Concerning the superconductivity of amorphous vanadium films

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The influence of gas impurities on the electronic properties of amorphous and crystalline vanadium films is investigated. The superconducting temperature $T_c{}^b$ of "bulky" pure amorphous vanadium is much lower than that of crystalline vanadium and is estimated at ~3.4 K. Numerical estimates show that amorphous vanadium has a density of states on the Fermi surface lower by about 2.5 times than the stable crystalline phase. The upper critical magnetic field of pure amorphous vanadium (as $T \rightarrow 0$ K) is given by the expression $B_{c0} \approx 1.2 T_c{}^b$. The gas impurities decrease the electron mean free path, lower the temperature of the superconducting transition, and increase B_{c0} of both amorphous and crystalline vanadium.

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1. INTRODUCTION

It is known that condensation of vanadium vapor in high vacuum on a substrate cooled with liquid helium leads to formation of a new modification of this metal.[1] Preliminary electron-diffraction investigations[2] have shown that this modification has a completely disordered amorphous structure. The electronic properties of the amorphous phase of vanadium—superconductivity, Hall effect, magnetoresistance—have been for the most part investigated.[3] It was shown, in particular, that crystallization of amorphous vandium films is accompanied by a substantial rise in their superconducting temperature T_c. Amorphous vandium exhibits an anomalous temperature dependence of the critical magnetic field $H_{c\perp}$ (directed perpendicular to the film surface):

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

H_{c0} is the value of $H_{c\perp}$ at $T=0$ K and exceeds 50 kOe. It was also found that in contrast to most amorphous and liquid metals[4,5] the amorphous modification of vanadium is characterized by a positive Hall coefficient.

The present study is a continuation of earlier investigations[3] of the properties of low-temperature condensates of vanadium. We consider the effect of impurities on the electronic (and particularly superconducting) properties of amorphous vanadium, and attempt to explain qualitatively the reasons why its superconducting characteristics differ from those of the stable crystalline phase.

2. PROCEDURE

The procedure used to obtain and investigate films condensed in ultrahigh vacuum on a substrate cooled by liquid helium was described earlier.[6] Prior to the condensation of the films, the vacuum in the working ampuls corresponded to a pressure ~10^{-12} mm Hg. The vanadium evaporators were made of purified tungsten wire. Despite the preliminary outgassing of the evaporator and of the charge, the vacuum conditions in the ampul deteriorated during the evaporation because hydrogen was released from the tungsten. It appears that hydrogen and helium (assuming microleakage to take place into the ampul) are the main impurities that land in the film in the course of condensation. The partial pressure of the remaining gases at $T=4.2$ K is negligibly small, and the purity of the original vanadium is high enough (~99.99%). In the present study we assessed the degree of contamination of the film from the ratio of their resistance $R_{300\text{K}}$ at room temperature to the residual resistance $R_{6\text{K}}$. The purest sample investigated before [3] and in the present study had a ratio $R_{300\text{K}}/R_{6\text{K}}=3-4$. Comparison with results by others (see[3]) show that these film samples can contain ~0.2 at.% of gas impurities. Another purity criterion of the investigated films was their resistivity in both the amorphous and the crystalline state. The film thickness was determined by an electric method.[7] Additional control was by interferometry with the aid of the optical-density method. The thickness, the resistivity, and the Hall constant of the investigated films were determined accurate to ±15–20%.

The magnetic field was produced with a superconducting solenoid rated 40 kOe. The film plane was perpendicular to the field direction.

3. EXPERIMENTAL RESULTS

A. Resistivity and Hall effect

As shown earlier[3], the resistivity of pure amorphous vanadium films, ρ, is ~200×10^{-8} Ω-m and remains practically constant in the investigated thickness interval, $d=20-300$Å. The Hall coefficient R_H of such films is $+0.8\times10^{-10}$ m^3/C. Contaminated (presumably with helium and hydrogen) amorphous vanadium films have a higher resistivity and a larger (absolute) value of the Hall constant (Table I).

As seen from Table I, films with large resistivity have a higher temperature of transition to the crystalline state $T_{a\to c}$. This only confirms the general rule[6] that the impurities stabilize the amorphous modifications of metals.

In analogy with other amorphous metals,[8] amorphous vanadium films are characterized by a negative temperature coefficient of resistivity (TCR) β (Fig. 1, curve 1). Heating to the midpoint of the $a\to c$ transition[1)] leads to appearance of a minimum on the $R(T)$ curve, due to the competition of the phases with pos-

TABLE I. Electronic characteristics of amorphous vanadium films in the normal state.

Sample	d, Å	ρ_{6K}, 10^{-8} Ω-m	β, 10^{-4} deg^{-1} ($T=15$ K)	R_H 10^{-10} m^3/C	$T_{a\to c}$, K
V-3	60	215	−4.7	+0.8	74
V-8	150	180	−3.5	+0.8	46
V-19	90	350	−5.2	+2.52	150
V-21	110	560	−4.7	+3.37	>300

itive and negative TCR (Fig. 1, curve 2). Finally, after a complete transformation of the amorphous phase of vanadium into the crystalline phase, a positive TCR is observed (Fig. 1, curve 3). The resistivity of the pure films decreases in this case to (20–25 × 10^{-8} Ω-m, and the Hall coefficient approaches the bulk-metal value. At room temperature the resistivity $\rho_{300\,K}$ of pure crystalline films is ~(35–40) × 10^{-8} Ω-m, much higher than the resistivity of bulk vanadium. This is evidence of a large number of structure defects. To eliminate the lattice defects and the stresses produced in the $a \to c$ transition, annealing at higher temperature is necessary.

It should be noted that, in contrast to the resistivity and the Hall coefficient, the TCR of amorphous vanadium films is not very sensitive to their purity (see Table I). The Hall coefficient of amorphous films in the temperature region of their existence ($T < T_{a\to c}$) is practically independent of temperature (within ±1%).

B. Superconducting temperature

It follows from the earlier[3] brief survey of the experimental research on the superconductivity of vanadium in its stable modification, this metal is extremely sensitive to impurities. Both metallic and gaseous impurities lower greatly its superconducting temperature. The existing investigations of amorphous vanadium films also attest the decrease of T_c with increasing impurity content. Thus, for films condensed on a cold substrate in a vacuum of ~10^{-7} mm Hg, the value of T_c of a hypothetical amorphous layer of "of infinite thickness" is estimated at 2.5 K.[9] At the same time, films obtained in the best vacuum have $T_c \approx 3$ K already at a thickness ~300 Å.[3]

We have investigated the superconductivity of amorphous vanadium films of varying purity (Fig. 2). Each of the plots of T_c against $1/d$ in this figure was obtained in a single experiment by successively adding-on material and measuring T_c after each additional evaporation. The intermediate thicknesses were determined from the condensation time. Plot 1 was constructed for films obtained from a thoroughly outgassed evaporator. Curve 2 characterizes T_c of films contaminated presumably by hydrogen. The resistivities of the amorphous films in the two cases were ~190 × 10^{-8} and ~250 × 10^{-8} Ω-m, respectively. The thickest film has $R_{300\,K}/R_{6\,K}$ values ~3.6 and ~2, respectivly. Since the plots of T_c against $1/d$ in Fig. 2 are straight lines at thicknesses above 100 Å, extrapolation of these lines to the ordinate axis yields the "bulk" value T_c^b of the amorphous modification of vanadium. In the case of the purest films (curve 1) $T_c^b \approx 3.4$ K; for the "dirty" variant (curve 2) $T_c^b \approx 2.3$ K. Immediately after heating to the crystalline state, the superconducting temperature of vanadium rises and reaches 4.5 K for the purest films of 400–500 Å thickness. This is 0.9 K lower than T_c of pure bulky vanadium. Such a difference is attributed to the presence of the aforementioned strong distortions of the lattice and to the relatively small thickness of the investigated films. In addition, the purity of even the best of the investigated samples was apparently not better than 99.7–99.8%. For all that, high temperature annealing under ultrahigh vacuum conditions would obviously lead to an appreciable rise of T_c of the crystalline films investigated in this study. The employed procedure, however, does not afford such a possibility.

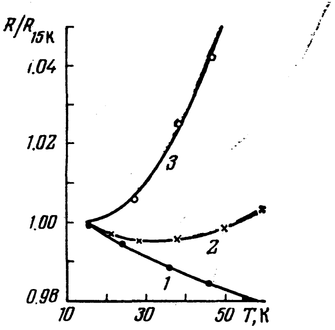

FIG. 1. Temperature dependence of the relative resistance $R/R_{15\,K}$ ($R_{15\,K}$ is the resistance at $T = 15$ K) for a vanadium film ~60 Å thick: 1—amorphous state, 2—mixture of amorphous and crystalline phases, 3—crystalline state.

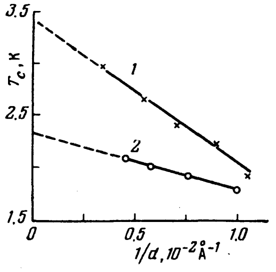

FIG. 2. Plot of T_c against the thickness of amorphous vanadium films of varying purity: 1—pure films, 2—films contaminated by hydrogen.

Moreover, the ultrahigh vacuum is maintained in the working ampul only so long as the ampul is in the liquid helium. When heated to room temperature, the pressure of the residual gases in the ampul increases at least to the value it had when sealed off from the vacuum unit (~10^{-6} mm Hg). The temperature T_c of films heated to room temperature decreased by several tenths of a degree compared with the superconducting temperature measured immediately after the $a \to c$ transition (Fig. 3). The possible assumption that this behavior is due to partial oxidation of the film is apparently inconsistent. Control experiments in which the samples were rapidly heated to room temperature when the lower part of the ampul was in liquid helium, so that the partial pressure of the oxygen was negligibly small, revealed a similar decrease ΔT_c of the superconducting temperature. The decrease of T_c was accompanied as a rule by an increase $\Delta\rho$ from the value $\rho_{6\,K}$ immediatly after the $a \to c$ transition. The Hall coefficient (at $T = 6$ K) decreased somewhat in the course of the additional heating of the film after the $a \to c$ transition (by an amount ΔR_H), or else remained unchanged. Table II lists the changes of the indicated characteristics for

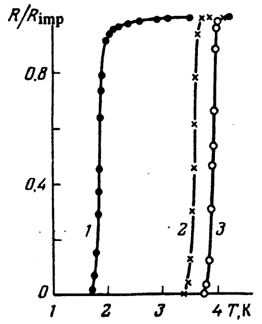

FIG. 3. Superconducting transition curves of vanadium film ~70 Å thick: 1—amorphous state, 2 and 3—crystalline state after heating to $T = 300$ K and $T = T_{a\to c}$, respectively.

several crystalline vanadium films in the course of their heating from the crystallization temperature to $T = 300$ K.

Since only helium and hydrogen have a noticeable vapor tension at 4.2 K, it can be assumed that the decrease of T_c and the increase of the resistivity of the films as they are heated are due to absorption of these gases by the film. Since the partial pressure of helium in the ampul is small in the absence of leakage (~10^{-12} mm Hg), the most probable is the absorption, by the films, of the hydrogen released from the tungsten wire in the course of the evaporation. Nor can we exclude the diffusion of the gases from the glass substrate into the films. It must be noted that the described behavior of T_c in the course of heating was observed only for thin films ($d < 300$ Å). Layers 400–500 Å thick underwent no change of the superconducting temperature when heated to room temperature.

C. Critical magnetic field

As noted above, the temperature dependence of the critical magnetic field of amorphous vanadium films is satisfactorily described by a cubic law (see the Introduction). Regardless of the thickness (at least in the interval 140 Å $< d <$ 300 Å) films of like purity have the same value of H_{c0}.[3] Further investigations have shown, however, that the impurities increase the critical magnetic field substantially. Figure 4 shows plots of the magnetic-field induction $B_{c\perp}$ against $(T/T_c)^3$ for three amorphous vanadium films of different purity. It is seen that the smaller the ratio $R_{300\text{ K}}/R_{6\text{ K}}$, i.e., the "dirtier" the films, the larger $|dB_{c\perp}/dT|_{T_c}$ and B_{c0}. Heating to a temperature above the crystallization temperature $T_{a\to c}$ decreases these magnetic-field parameters (Fig. 5, curve 2). After heating to room temperature, B_{c0} decreases even more (Fig. 5, curve 3). The form of the temperature dependence of $B_{c\perp}$ of annealed films differs from that of amorphous vanadium. The value of B_c varies with the temperature linearly near T_c, and at lower temperatures the dependence comes closer to quadratic:

$$B_{c\perp} = B_{c0}[1 - (T/T_c)^2].$$

TABLE II. Change of the electronic characteristics of crystalline vanadium films when heated from $T = T_{a\to c}$ to $T = 300$ K.

Sample	d, Å	$R_{300\text{ K}}/R_{6\text{ K}}$	ΔT_c, K	$\Delta\rho$, %	ΔR_H, %
V-1	60	1.7	0.4	0	20
V-3*	60	2.2	0.27	3	0
V-5*	70	3.5	0.35	12	–
V-6*	150	3.3	0.39	2	2.9
V-11	250	2.8	0.77	11	–
V-7	500	4	0	0	–

*The asterisks mark the films heated to room temperature in ultrahigh vacuum.

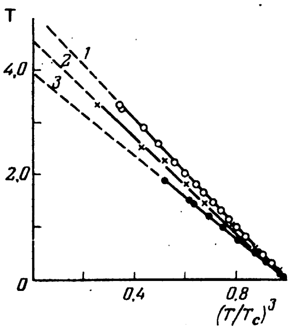

FIG. 4. Magnetic field induction vs. the relative temperature for amorphous vanadium films of varying purity ($d = 200$ – 300 Å). The ratio $R_{300\text{ K}}/R_{6\text{ K}}$ for curves, 1, 2, and 3 is 2.4, 2.8, and 3.3, respectively.

The increase of the impurity content increases $|dB_{c\parallel}/dT|_{T_c}$ and B_{c0} substantially not only in amorphous crystalline vanadium films, but also in those heated to room temperature. The dependence of the critical field on the temperature remains close to quadratic in this case.

4. DISCUSSION OF RESULTS

A. Electric properties

Amorphous metals have as a rule a structure similar to the structure of their melts.[4,10] This is obviously the reason why the resistivities of amorphous metals are close to those of the corresponding liquid metals.[4,8,11] Although we have no data on the electric conductivity of molten vanadium, it appears that this metal is likewise no exception from the general rule. At any rate, a rough calculation shows that ρ of pure amorphous films (~200×10^{-8} Ω-m).

According to present-day concepts,[5] the negative TCR in liquid or amorphous conductors can be due to "hopping" conductivity effected by thermally activated

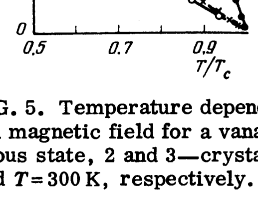

FIG. 5. Temperature dependence of the induction of the critical magnetic field for a vanadium film ~250 Å thick: 1—amorphous state, 2 and 3—crystalline state after heating to $T = T_{a\to c}$ and $T = 300$ K, respectively.

hops of the electrons from one localized state to another. In the case of amorphous vanadium this mechanism has low probability, since the observed conductivity of the amorphous films is quite high. However, as noted by Mott and Davis,[5] a small negative coefficient of resistivity does not necessarily mean hopping conductivity. The point is that fluctuations of the density or of the coordination number should produce in the amorphous or liquid metal a small number of deep potential wells, in which the states are localized. Localized states are separated from the non-localized ones by a critical energy E_c. If the scattering decreases rapidly with increasing energy, as can happen if the Fermi energy is close to E_c on the side of the nonlocalized states, then one should expect the conductivity to increase with increasing temperature. It appears that it is this mechanism which explains the negative TCR of amorphous metals and alloys with large resistivities.

The simplest explanation of the positive Hall coefficient in liquid and amorphous metals is based on the assumption that the energy E has a parabolic dependence on the wave vector k, with a negative effective (hole) carrier mass independent of k. In this case R_H is determined by the formula of the theory of free electrons and has a positive sign. But the physical meaning of such holes in an amorphous or liquid metal is not clear. The existing more rigorous analyses have qualitative character and they are extremely difficult to verify experimentally.[12]

B. Superconductivity

The experimental dependence of the upper critical field on temperature, obtained in the present study, and the resistivity of the investigated vanadium films, make it possible to obtain numerical estimates for a number of important electronic parameters of the amorphous modification of this metal. Both amorphous and crystalline vanadium films are characterized by a small mean free path l at low temperature. Even for pure crystalline films, the relation $l \ll \xi_0$ is satisfied,[13,14] where $\xi_0 = 0.18\hbar v_F/k_B T_c$ is the coherence length for pure bulk metal, v_F is the electron velocity on the Fermi surface, K_B is the Boltzmann constant, and T_c is the superconducting temperature.

It is known that the properties of superconductors with such small mean free paths can be described by the Ginzburg-Landau-Abrikosov-Gor'kov theory. Tinkham[15] derived on the basis of this theory an expression for a magnetic field perpendicular to a thin film:

$$B_{c\perp}=4\pi\lambda^2 B_{td}{}^2/\Phi_0=2^{1/2}\varkappa B_{td}\,. \tag{1}$$

Here $B_{c\perp}$ is the induction of the upper critical field, B_{td} is the induction of the thermodynamic critical magnetic field, λ is the penetration depth, $\Phi_0 = h/2e = 2.07\cdot 10^{-15}$, T-m^2 is the flux quantum, and $\varkappa$ is the Ginzburg-Landau parameter.

Using the relation[16]

$$\Phi_0 = 2^{3/2}\pi\lambda\xi B_{td} \tag{2}$$

we can rewrite (1) in the form

$$B_c = \Phi_0/2\pi\xi^2(T). \tag{3}$$

Near the critical temperature, the function $\xi(T)$ is given by

$$\xi(T)=\xi(0)(1-T/T_c)^{-1/2}. \tag{4}$$

In accord with the BCS theory we can write in the limit $l \ll \xi_0$[17]

$$\xi(0)=0.85(\xi_0 l)^{1/2}. \tag{5}$$

It follows from (3) and (4) that

$$B_{c\perp}=\Phi_0(1-T/T_c)/2\pi\xi^2(0). \tag{6}$$

Using this relation, we can estimate from the experimental relations $B_{c\perp}(T/T_c)$ (Fig. 5) the coherence length $\xi(0)$ for the amorphous and crystalline vanadium films investigated in the present study. We choose for this purpose the values of $\xi(0)$ such that the $B_{c\perp}$ calculated from (6) agree best with the experimental curve near T_c. Table III gives the coherence lengths obtained in this manner for two investigated vanadium films in the amorphous and crystalline states. The value of $\xi(0)$ for amorphous vanadium is ~50-60 Å, which is close to the coherence length of amorphous bismuth.[18] Assuming $\xi_0 = 450$ Å,[19], we can estimate from (5) the electron mean free path in crystalline vanadium films. It is equal to 25-35 Å (Table II). The mean free path calculated for these films from the relation $\rho l = 3.5 \times 10^{-12}$ Ω-cm^2 [19] amounts to 20-25 Å, in satisfactory agreement with the values of l estimated from ξ_0 and $\xi(0)$. It is difficult to estimate l for amorphous vanadium [from (5)] because ξ_0 cannot be correctly determined in this case. It is known that $\xi_0 \sim v_F/T_c$, and although T_c is known for both vanadium phases, it is difficult to assess the extent to which their electron velocities on the Fermi surface differ. It can only be

TABLE III. Experimental and calculated electronic parameters of vanadium films in the amorphous and crystalline states.

Sample	d, Å	ρ_{6K}, 10^{-8} Ω-m		$\rho_{300K}-\rho_{6K}$, 10^{-8} Ω-m	T_c, K		$\lvert dB_{c\perp}/dT\rvert_{T_c}$, T/K		$N(0)$, 10^{47} J^{-1} m^{-3}		$\xi(0)$, Å		l, Å	
		A*	C**	C	A	C	A	C	A	C	A	C	A	C
V-10	300	200	14,2	25.6	2.55	3.87	5.18	1.07	9.2	23.7	50	108	<20	34
V-3	60	215	20.4	25,3	1.97	3.35	5.02	1.3	8.3	22	60	88	<20	24

*A—amorphous phase.

**C—crystalline phase.

started with assurance that in amorphous vanadium, at most, $l<20$ Å, so that decreasing the film thickness to this value produces practically no increase of ρ. In addition, since it can be assumed that ρl is constant also for amorphous vanadium, contaminated films, whose resistivity is larger, have a smaller electron mean free path.

Of the many hitherto investigated amorphous transition metals,[20] only V, Nb, and Ta have a superconducting temperature lower than in the crystalline state. Crow *et al.* have shown[21] that such a behavior of these metals can be qualitatively attributed to a decrease of the density of the states on the Fermi surface because of the decreased mean free path in the amorphous state. The Fermi level of bulky V, Nb, and Ta is on the "top" of the energy distribution of the density of the electronic states. Formation of the amorphous phase should cause a "smearing" of this curve and by the same token a shift of the Fermi level towards lower state densities. The result should be a lowering of the critical temperature compared with the bulk metal. On the contrary, transition metals that are characterized in the equilibrium state by a low density of the electronic states (W, Mo, and others) should have in the amorphous state a higher state density on the Fermi surface and a higher T_c. The state density $N(0)$ (in the case $l \ll \xi_0$) is easiest to estimate from the initial slope of the upper critical field as a function of the temperature, and from the resistivity.[13,22]

From the microscopic theory developed by Gor'kov for weakly bound superconductors in a magnetic field[23] it follows that the density of the electron states on the Fermi surface (with account taken of the two spin directions) is given by[22]

$$N(0)=\frac{\pi\,|dB_{c2}/dT|_{T_c}}{4k_Be\rho}, \tag{7}$$

where e is the electron charge and $B_{c2}=B_{c\perp}$ according to[15]. Crystalline vanadium is a weakly bound superconductor[19] and formula (7) is therefore valid for the crystalline films investigated here. In the case of tight or intermediate binding it is necessary to introduce in the denominator of the right-hand side of (7) a certain coefficient η of the order of unity.[24] We have no data to indicate whether amorphous vanadium is a tightly or weakly bound superconductor. Calculations performed for tightly bound amorphous superconductors,[25] however, yielded for η a value 1.0 ± 0.05. We have therefore used (7) also for the calculation of the state density in amorphous vanadium. The results of the calculations are shown in Table III, from which it follows that the state density for amorphous vanadium is smaller by approximately a factor 2.5 than that of crystalline vanadium. The latter agrees satisfactorily with results obtained by others for crystalline ϰ vanadium films and with the state density calculated from the electronic component of the heat capacity for the bulk metal[13] (with allowance for the spin directions). Thus, although the coefficient η has been neglected in (1) despite its known value, it is quite obvious that the density of states in the amorphous modification is substantially lower than in the crystalline one. This is apparently also in agreement with the main reason suggested by Crow *et al.*[21] for the decrease of T_c in the amorphous modification of vanadium.

It follows, however, from the expression proposed by the BCS theory for T_c that the obtained difference between the state densities of amorphous and crystalline vanadium should lead to a much lower superconducting temperature of the amorphous state than observed in the experiment. This disparity can be explained by assuming that the constant that characterizes the electron-phonon interaction is much larger for the amorphous vanadium than for the crystalline one. It appears that this assumption is correct, since all the hitherto investigated amorphous superconductors have a strong electron-phonon interaction.[4]

It was noted earlier[3] that the dependence of the upper critical magnetic field on the relative temperature for amorphous vanadium films of varying thickness (but of equal purity) is described by the same single curve. It follows from (5) and (6) that this is due to the equality of the electron mean free paths in such films. Contamination of the films by foreign atoms decreases the mean free path and increases the magnetic field (Fig. 4).

Clogston[26] has proposed that the maximum of the field is determined by the condition that the energy, in the magnetic field, of the spins of the electrons constituting the Cooper pair be equal to the binding energy of the pair

$$\mu B_{c0}\sim k_BT_c \tag{8}$$

($\mu=9.27\times10^{-24}$ A-m^2 is the Bohr magnton), i.e., $B_{c0}\sim1.5T_c$. (B_{c0} is expressed here in tesla units and T_c in degrees Kelvin.) Gor'kov has shown[27] that fields of this order of magnitude are obtained if it is assumed that the mean free path becomes comparable with the interatomic distances. An estimate $B_{c0}\approx1.2T_c^b$ is obtained for hypothetical pure amorphous vanadium in bulk form, having $T_c^b\approx3.4$ K and $\rho\approx190\times10^{-6}$ Ω-cm (see Fig. 2). Decreasing the mean free path by introducing impurities increases the coefficient of T_c^b, and for films with $\rho\approx250\times10^{-6}$ Ω-cm we already have

$$B_c\approx2.1T_c^b.$$

It appears that decreasing the electron mean free path in amorphous vanadium films to the limit can lead to further increase of the ratio B_{c0}/T_c^b. This fact, together with experimental results of others[28,29] (who obtained $B_{c0}/T_c\approx3-6$), casts doubts on Clogston's interpretation of the paramagnetic limitation,[26] according to which the limiting value of B_{c0}/T_c is 1.84.

[1] Transition from the amorphous to the crystalline state.

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[1] J. C. Suits, Trans. Ninth National Vacuum Symposium, 1962, p. 74.

[2] J. Hasse and K. Weber, Proc. Fourteenth Intern. Conf. on Low Temp. Phys., Otaniemi, Finland, Vol. 2, 1975, p. 79.

[3] V. M. Kuz'menko, B. G. Lazarev, V. I. Mel'nikov, and A. I. Sudovtsov, Zh. Eksp. Teor. Fiz. **67**, 801 (1974) [Sov. Phys. JETP **40**, 396 (1975)].

[4] G. Bergman, Phys. Rep. **27**, 159 (1976).

[5] N. F. Mott and E. A. Davis, Electronic Processes in Non-Crystalline Materials, Oxford U. Press, 1971.
[6] V. M. Kuz'menko, B. G. Lazarev, V. I. Mel'nikov, and A. I. Sudovtsov, Ukr. Fiz. Zh. **21**, 883 (1976).
[7] A. M. Toxen, Phys. Rev. **123**, 442 (1961).
[8] B. G. Lazarev, V. M. Kuz'menko, A. I. Sudovtsov, and V. I. Mel'nikov, Dokl. Akad. Nauk SSSR **206**, 327 (1972) [Sov. Phys. Dokl. **17**, 917 (1973)].
[9] W. Felsch, Proc. Low Temp. Conf. LT 13, Plenum Press, New York, Vol. 3, 1974, p. 543.
[10] G. Breitling, S. Mader, and H. Richter, Z. Naturforsch. Teil A **28**, 1120 (1973).
[11] J. R. Bosnell, Thin Solid Films **3**, 233 (1969).
[12] G. Busch and H. J. Güntherodt, Solid State Phys. **29**, 235 (1974).
[13] A. A. Teplov, M. N. Mikheeva, V. M. Golyanov, and A. N. Gusev, Zh. Eksp. Teor. Fiz. **71**, 1122 (1976) [Sov. Phys. JETP **44**, 587 (1976)].
[14] N. E. Alekseevskiy, V. M. Sakosarenko, K. Blüthner, and H. J. Köhler, Phys. Status Solidi A **34**, 541 (1976).
[15] M. Tinkham, Phys. Rev. **129**, 2413 (1963).
[16] F. E. Harper and M. Tinkham, Phys. Rev. **172**, 441 (1968).
[17] D. Saint-James, G. Sarma, and E. J. Thomas, Type II Superconductivity, Pergamon Press, 1969.
[18] R. E. Glover III, Physica (Utrecht) **55**, 3 (1971).
[19] R. Radebaugh and P. H. Keesom, Phys. Rev. **149**, 209, 217 (1966).
[20] M. M. Collver and R. H. Hammond, Phys. Rev. Lett. **30**, 92 (1973).
[21] J. L. Crow, M. Strongin, R. S. Thompson, and O. F. Kammerer, Phys. Lett. A **30**, 161 (1969).
[22] G. Bergman, Phys. Rev. B **7**, 4850 (1973).
[23] L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **37**, 1407 (1959) [Sov. Phys. JETP **10**, 998 (1960)].
[24] G. Eilenberger and V. Ambegaokar, Phys. Rev. **158**, 332 (1967).
[25] D. Rainer and G. Bergmann, J. Low Temp. Phys. **14**, 501 (1974).
[26] A. M. Clogston, Phys. Rev. Lett. **9**, 266 (1962).
[27] L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **44**, 767 (1963) [Sov. Phys. JETP **17**, 518 (1963)].
[28] B. G. Lazarev, L. S. Lazareva, E. E. Semenenko, V. I. Tutov, and S. I. Goridov, Dokl. Akad. Nauk SSSR **196**, 1063 (1971) [Sov. Phys. Dokl. **16**, 147 (1971)].
[29] H. Jones, D. Fischer, and G. Bongi, Proc. Fourteenth Intern. Conf. on Low Temp. Phys., Otaniemi, Finland, Vol. 2, 1975, p. 20.

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Relaxation processes and characteristics of the luminescence spectra of ZnTe and $Zn_xCd_{1-x}Te$ crystals

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An investigation was made of the features of the luminescence spectra ZnTe and $Zn_xCd_{1-x}Te$ crystals at low rates of resonant pumping with sources of half-width $\Delta\Omega$ much smaller than the natural exciton-level width γ. An analysis of the polarization and energy correlations between the structure of the observed emission spectra and the excitation photons yielded information on the longitudinal and transverse relaxation times. The problem of the relationship between resonance Raman scattering and luminescence was considered from the point of view of the relaxation theory. It was found that for $\Delta\Omega < \gamma$ there was a possibility of a change from the resonance Raman scattering to the usual thermalized luminescence via various stages of hot luminescence.

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1. INTRODUCTION

In studies of radiative recombination in crystals under resonance excitation conditions much attention is usually given to the question of the relationship between resonance Raman scattering and hot and ordinary luminescence.[1,2] Recently, this relationship has become particularly important because its studies may solve one of the most difficult problems in the physics of interacting excitons, which is the experimental realization of the Bose–Einstein condensation.

If we follow the Heitler theory of resonance fluorescence,[3] we find that luminescence can be obtained only if we use a source whose excitation band is of half-width $\Delta\Omega > \gamma$, where γ is the natural width of an electron (exciton, biexciton) level. In the opposite case, i.e., for $\Delta\Omega < \gamma$, the structure of the spectra should be governed by the light scattering processes. Nagasawa *et al.*[4] investigated only the correlation between the luminescence spectra and the excitation photons from a tunable laser, and they concluded that this behavior was exhibited by their CuCl crystals in the case of two-photon resonance excitation of the biexciton energy band.

However, the validity of the Heitler results[3] in the case of an exciton system is not self-evident and these results may be even incorrect because in solids there is a possibility of going over from light scattering processes to luminescence for any nonzero value of $\Delta\Omega$ smaller than γ and this can occur as follows. During a time interval γ^{-1} there exist scattering complexes for which the absorption and luminescence processes are, in principle, indistinguishable.[5] The luminescence appearing before the completion of the relaxation processes is known as the hot luminescence. The ordinary luminescence is the radiation which appears after the relaxation is complete. It thus follows from Toyozawa's