0°K. This dependence differs strongly from the behavior not only of the amorphous[24, 25] but also of the bulk crystalline superconductors, including the stable phase of vanadium.

It is important to note that, as seen from Fig. 5, the films of the amorphous vanadium of different thickness, and consequently with different T_c, seem to have the same value of H_{c0}. It follows therefore that

$$(\partial H_c/\partial T)_{T_c} = \text{const}/T_c, \quad \text{const} = -3H_{c0}, \qquad (2)$$

i.e., the thinner the film, the steeper the $H_c(T)$ plot.

The values of H_c shown in Fig. 5 correspond to the magnetic fields that restores the normal resistance to half its value. In essence, it would be necessary to obtain the field required for a complete restoration of the resistance. As seen from Fig. 6, transitions in a perpendicular magnetic field are very greatly stretched out. It is possible to estimate from their behavior, however, that the field H_{c0} needed to destroy the superconductivity completely is ≥ 55 kOe. Thus, the critical magnetic field H_{c0} for amorphous vanadium films of thickness below critical is $\sim 2 \times 10^4\ T_c$. The coefficient of T_c increases with decreasing thickness to a value $> 3 \times 10^4$ for the thinnest films. It appears that the obtained value of H_{c0} is close to the limiting critical field of vanadium. The limiting field was heretofore observed only for thin amorphous films of bismuth[24]. In order of magnitude, the obtained values agree with the theoretical estimates for a metal in which the conduction-electron mean free path l is close to the interatomic distances ($H_{c0} \sim (1-2) \times 10^4 T_c$)[26, 27]. (As is well known, l = 5–10 Å for amorphous metals[28, 29].)

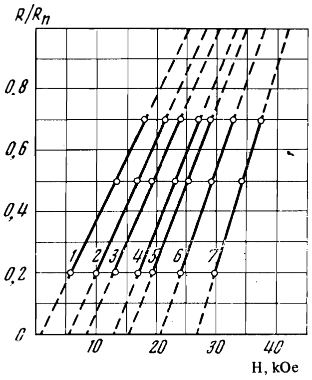

FIG. 6. Variation of the relative resistance of amorphous vanadium of thickness $0.91d_{cr}$ (see Fig. 5) following application of a perpendicular magnetic field at the following temperatures): 1–2.43 K, 2–2.35 K, 3–2.29 K, 4–2.21 K, 5–2.15 K, 6–2.04 K, 7–1.87 K.

We note that, just as in the other investigated transitions from the amorphous to the crystalline state[7], to obtain further corroboration we used measurements of the electromagnetic properties of the vanadium films. The transitions from the amorphous to the crystalline state, in addition to the jump of the resistivity and of T_c, were characterized by a jumplike change of the Hall constant[7]. The Hall coefficient, which is practically independent of the layer thickness and of the temperature, amounts to $+0.8 \times 10^{-10}$ m³/C for amorphous vanadium. On going to the crystalline state, the Hall coefficient decreases jumpwise to $+0.6 \times 10^{-10}$ m³/C (at T = 6°K), corresponding to the value for the stable bcc phase of vanadium in the bulk state[30]. The magnetoresistance of the vanadium films is very slight and is not very sensitive to the transition from the amorphous to the crystalline state. In the investigated films, the ratio $\Delta\rho_H/\rho$ (where ρ is the resistivity at H = 0 and ρ_H is the increase of ρ following application of the field H) in a field of 40 kOe amounts to $(3-3.5) \times 10^{-3}$ for both the amorphous and the crystalline state.

In conclusion, we list the obtained features of the amorphous layers of vanadium:

1) Vanadium is so far the only metal whose amorphous films have in the entire range of thickness values of T_c lower than the crystalline films (stable).

2) A temperature dependence of $H_c(T)$ in the form (1) is observed only for amorphous vanadium layers.

3) Amorphous vanadium, just as amorphous bismuth, has the highest obtained value of the critical magnetic field, $H_{c0} \geq 3 \times 10^4 T_c$.

[1)] The superconducting temperature corresponds to the temperature at which the sample resistance R becomes equal to half its resistance R_n in the normal state.

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92