SOVIET PHYSICS JETP VOLUME 21, NUMBER 4 OCTOBER, 1965

IMPURITY EFFECT IN THE PRESSURE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE OF THALLIUM. I

B. G. LAZAREV, L. S. LAZAREVA, V. I. MAKAROV, and T. A. IGNAT'EVA

Physico-technical Institute, Academy of Sciences, Ukrainian S.S.R.

Submitted to JETP editor November 20, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) **48**, 1065-1070 (April, 1965)

The effects of the valence and concentration of impurities on the pressure-induced shift of the superconducting transition temperature of thallium is investigated. Even small Bi, Sb, or Hg impurity concentrations can reverse the sign of the pressure effect in thallium, making it negative. The results indicate a complex energy dependence of the electron state density near the Fermi surface, and a sharp impurity effect in the energy spectrum of thallium conduction electrons.

THE superconducting transition temperature T_c is lowered by pressure in most superconductors (Sn, Cd, Pb, In etc.),[1] but in some, such as zirconium,[2] vanadium,[3] and titanium [1)] the transition temperature is elevated under pressure. Thallium exhibits still different behavior; at pressures up to 2000 kg/cm^2 we observe $dT_c/dP > 0$,[4] followed by a sign reversal at still higher pressures.[5]

Since the sign of dT_c/dP is reversed at relatively low pressures, it can be assumed that one of the parameters determining T_c for thallium is very sensitive to external influences. In addition, the superconducting transition temperature of thallium is more strongly influenced by the valence of impurities than in the cases of other superconductors.[6] In the present work we investigate the effects of different impurities on the pressure-induced shift ΔT_c of the superconducting transition temperature of thallium.

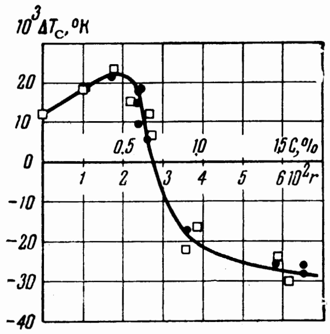


FIG. 1. ΔT_c versus $r = R(4.2°K)/R(300°K)$ for thallium-mercury alloys at 1730 kg/cm^2 pressure. The different symbols pertain to separately prepared series of samples.

SAMPLES AND EXPERIMENTAL TECHNIQUE

Our solid solutions were prepared with 99.998% pure thallium ($r \equiv R(4.2°K)/R(300°K) \sim (1-2) \times 10^{-4}$) and high-purity bismuth, mercury, and antimony. Thallium together with an impurity was melted in a test tube under a vacuum of $(1-2) \times 10^{-5}$ mm Hg. The melt was then sealed in a vial under the same vacuum and was maintained more than one day in an oven at a temperature above the melting point. After being homogenized by prolonged shaking the melt was cooled suddenly. Low-concentration alloys were prepared by the dilution of higher concentrations.

Wire samples 0.4 mm in diameter and 15—20 mm long were prepared by extrusion, and were annealed for several days at 80—100° C. The samples were of very good quality, having a homogeneous impurity distribution as indicated by the $(2-3) \times 10^{-3}$° K width of the superconducting transition.

High pressures were generated by the ice-bomb technique, using water and water-alcohol solutions,[7,8] with pressure monitoring in the vessel by a superconducting manometer of ±50 kg/cm^2 accuracy. The pressure effect was measured differentially, by a potentiometer method, using two samples, inside and outside of the pressure vessel, respectively.

RESULTS

A. Thallium-mercury. Figure 1 shows the dependence of ΔT_c, the shift of the superconducting

---

[1)] Reported by N. B. Brandt and N. I. Ginzburg at the Eleventh All-Union Conference on Low-Temperature Physics, Minsk, 1964.

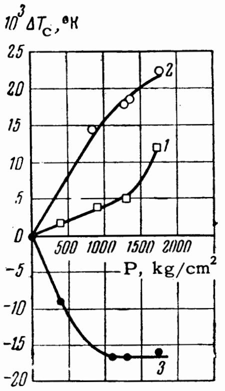


FIG. 2. Pressure dependence of ΔT_c for thallium alloyed with different concentrations of mercury. 1 – pure Tl; 2 – Tl + ~0.45 at% Hg ($r \sim 1.8 \times 10^{-2}$); 3 – Tl + ~0.9 at% Hg ($r \sim 3.6 \times 10^{-2}$).

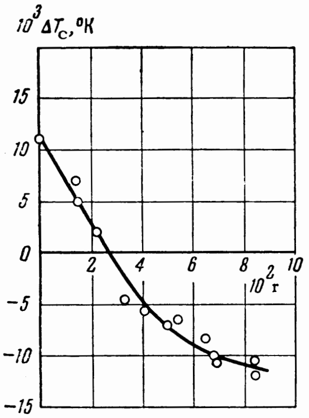


FIG. 3. ΔT_c versus r for thallium-bismuth alloys at 1730 kg/cm² pressure.

transition temperature of thallium-mercury alloys at a pressure of 1730 kg/cm², on the residual resistance r, which is a measure of the mercury concentration. With increasing r up to $\sim 2 \times 10^{-2}$ the pressure effect is seen to increase. With further increase of the impurity concentration the sign of the effect is reversed; comparatively little variation is observed in the range of r from $\sim 4 \times 10^{-2}$ to $\sim 6 \times 10^{-2}$.

Figure 2 shows the pressure dependence of ΔT_c for thallium alloyed with different concentrations of mercury in the pressure range 0–1730 kg/cm². It is noteworthy that the pressure dependence is nonlinear in this range.

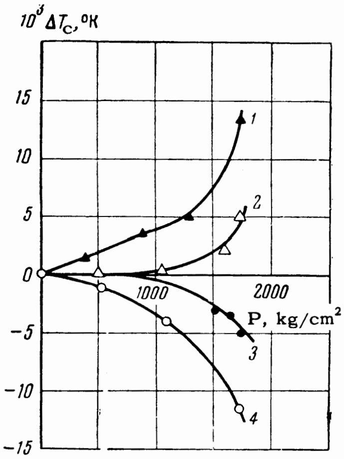


FIG. 4. Pressure dependence of ΔT_c for thallium alloys. 1 – pure thallium; 2 – Tl-Bi with $r = 1.5 \times 10^{-2}$; 3 – Tl-Bi with $r = 2.3 \times 10^{-2}$; 4 – Tl-Bi with $r = 6 \times 10^{-2}$.

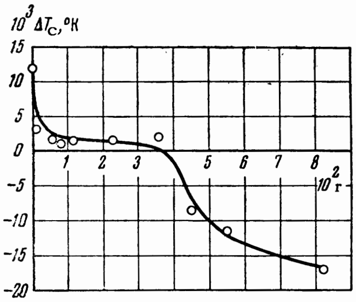


FIG. 5. ΔT_c versus r for thallium-antimony alloys at 1730 kg/cm² pressure.

B. Thallium-bismuth. Figures 3 and 4 show similar measurements for thallium-bismuth alloys. Unlike the thallium-mercury alloys, a thallium alloy containing a relatively small bismuth concentration, with $r = 1.5 \times 10^{-2}$ (~0.1 at% Bi), already exhibits a reduced pressure effect. Further increase of the bismuth concentration reverses the sign of the effect, as in the case of the thallium-mercury alloys.

Figure 4 shows that the pressure dependence of ΔT_c in the range 0–1730 kg/cm² for different bismuth concentrations is also nonlinear, but is of different character than for the thallium-mercury alloys.

C. Thallium-antimony. The pressure effect in thallium is even more strongly influenced by an admixture of antimony (Fig. 5). The pressure effect is reduced to 1.5×10^{-3}°K by as little as 0.02 at% Sb ($r \sim 3 \times 10^{-3}$), with almost no variation as the concentration is increased to ~0.22 at% Sb ($r \sim 3.5 \times 10^{-2}$). With still further increase of the impurity concentration the pressure effect becomes negative.

The pressure dependence of ΔT_c for the thallium-antimony alloys (with $r \sim 5.8 \times 10^{-2}$) in Fig. 6 resembles the analogous curve for a thallium-bismuth alloy in Fig. 4.

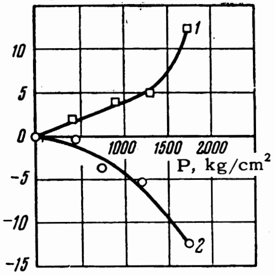


FIG. 6. ΔT_c versus pressure. 1 – pure thallium; 2 – Tl-Sb with $r = 5.8 \times 10^{-2}$.

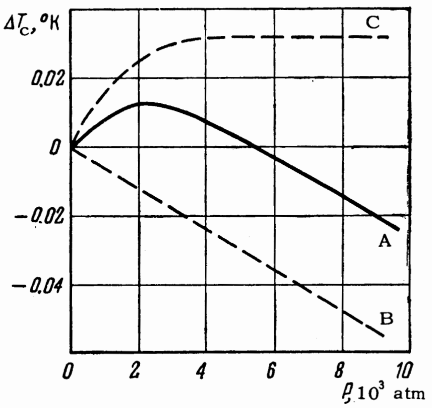
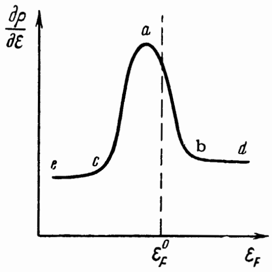


FIG. 7. Pressure dependence of ΔT_c for pure thallium[4] (curve A). Curves B and C are the linear and nonlinear components, respectively, of A.

FIG. 8. Variation of $\partial\rho/\partial\epsilon$ near $\epsilon_F{}^0$ ($\rho = V\partial N/\partial\epsilon$).



DISCUSSION OF RESULTS

Cody's hypothesis of anisotropic elastic moduli ($|S_{13}| > S_{11} + S_{12}$)[9] seems to be an interesting possible means of accounting for the behavior of thallium under pressure. However, subsequent experimental measurements of the elastic constants of thallium single crystals[10] have not confirmed the foregoing inequality, $|S_{13}| > S_{11} + S_{12}$.

We present here a different explanation of the anomalous behavior of thallium. The curve representing the pressure dependence of T_c for thallium[4] can be decomposed formally into two components:[11] a linear component having a negative slope $\partial T_c/\partial P$, and a nonlinear component having a positive slope at low pressures (Fig. 7). At the pressures used in the present work (up to 2000 kg/cm^2) the nonlinear component is more important; the pressure effect is also very sensitive to the impurity content.

A strong valence effect is evident even at low impurity concentrations. The pressure effect is enhanced (Fig. 1) by an impurity (mercury) of valence lower than that of thallium, whereas higher valences (bismuth and antimony) reduce the pressure effect (Figs. 3, 5). This influence of valence for low concentrations in the given pressure range suggests that impurities affect only the electronic properties of a metal through the parameters that determine the superconducting transition temperature:[12] $T_c \sim \Theta e^{-1/\rho}$, where Θ is the Debye temperature and $\rho = V\partial N/\partial\epsilon$. We have such parameters in the density of electronic states on the Fermi surface ($\partial N/\partial\epsilon$) and the electron-phonon interaction constant V. Therefore $\rho(\epsilon_F)$ in thallium is extremely sensitive to variations of energy (or electron density) near the Fermi level.

Only the second term in the equation

$$\frac{dT_c}{dP} = \frac{T_c}{\Theta}\frac{\partial\Theta}{\partial P} + \frac{T_c}{\rho^2}\frac{\partial\rho}{\partial P}$$

will be important for our subsequent discussion; this term is associated with the variation of electronic properties, i.e., the variation dT_c/dP depends on $\partial\rho/\partial P = (\partial\rho/\partial\epsilon)(\partial\epsilon/\partial P)$. Since $\partial\epsilon/\partial P$ is a slowly varying function of pressure,[13] the magnitude of $\partial\rho/\partial\epsilon$ near ϵ_F^0 is responsible for all the characteristics of dT_c/dP that are associated with the influence of impurities. Figure 8 shows the qualitative form of the dependence of $\partial\rho/\partial\epsilon$ on ϵ_F, representing the results of the present work and data for thallium reported in the literature.[4]

Both pressure and impurities change the electron density $n = N/v$, where N is the number of electrons in a volume v and n varies with either N or v. Hydrostatic compression reduces the volume v; this corresponds to an increase of n. With the addition of an impurity both v and N vary, the change of v being smaller than that of N (for the considered impurities, in any event). In this case the sign of the change in n depends on the valence of the impurity; a higher impurity valence increases n, while a lower valence reduces n. Since n depends on ϵ_F, the variation of n can be related to the variation of ϵ_F; for example, in the case of quadratic dispersion of conduction electrons we have $n \sim \epsilon_F^{3/2}$. We shall now consider our experimental results on this basis.

When an impurity (Bi, Sb) of higher valence than thallium is added, ϵ_F is enhanced, the derivative $\partial\rho/\partial\epsilon$ becoming smaller (segment Ob in Fig. 8). Experimentally this corresponds to a decrease of dT_c/dP. With further increase of the impurity concentration the linear mechanism of the pressure effect on T_c for thallium, with the negative value of $\partial T_c/\partial P$, begins to contribute, while the contribution of the nonlinear component is reduced and approaches a constant limit. This corresponds to the negative sign of the pressure effect (Figs. 3, 5) and the nearly constant derivative $\partial\rho/\partial\epsilon$ (segment bd in Fig. 8).

When the lower-valence impurity, mercury, is added the pressure effect is enhanced. This corresponds to a larger value of the derivative $\partial\rho/\partial\epsilon$ near ϵ_F^0 when the Fermi energy is reduced (segment Oa in Fig. 8).

With further increase of the impurity concentration, the pressure effect reaches its maximum and begins to decrease; this corresponds to the decrease of $\partial\rho/\partial\epsilon$ in segment ac of Fig. 8. At a still higher concentration the sign of ΔT_c is reversed and a constant value is approached (Fig. 1); this corresponds to segment ce of Fig. 8.

Therefore the way in which the pressure dependence of T_c for thallium varies with the kind and concentration of the impurity is represented by the complex dependence of ρ on energy near the Fermi surface (Fig. 8). One possible cause would be an electron transition in thallium, i.e., a transition through a critical energy in the electron spectrum that is close to ϵ_F^0.[13]

If the electron transition is the main mechanism, we can expect it to affect other electronic properties of the metal, such as galvanomagnetic properties and the electronic component of the thermal expansion coefficient.[13] These ideas can be developed greatly by investigating impure thallium at much higher pressures.

The authors wish to thank V. G. Bar'yakhtar for a discussion of the results.

---

[1] J. L. Olsen and H. Rohrer, Helv. Phys. Acta **33**, 872 (1960).

[2] N. B. Brandt and N. I. Ginzburg, JETP **46**, 1216 (1964), Soviet Phys. JETP **19**, 823 (1964).

[3] G. K. White, Cryogenics **2**, 292 (1962).

[4] Kan, Lazarev, and Sudovtsov, DAN SSSR 69, 173 (1949).

[5] L. D. Jennings and C. A. Swenson, Phys. Rev. **112**, 31 (1958); D. H. Bowen and G. O. Jones, Proc. Roy. Soc. (London) **A254**, 522 (1960).

[6] Lazarev, Lazareva, Makarov, and Ignat'eva, JETP **46**, 829 (1964), Soviet Phys. JETP **19**, 566 (1964).

[7] B. G. Lazarev and L. S. Kan, JETP **14**, 463 (1944).

[8] N. B. Brandt and A. K. Tomashchik, PTÉ No. 2, 113 (1958).

[9] G. D. Cody, Phys. Rev. **111**, 1078 (1958).

[10] Ferris, Shepard, and Smith, J. Appl. Phys. **34**, 768 (1963).

[11] Kan, Lazarev, and Makarov, JETP **40**, 457 (1961), Soviet Phys. JETP **13**, 317 (1961).

[12] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957).

[13] I. M. Lifshitz, JETP **38**, 1569 (1960), Soviet Phys. JETP **11**, 1130 (1960).

Translated by I. Emin
154