SUPERCONDUCTIVITY OF COLD-DEPOSITED FILMS OF ALLOYS OF GERMANIUM WITH PLATINUM-GROUP ELEMENTS

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Superconducting modifications of alloys of germanium with platinum-group elements were found in the form of cold-deposited films of Ge-Pt and Ge-Pd alloys. The Ge-Pd system is used to investigate the dependence of the critical temperature on the composition and to measure the critical magnitude.

It is known that by condensation on cold substrates it is possible to obtain extremely unstable modifications of metals and alloys, many of which become superconducting. For example, cold-deposited films of the alloys of Ge with Cu, Ag, and Au are superconductors, although these alloys exhibited no superconductivity in the equilibrium state [1, 2].

We have investigated films of Ge alloyed with elements of the platinum group. The alloys were prepared from powders of the initial metals, with purity not worse than 99.97%.

The alloys were evaporated with a pulsed free-running neodymium laser. The films were condensed on a mica substrate in contact with liquid helium. Before the condensation, platinum contacts with which to measure the film resistance were deposited on the substrate. In some cases the films were evaporated not from a piece of the alloy, but from a compressed pellet of a mixture of the powdered metals. Within the framework of the experimental error, the T_c of such films did not differ from the T_c of films obtained by evaporation from a piece of alloy. Plots of the superconducting transition of the films could be obtained either by observing the change of the resistance or the change of the inductance of a coil placed near the film. The sample preparation and measurement procedure is described in greater detail in [1, 3].

From among the alloys of Ge with Ru, Os, Rh, Pd, and Pt, superconductivity was observed only in the systems Pd-Ge and Pt-Ge. The alloy films $Ru_{0.5}Ge_{0.5}$, $Os_{0.5}Ge_{0.5}$, and $Rh_{0.5}Ge_{0.5}$ were not superconducting down to 1.1°K.

The cold-deposited $Pt_{0.5}Ge_{0.5}$ films had T_c = 1.4°K, whereas the films heated to 300°K did not become superconducting down to 1.0°K. The dependence of T_c on the composition was traced for the Pd-Ge system, and is shown in Fig. 1[1)]. The abcissas show the batch composition of the alloy from which the film was prepared. The maximum value of T_c corresponds to the composition Pd_2Ge_3 and is equal to 3.1°K. Curve (a) corresponds to T_c of cold-deposited films, determined from the change of the resistance (circles) and from the change of the inductance (squares). The difference between the values of T_c obtained by these methods, as seen from

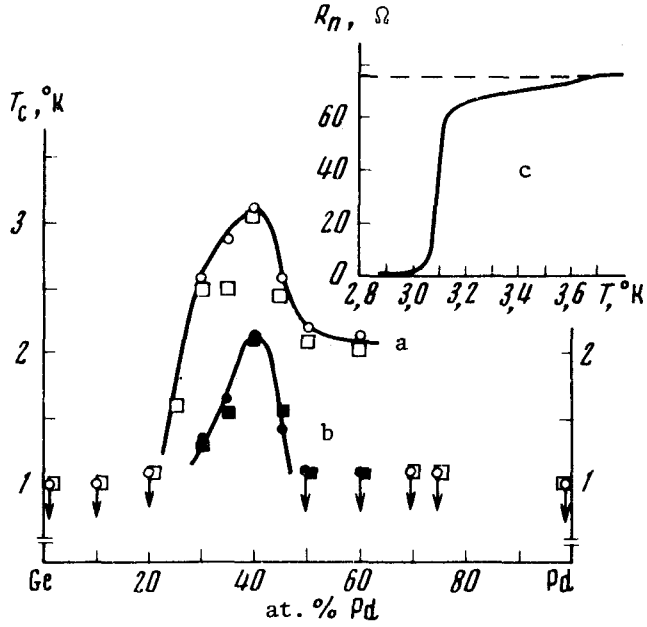

Fig. 1. T_c of Pd-Ge films vs the Pd concentration: a) T_c of cold-deposited films, determined by measuring the resistance (○) and the inductance (□). b) T_c of films after heating to 300°K, determined by measuring the resistance (●) and the inductance (■). c) Transition curve of cold-deposited Pd_2Ge_3 film. The points with arrows denote the temperatures down to which no superconductivity was observed.

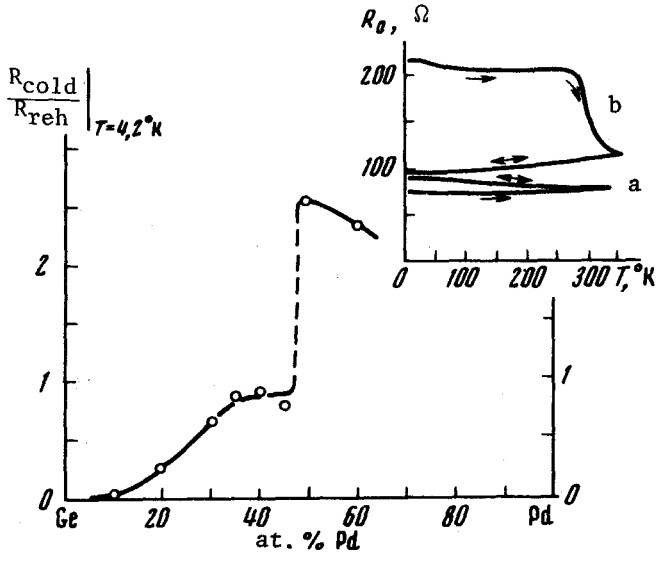

Fig. 2. Ratios of resistance of cold-deposited film to the resistance of the film after reheating to 300°K, taken at 4.2°K, vs. the Pd concentration, and the temperature dependence of the resistance of $Pd_{0.4}Ge_{0.6}$ (a) and $Pd_{0.6}Ge_{0.4}$ (b). The single and double arrows show the temperature dependences immediately after condensation and after reheating, respectively.

the figure, is not very large, but it should be noted that in measurements based on resistance the first deviations from R_n are observed at appreciably higher temperatures (in some cases 1.5° above T_c). In the upper right corner of Fig. 1 is shown the transition curve of one of the films with composition Pd_2Ge_3.

After being heated to 300°K, films containing from 30 to 50% Pd remained superconducting, but their critical temperatures were much lower than those of the cold-deposited films. The dependence of T_c of the annealed films on the composition is shown by curve b of Fig. 1. Here, too, just as in the case of cold-deposited films, the variation of the resistance begins at temperatures much higher than T_c.

Measurement of the film resistances at temperatures 4.2 - 300°K have shown that heating produces irreversible changes in the cold-deposited films. Figure 2 shows the ratio of the resistance of a cold-deposited film to the film resistance measured at 4.2° after heating the film to room temperature, as a function of the film composition. In the case of annealed films with Pd concentration less than 50%, the resistance exhibits a weak semiconductor-like variation. In the upper right corner of Fig. 2 is shown the temperature dependence of the resistance of a $Pd_{0.4}Ge_{0.6}$ film (curve a). The R(T) curve of reheated films with larger Pd contents show an abrupt change of resistance (Fig. 2, curve b for $Pd_{0.6}Ge_{0.4}$), which is apparently the consequence of the transition of the film into a stable modification. After reheating, these films did not become superconducting down to 1.0°K. We measured the critical magnetic fields perpendicular to the $H_{c\perp}$ plane for Ge_3Pd_2 films, by constructing the R(T) curves in different magnetic fields and plotting the function $H_{c\perp}$ (t), where T_c was defined, as before, to be the center of the transition. The $H_{c\perp}$ (T) plots were practically linear and $dH_{c\perp}/dT$ assumed values 6190 Oe/°K ± 5% for annealed films and 5760 Oe/°K ± 8% for cold-deposited ones. Measurements of the resistivity of the films with this composition have shown that $\rho = 0.78 \times 10^{-3}$ and 1.08×10^{-3} Ω-cm for cold-deposited and annealed films, respectively. The film thickness was determined with a quartz thickness gauge, and the film density was assumed to be [2] 8 g/cm³.

If we assume that $H_{c\perp} - H_{c2}$ (see, e.g., [4]) and use the formula [3]

$$\gamma = 2{,}2 \cdot 10^{-5} \frac{1}{\rho} \frac{dH_{c2}}{dT}, \qquad (1)$$

where γ is the coefficient in the linear law for the specific heat (erg/cm³deg²), ρ is the resistivity (Ω-cm), and H_{c2} is the critical field (gauss), then we get γ = 161 and γ = 127 erg/cm³deg² for the cold-deposited film and the film heated to 300°K respectively. A 20% change in γ is quite sufficient to explain why T_c of the reheated film decreases by a factor [4] 1.5. However, the absolute value of γ obtained from (1) should be treated with some caution, since the applicability of formula (1) to our case is not free of doubts.

On the basis of the presented data and of our earlier results, we can conclude that rapid condensation of vapor on a cold substrate results in the production of unstable phases in the systems Cu-Ge, Ag-Ge, and Au-Ge, as well as in the systems Pd-Ge and Pt-Ge. In some of the systems there exist at least two unstable modifications with different T_c (e.g., Au-Ge and Pd-Ge),

the compound with higher degree of instability having the higher critical temperature.

As already noted, the superconductivity may occur in non-equilibrium phases because the electron-phonon interaction parameter may turn out to be larger for these phases than for the equilibrium phases; this is apparently also the cause of their instability.

Unstable phases should probably be characterized by weaker interactions between the atoms in these phases, i.e., the quasielastic coupling constant should be smaller than in the stable phases. It can then be assumed that the average oscillation frequency in them is lower, and the average distance between the atoms is larger, than in the stable phases. The latter circumstance should lead to a smaller overlap of the electron ψ-functions, and consequently to the formation of narrower bands. These may be precisely the factors that play the major role in the onset of their superconductivity.

[1])T_c was defined as the midpoint of the transition curve.

[2])Naturally, the accuracy of the absolute value of ρ is governed by the validity of this assumption.

[3])This formula can be easily obtained from the Gor'kov formula [5] for χ and from the BCS expression for the jump of the specific heat.

[4])Indeed, following such a change of γ the difference in T_c should be larger than the observed one. It is not excluded that the actually observed smaller difference in T_c is a consequence of the low value of the Debye temperature of a freshly-condensed film.

[1] N. E. Alekseevskii, V. M. Zakosarenko, and V. I. Tsebro, ZhETF Pis. Red. 12, 228 (1970); 13, 412 (1971) [JETP Lett. 12, 157 (1970); 13, 292 (1971)].
[2] B. Stritzker and H. Wuhl, Z. Physik 243, 361 (1971).
[3] N. E. Alekseevskii and V. I. Tsebro, J. Low Temp. Phys. 4, 679 (1971).
[4] M. Tinkham, Phys. Rev. 129, 2413 (1963).
[5] L. P. Gor'kov, Zh. Eksp. Teor. Fiz. 37, 1407 (1959) [Sov. Phys.-JETP 10, 998 (1960)].

EMISSION OF ELECTRON-HOLE DROPS IN GERMANIUM AT 0.5°K

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We have investigated the radiative recombination of electron-hole (e-h) drops in pure Ge at 1.3 - 0.5°K, for the purpose of constructing the phase diagram of an electron-hole liquid and a free-exciton gas at 0.5°K. The threshold concentration of the excitons at which the e-h drops are produced at 0.5°K is estimated at $\lesssim 3 \times 10^{12}$ cm^{-3}. No new emission lines (e.g., exciton-molecule lines) were observed. The broadening of the e-h drop emission lines is attributed to the influence of deformations in the region of the condensation nuclei.

At temperatures 1.5 - 4.2°K there appears in the photoluminescence of pure Ge a new emission line of energy E_{max} = 708.5 meV [1], due to radiative annihilation of electron-hole (e-h) drops [2 - 4].

It is also known that a number of broad-band semiconductors (CuBr, CuCl, Cu_2O, CdSe) have in their emission spectra, at certain excitation levels, a line due to exciton-molecule