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THE EFFECT OF IMPURITIES ON THE PRESSURE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE OF THALLIUM. III

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The effect of an admixture of indium on the pressure dependence of the superconducting transition temperature of thallium is investigated. It is found that the effect of indium (which has the same valency as thallium) on the $T_c(p)$ dependence of thallium is similar to that of antimony and bismuth (the valency of which is greater than that of thallium). For thallium alloys containing 3.57 and 7.15 at.% of indium the dependence $T_c(p)$ is linear, the values of dT_c/dp being -1.5×10^{-5} and -1.6×10^{-5} deg/atm respectively; these values are close to that of pure thallium ($dT_c/dp = -1.4 \times 10^{-5}$) at pressures from 20,000 to 28,000 atm. The experimental data obtained confirm the previously expressed opinion[1, 3, 5] that the electron spectrum of thallium is sensitive to impurities and pressure.

In investigating the effect of impurities on the temperature of the superconducting transition (T_c) of thallium under pressure[1] it was noted that the pressure effect in thallium is sensitive to the valency of the impurity atom, and that even small concentrations of bismuth, antimony, and mercury change the sign of the shift of T_c under pressure from positive to negative.

It was important therefore to investigate the behavior of T_c of thallium on adding an impurity of the same valency as thallium. The results of an investigation of the effect of such an impurity (indium) under pressure are presented below.

THE SAMPLES AND THE METHOD OF MEASUREMENT

In the preparation of the solid solutions we used 99.9997% pure thallium [$r \equiv R(4.2°K)/R(300°K) = (1-2) \times 10^{-4}$], and indium of very high purity (better than 99.999%).

The alloys were prepared by a method described previously in [1]—by careful mixing of the solution in the liquid phase and prolonged annealing of the samples. Prolonged annealing (lasting several days) at 80–100°C made it possible to obtain in accordance with the thallium-indium diagram of state homogeneous hexagonal-phase samples. Thallium alloys with 7.15 at. % of indium were investigated. The homogeneity of the impurity distribution was borne out by the proportionality of the residual resistivity r and the impurity concentration (Fig. 1), the very small width of the superconducting transition, [$(2-3) \times 10^{-3}$; Fig. 2], and the monotonic variation of the lattice parameters with increasing concentration (see Fig. 7 below).

We note that because of a narrowing of the solubility region annealing at higher temperatures gives rise to precipitation of indium from the solid solution at the grain boundaries, and naturally under these circumstances the residual resistivity will not be proportional to the impurity concentration.[2]

The pressure was obtained, as previously,[1] by the ice method, using water and water-alcohol solutions. The measurements were differential: one sample was inside the bomb and the other outside.

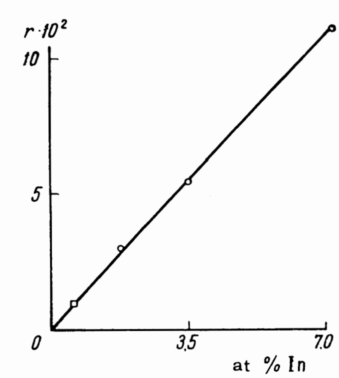


FIG. 1. The residual resistivity $r = R(4.2°K)/R(300°K)$ of thallium alloys as a function of the indium concentration: ○ – present work, □ – data from[2].

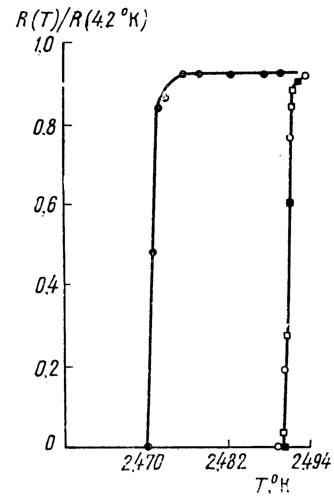


FIG. 2. Superconducting-transition curves of Tl – In alloy with r = 3.1×10^{-2}. The sample was placed inside a bomb: □ – p = 0, ● – p = 1730 kg/cm², ■ – p = 0 (after taking off the pressure); ○ – sample placed outside the bomb.

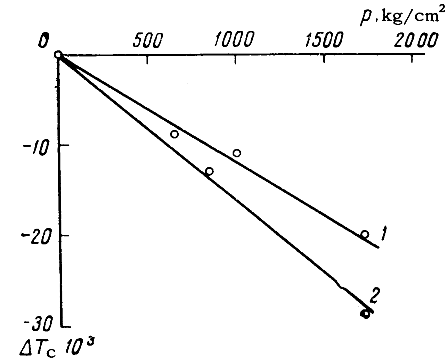
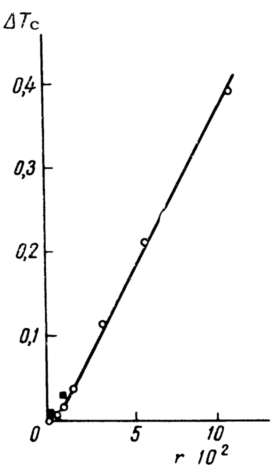


FIG. 5. Pressure dependence of ΔT_c of thallium. Curve 1 – thallium with a 3.57 at. % content of indium, 2 – thallium with a 7.15 at. % content of indium.



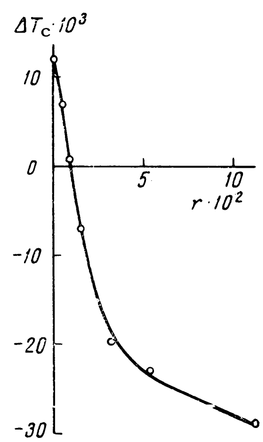


FIG. 3 FIG. 4

FIG. 3. The dependence of ΔT_c of thallium on the residual resistivity: ○ – present work, ■ – from[2].

FIG. 4. The dependence of ΔT_c of thallium on r at a pressure of 1730 kg/cm².

RESULTS OF THE MEASUREMENTS AND DISCUSSION

The dependence of the shift of the superconducting transition temperature ΔT_c of thallium-indium alloys on the residual resistivity is shown in Fig. 3.

Figure 4 shows the dependence of ΔT_c of thallium under a pressure of 1730 kg/cm^2 on the residual resistivity (on the impurity concentration). As can be seen from the figure, the indium impurity decreases immediately the positive effect of the pressure. An analogous dependence was observed in alloys of thallium with antimony and bismuth.[1]

The pressure dependence of ΔT_c for alloys of thallium and indium is presented in Fig. 5. It should be noted that the pressure dependence of ΔT_c for these alloys with an r of 3.1×10^{-2} and 11.2×10^{-3} is linear with values of dT_c/dp of $(-1.2 \pm 0.1) \times 10^{-5}$ and $(-1.6 \pm 0.1) \times 10^{-5}$ deg/atm respectively. These values are very close to the value of $dT_c/dp = -1.4 \times 10^{-5}$ deg/atm for pure thallium in the pressure range of 20,000–28,000 atm.[3]

In discussing the results of the effect of bismuth, antimony, and mercury impurities on the superconducting transition temperature of thallium under pressure, account was taken only of the valency difference between thallium and the impurity and the change of the unit-cell volume was neglected.[1] To explain the aggregate of all the experimental data it was assumed that an impurity whose valency is greater than that of thallium changes the electron density n = N/v (N is the number of electrons per unit volume) in the same direction as the pressure, whereas an impurity

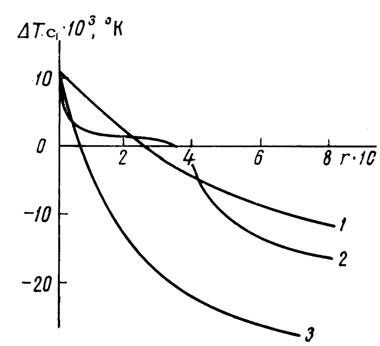


FIG. 6. Dependence of ΔT_c of thallium on r at a pressure of 1730 kg/cm²: curve 1 – thallium with an admixture of bismuth,[1] 2 – thallium with an admixture of antimony,[1] 3 – thallium with an admixture of indium.

whose valency is smaller than that of thallium changes n in the opposite direction to the pressure. On adding an impurity with the same valency as the main metal, the change in n is due solely to the change in the unit-cell volume.

It is seen from Fig. 6 that indium whose valency is the same as that of thallium influences the pressure effect in thallium qualitatively in the same way as impurities with a greater valency; therefore the volume of the unit cell of thallium should decrease on adding indium.

In order to verify this assumption, thallium-indium alloys with various impurity concentrations were studied with the aid of x-rays. The alloys were investigated by the back-reflection technique using copper radiation. The a and c parameters of the alloys were determined from the $K\alpha_1$ and $K\alpha_2$ doublets of the (125) and (206) lines. Pure thallium with a = 3.4565 Å and c = 5.5249 Å served as the standard.[4] The accuracy of the determination of a and c was $\pm 7 \times 10^{-4}$ Å.

The results of these investigations are presented in Fig. 7. It is seen that the a parameter decreases considerably more rapidly with increasing impurity concentration than the c parameter—the c/a ratio increases. The change in the volume of the metal ($-\Delta v/v$) with an indium content of 3.57 and 7.15 at.% is 1.54×10^{-3} and 3.94×10^{-3} respectively. With these volume changes dT_c/dp lies between the limits of $(1.2-1.6) \times 10^{-5}$ deg/atm. Such a value of dT_c/dp is observed in pure thallium at pressures of 20,000–28,000 atm [$\Delta v/v = (50-70) \times 10^{-3}$].

It is important that volume changes due to the impurities exert a considerably stronger influence on the $\Delta T_c(p)$ dependence in thallium than volume changes produced by uniform compression. This is apparently connected with the following circumstance. Because of the comparatively small anisotropy of the compressibility ($\kappa_c = 0.75\,\kappa_a$) a more uniform change of the lattice takes place in uniform compression than under the influence of the impurity, where with a practically unchanged c parameter all volume changes are due to changes in the a parameter. Such an action of the impurity is more effective in removing the nonlinear component of the effect of pressure in thallium.[1] As can be seen from Fig. 5, at low pressures a linear dependence, such as is observed in thallium at high pressures, is observed in thallium with an indium impurity. It is conceivable that the linear dependence of $\Delta T_c(p)$ is also preserved at considerably higher pressures.

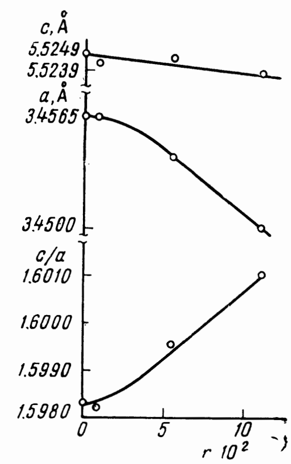


FIG. 7. Dependence of the lattice parameters a and c and of the c/a ratio on the indium concentration.

It appears that the results concerning the effect of an indium impurity on the pressure effect in thallium do not alter qualitatively the previously expressed view on the sensitivity of the electron spectrum of thallium to external—impurity and pressure—effects. However, to consider the effects of impurities with different valency on the transition temperature in thallium under pressure quantitatively, one must take into account the effect of volume changes brought about by these impurities.

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