SUPERCONDUCTIVITY IN THE Ag—Ga *SYSTEM*

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It is shown that Ag—Ga alloys containing ≈ 30% Ga can become superconducting. The characteristic features of the superconducting properties and phase composition of these alloys are discussed.

GALLIUM alloys include a considerable number of superconductors, some of which become superconducting at quite high temperatures.[1] But, as far as the author is aware, alloys of gallium and silver have not as yet been investigated in this context, and therefore a study of the alloys of this system was undertaken.

According to the published data,[2] this system has two phases (ζ and ζ') near 30 at.% Ga, while at 60 at.% the existence of a δ-phase is postulated. The structures of these phases are as follows: ζ is hexagonal close-packed, a = 2.936 Å, c = 4.757 Å, c/a = 1.620; ζ' is hexagonal and isomorphous with the ζ-phase of Ag—Zn, a = 7.816 Å, c = 2.886 Å (the phases ζ and ζ' are sometimes called β and γ). The ζ and ζ' phases are n-type compounds, in which the number of electrons per atom should be 3/2.

Samples of alloys of the Ag—Ga system were prepared from pure Ag and Ga, for which the change in the resistance from room temperature to 4.2°K was $\rho_{300°}/\rho_{4.2°} \approx 1000$ for Ag, and about 10 000 for Ga. The samples were prepared by melting in a high-frequency furnace in quartz ampoules (some of the samples were melted in the flame of an oxygen torch). After melting, the samples were usually subjected to annealing.

We prepared alloys containing from 5 to 98 at.% Ga. The measurements of the magnetic moment, carried out on samples of these alloys, showed that the alloys containing from 20 to 70 at.% Ga and annealed at 220—270°C, had superconductor-type dependences of the magnetic moment on an external field. (The maximum value of the magnetic moment was exhibited by the alloys with 35 at.% Ga.) Superconductivity was not found in the alloys whose composition was outside the stated range. The alloys containing 60% Ga consisted of two phases and did not have the δ-phase structure, which, as mentioned in [3], was very difficult to obtain because of the narrow homogeneity region.

Figure 1 shows the dependences of the magnetic moment on an external field for one of the annealed samples of the 35% Ga alloy. To determine the critical temperature, we plotted the dependences $H_{c1}(T)$ (cf. Fig. 2), where H_{c1} was determined by the extrapolation of that part of the M(H) dependence in which M decreased linearly as the field increased. The characteristic feature of the investigated Ag—Ga alloy samples was, as is evident from Fig. 1, the lack of hysteresis in the curves representing the dependence of the magnetic mo-

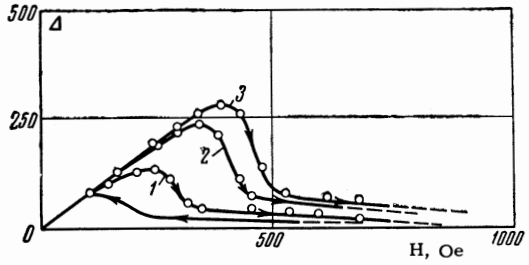

FIG. 1. Field dependence of the magnetic moment for one of the Ag–Ga alloy samples containing 35 at.% Ga: 1) T = 4.2°K; 2) T = 2.8°K; 3) T = 1.5°K (Δ denotes the deflection, in millimeters, on the scale of a ballistic galvanometer).

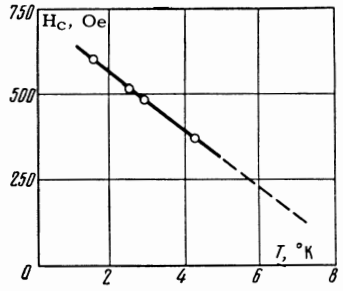

FIG. 2. Temperature dependence of H_{c1} for a sample of the Ag–Ga alloy containing 35 at.% Ga (the same as in Fig. 1).

ment on the external field; when the magnetic field was reduced, the return run curves were found to lag in the region near the critical field, usually due to supercooling. It should be mentioned that in some samples, after a time, a second, less sharp maximum appeared in the M(H) curve, which could be explained by a change in the phase composition of the sample.[4] For the majority of the samples, the values of T_c, estimated from the $H_{c1}(T)$ curve, were within the temperature range 6.5—8°K.

To determine directly the critical temperature, we measured the resistance in the intermediate range of temperatures. For this purpose, we used an apparatus having an additional internal Dewar flask, in which the temperature was varied by altering the degree of vacuum between the walls of the inner Dewar and the power supplied to the heater. To pump the space between the walls of the inner Dewar, we used a carbon sorption pump, placed in liquid helium.

Usually, no discontinuity was observed in the temperature dependence of the resistance r in the temperature range 6.5—8°K. Only the samples which underwent recrystallization had an r(T) dependence typical of a superconductor, but the region in which the resistance changed rapidly was close to 4°K (cf. Fig. 3).[1)]

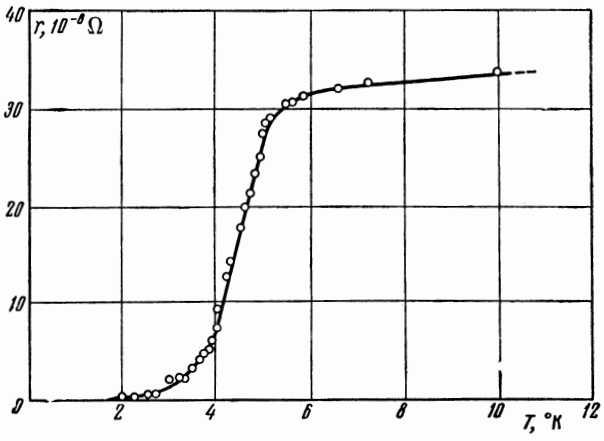

FIG. 3. Temperature dependence of the resistance for a sample of the 30 at.% Ga alloy, which has undergone crystallization.

Experiments on the determination of the magnetic moment were carried out also on a doubly-connected sample. In these experiments, an alloy sample was prepared in the form of a short thick-walled hollow cylinder. When the alloy resistance vanished, the M(H) curve should have been similar to the curve for a ring. It is evident from Fig. 4 that this was not so.

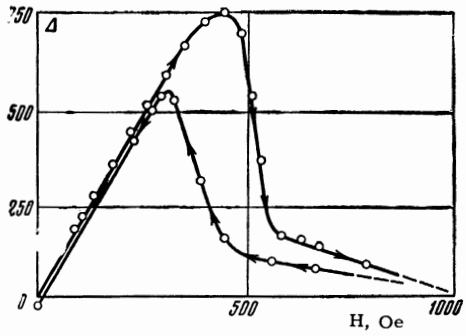

FIG. 4. Field dependence of the magnetic moment for a hollow cylinder made of the Ag–Ga alloy containing 30 at.% Ga.

Apart from alloys of the Ag—Ga system, we also investigated alloys with an admixture of a third component, and other n-type compounds, such as Ag_3In, $AgSi_2$ and Cu_3Ga. None of the investigated n-type compounds of other systems exhibited large values of the diamagnetic moment—characteristic of a superconductor—right down to 1.4°K.

In ternary alloys, in which 10 at.% Ga was replaced with In, Zn, or Sn, a sharp reduction in T_c to 4.2°K occurred only in the case of Sn, while the other two admixtures did not alter T_c greatly.

The appearance of superconductivity in the Ag—Ga system may be due to the fact that these alloys contain the finely dispersed β-Ga, which, as indicated by the data on freshly condensed Ga films,[5] becomes superconducting at a temperature close to the critical temperature of the investigated alloys of the Ag—Ga system. However, in this case, we would expect the samples, quenched from the liquid state, to have a high concentration of β-Ga, while in fact they had lower values of $|M|$ and in some cases did not become superconducting even at 1.6°K.

The determination of the temperature dependence of the resistance of the Ag—Ga alloys showed that the resistance decreased only by a factor of five in the range from room temperature to 4.2°K. The hypothesis most likely to be correct is that the very finely dispersed superconducting phase ζ' is surrounded by a nonsuperconducting, high-resistance shell. If the fraction of the normal phase decreases on cooling, the resistance decreases smoothly. This, in fact, is observed (cf. Fig. 3). It is also possible that a change in the fraction of the normal phase with the magnetic field is the cause of a quite strong dependence of r on H; this dependence is difficult to explain otherwise since a very small value of the mean free path, and,

[1)] The value of T_c corresponding to $\frac{1}{2}r(17°)$ amounted to ≈ 4.6°K, while the magnetic moments gave $T_c \approx 7.5$°K. According to the x-ray diffraction data, the main phase in all the samples was the ζ'-phase.

consequently, low values of the effective field, could only alter the resistance very slightly. Detailed investigations of the phase composition, which will be carried out in the near future, should make it possible to determine the true cause of the observed features of the properties of the Ag—Ga alloy system.

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[3] E. Hellner, Fortschritte der Mineralogie, Stuttgart, 1950, Vol. 29-30, p. 58.

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[5] W. Buckel and R. Hilsch, Z. Physik **138**, 109 (1954).

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