Effect of impurities and pressure on the superconducting transition temperature of thallium. V

T. A. Ignat'eva, V. I. Makarov, and Yu. A. Cherevan'

Physico-technical Institute, Ukrainian Academy of Sciences

(Submitted June 25, 1973; resubmitted April 11, 1974)
Zh. Eksp. Teor. Fiz. 67, 994–1005 (September 1974)

The effect of impurities of different valencies and of pressures up to 12 katm on the T_c of thallium is investigated in ternary solid solutions (thallium containing impurities of mercury and indium). It is shown that investigation of ternary solid solutions makes it possible to experimentally separate and estimate the contributions of two possible nonlinear mechanisms whereby they affect T_c, one due to a reduction in the anisotropy of the electron-electron interaction in the scattering of electrons by impurities, and the other due to changes in the topology of the Fermi surface.

At the present time there exist rather detailed experimental data on the effect of impurities on the superconducting transition temperature of nontransition metals.[1] For the majority of investigated metals, for example, for Al, Sn, and In, the nonlinear reduction of the superconducting transition temperature under the influence of impurities is qualitatively explained by a decrease in the anisotropy of the effective electron-electron interaction parameter associated with the scattering of electrons by impurities.[2] However, in connection with an investigation of certain ternary solutions of thallium (a metal containing two impurities) it was found that the dependence of the superconducting transition temperature on the impurity concentration ($T_c(C)$) for this metal cannot be attributed to this mechanism only.[3-5]

Detailed investigations of the combined effect of impurities and pressure on T_c for thallium indicated that the experimentally observed maximum of the derivative $\partial T_c/\partial P(C)$ and the nonlinear dependence $T_c(P)$, which are correlated among themselves, can be attributed to a change in the topology of the Fermi surface of the metal.[6-8] Since in the present case both pressure and impurity are considered as parameters which change the Fermi energy of the metal, one would naturally also expect a manifestation of this same mechanism in the $T_c(C)$ dependence.

Therefore, in studying the effect of impurities on the superconducting transition temperature of metals, experimental separation of the two possible mechanisms for the effect of impurities on T_c is essential: one mechanism is due to a decrease in the anisotropy of the effective electron-electron interaction parameter,[2] and the other mechanism is due to a change in the topology of the Fermi surface under the influence of impurities.[5, 7] As is shown in the present work, it is possible to separate these two mechanisms in an investigation of $T_c(C)$ for different ternary solutions. In addition, in this work detailed experimental data is obtained on the $T_c(P)$ dependences for thallium containing various impurities over a wide range of pressures (0 to 12,000 atm), enabling us to make a quantitative comparison of theory with experiment. Numerical values of the parameters, describing the nonlinear mechanisms for the effect of impurities and pressure on the superconducting transition temperature of thallium, are obtained as a result of the comparison of the experimental data with theory.

1. SAMPLE PREPARATION AND MEASUREMENT PROCEDURE

In this work the effect of impurities on T_c was investigated in solid solutions of Tl-Hg-In$_x$ and Tl-Hg-Sb$_x$, and the effect of pressure on T_c was studied over a range of pressures from 0 to 12,000 atm for the following solutions: Tl-Hg containing 0.5, 0.9, and 1.2 at.% mercury, Tl-In(0.5 at.%), and Tl-Hg(1 at.%)-In(0.5 at.%). The subscript x indicates that the amount of impurity in the investigated solutions is a variable parameter. The measure of the impurity concentration (C) is the residual resistance of the samples, $r = R_{4.2^\circ K}/R_{300^\circ K}$. For each of the impurities, the dependence of r on C is linear[9] in the range of concentrations investigated, which corresponds to the solid-solution range. The residual resistance of a ternary solution is equal to the sum of the residual resistances of binary solutions containing the same amount of each impurity. X-ray investigations of such solutions also attest to the single phase nature of the investigated solutions.

The samples were prepared in the same way as described earlier (see[3]). On a base of initial, binary alloys of Tl-Hg containing 0.7 and 1 at.% Hg impurities, a collection of ternary alloys containing variable concentrations of In or Sb impurities was prepared. The maximum content of In or Sb impurity was 3.5 or 0.55 at.%, respectively. Samples obtained by extrusion through a hole were annealed at a temperature of 80 to 100°C for a period of several days. The width of the superconducting transition, 2 to 3 mK, attests to the uniform distribution of the impurities and the absence of internal stresses in the samples.

An improved design[10] of the high pressure bomb[11] was used for the creation of pressures in the range from 0 to 12,000 atm. A plunger made of nonmagnetic material-sintered pure tungsten carbide–was used for precision measurements of T_c in the high pressure chamber.

The pressure created in the bomb was determined with a superconducting In-Tl (13 at.%) manometer with $\partial T_c/\partial P = 4.2 \times 10^{-5}$ deg/atm. The superconducting pressure gauge was first calibrated against a manganin manometer in the pressure range from 0 to 10,000 atm. The superconducting transition temperature of the indium manometer was measured to an accuracy of ± 2 to 3 mK. This allowed us to determine the pressure with an accuracy no worse than ± 0.1 katm over the entire range of pressures investigated. The constancy of the width of the superconducting transition, 2 to 5 mK, under pressure and without pressure attests to the uniformity of the created pressure.

The measurements were carried out by a potentiometer method. The change in the superconducting transition temperature (ΔT_c) under pressure was determined relative to a sample kept constantly under zero pressure outside the bomb according to the vapor pressure of liquid helium, with the aid of an oil manometer. The differential method of measurement allowed us to eliminate the error associated with the different level of helium in different experiments.

2. RESULTS OF THE MEASUREMENTS

A. The $\Delta T_c(r)$ dependence for ternary solid solutions of thallium. The experimental data on the $\Delta T_c(r)$ dependences for solid solutions of Tl-Hg-In$_x$ (Fig. 1b) and Tl-Hg-Sb$_x$ (fig. 2a) are shown in Figs. 1b and 2a. These dependences are plotted from the corresponding points of the $\Delta T_c(r)$ dependence for the binary Tl-Hg solution.

An increase of T_c, starting with very small concentrations of the indium or antimony impurities, is observed in the $\Delta T_c(r)$ dependences of the investigated ternary solid solutions with a mercury impurity content of 0.7 at.% (curve 2 of Fig. 1b, curve 2 of Fig. 2a). A change of the initial content of mercury impurity in ternary solutions to 1 at.% leads to the appearance of a nonlinearity in the initial segment of the dependence $\Delta T_c(r)$ for small admixtures of the other impurity (curve 3 in Fig. 1b). Upon a further increase in the concentration of indium or antimony impurities in the solutions Tl-Hg-In$_x$ and Tl-Hg-Sb$_x$, the dependences $\Delta T_c(r)$ of the investigated ternary and binary–Tl-In$_x$ and Tl-Sb$_x$–solutions become similar to each other in the region of large concentrations, with slightly differing derivatives $\partial T_c/\partial r$ (curves 1–3 in Fig. 1b, curves 1 and 2 in Fig. 2a). The observation of a nonlinear increase of ΔT_c with increasing r is significant in the obtained experimental result for ternary solutions of Tl-Hg with variable concentrations of In or Sb impurities.

The previously investigated[3] dependences $\Delta T_c(r)$ for solid solutions of Tl-In-Hg$_x$ and Tl-Sb-Hg$_x$ are presented on these same figures for comparison (curves 2, 3, 4 of Fig. 1a, and curves 2, 3, and 4 of Fig. 2b). These dependences are plotted from the corresponding points of the $\Delta T_c(r)$ dependences for the binary solutions Tl-In$_x$ and Tl-Sb$_x$ (curve 1 of Fig. 1a, and curve 1 of Fig. 2b). Here a nonlinear decrease of $\Delta T_c(r)$ is observed in the ternary solid solutions.

It is interesting to note that ternary solid solutions on a base of thallium with one and the same admixtures (Hg, In, Sb), differing only by variable components–in one case In or Sb (curves 2, 3 of Fig. 1b, curve 2 of Fig. 2a), in the other case Hg (curves 2, 3, 4 of Fig. 1a, curves 2, 3, 4 of Fig. 2b)–have different signs of the variation $\Delta T_c(r)$.

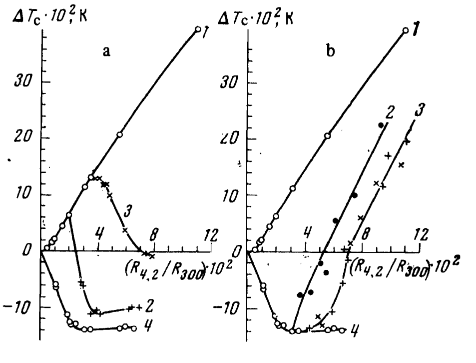

FIG. 1. The dependence of ΔT_c on r for solid solutions of thallium: a) 1–Tl-In$_x$, 2–Tl-In (1 at.%)-Hg$_x$, 3–Tl-In (2 at.%)-Hg$_x$, 4–Tl-Hg$_x$; b) 1–Tl-In$_x$, 2–Tl-Hg (0.7 at.%)-In$_x$, 3–Tl-Hg (1 at.%)-In$_x$, 4–Tl-Hg$_x$.

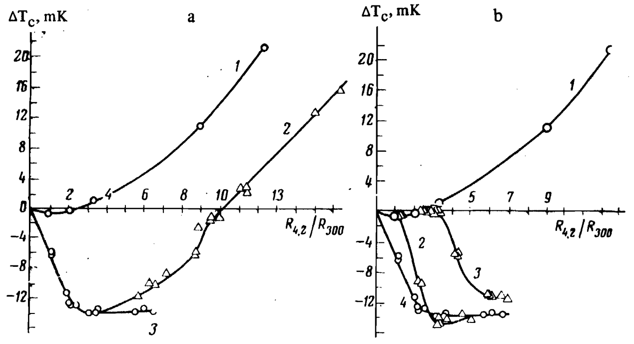

FIG. 2. The dependence of ΔT_c on r for solid solutions of thallium: a) 1–Tl-Sb$_x$, 2–Tl-Hg (0.7 at.%)-Sb$_x$, 3–Tl-Hg$_x$; b) 1–Tl-Sb$_x$, 2–Tl-Sb (0.042 at.%)-Hg$_x$, 3–Tl-Sb (0.084 at.%)-Hg$_x$, 4–Tl-Hg$_x$.

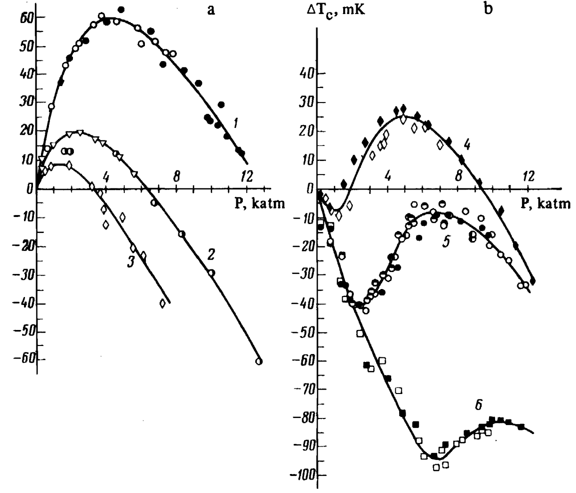

FIG. 3. The dependence of ΔT_c on the pressure P for solid solutions of thallium: a) 1–Tl-Hg (0.45 at.%), 2–pure Tl, [12] 3–Tl-In (0.5 at.%); b) 4–Tl-Hg (1 at.%)-In (0.5 at.%); 5–Tl-Hg (0.9 at.%); 6–Tl-Hg (1.2 at.%).

These experimental results indicate that in the present case it is not the change of the electron mean free path upon the addition of impurities which is important, but the change of the electronic concentration in the metal.

B. The $\Delta T_c(P)$ dependence for thallium containing impurities. The results of investigations of binary solid solutions of Tl with an impurity content of 0.45, 0.9, and 1.2 at.% Hg, with an impurity content of 0.5 at.% In, and of ternary solid solutions Tl-Hg(1 at.%)–In(0.5 at.%) under pressure are shown in Fig. 3. It is not difficult to observe that the $\Delta T_c(P)$ dependence for the solid solution Tl-Hg (0.9 at.%)[1] (curve 5 in Fig. 3b) contains all of the characteristic features inherent in the $\Delta T_c(P)$ dependences for other solutions: the practically linear decrease of ΔT_c in the region of small pressures (curves 4, 5, 6 of Fig. 3b), the section of an abrupt increase of ΔT_c, containing an inflection point (curve 1 in Fig. 3a, curves 4, 5, 6 of Fig. 3b), and the smooth decrease of ΔT_c associated with a further increase of the pressure.

It is clear from the cited figure that the $\Delta T_c(P)$ dependences for Tl solutions with a small amount of Hg impurities (0.45 at.%), with In impurities, and pure Tl (curves 1, 2, 3 of Fig. 3a) actually represent a portion of the more general $\Delta T_c(P)$ dependence under consideration (curve 5 of Fig. 3b). It should be emphasized that the most important feature in the graphs is the inflection point in the $\Delta T_c(P)$ dependences and, consequently, the presence of a maximum in the derivative $\partial T_c/\partial P(P)$, but not a maximum in the $\Delta T_c(P)$ dependences, which is a consequence of the combination of the two constituents–linear and nonlinear.[13]

The result for the ternary solid solutions Tl-Hg(1 at.%)-In(0.5 at.%) is interesting. Here the concentrations of the In and Hg impurities are chosen such that the dependence was unchanged in comparison with the solution Tl-Hg (0.9 at.%) (these curves can be superimposed), whereas the residual resistance increased by a factor 1.5.

3. DISCUSSION OF THE RESULTS

Before proceeding directly to a discussion of the experimental results (Figures 1–3), let us recall the fundamental mechanisms for the effect of impurities and pressure on the superconducting transition temperature. As is well known, in addition to linear changes of T_c as a function of the impurity concentration or pressure, which are due to linear corrections to the parameters which determine the superconducting transition temperature,[14] nonlinear corrections to T_c exist due to nonlinear mechanisms for the effect of impurities and pressure on T_c. At the present time it is known that the nonlinear variations of T_c under pressure can be related to a change in the topology of the Fermi surface.[6, 7] Whereas the effect of impurities on T_c may lead to the appearance of two nonlinear mechanisms, one of which is related to a change in the topology of the Fermi surface,[5] and the other is related to a decrease in the anisotropy parameter of the electron-electron interaction.[2] Therefore, in the general case one can write T_c as a function of the impurity concentration C and the pressure P in the form

$$T_c(P, C_1, C_2)={}^1/_2\tilde{v}T_c{}^0J(\tilde{\beta})-\langle a^2\rangle J_c(\chi) \\ +T_c{}^0(KP+K_1C_1+K_2C_2)+T_c{}^0, \tag{1}$$

where

$$\tilde{v}=\pm v, \quad \tilde{\beta}=\pm\beta, \quad \beta=(\varepsilon_F-\varepsilon_{\text{к}})/2T_c{}^0; \\ \chi=\lambda_1C_1+\lambda_2C_2, \quad v=\delta\nu(\varepsilon_c+2T_c{}^0)/\nu_0(\varepsilon_F),$$

T_c^0 denotes the superconducting transition temperature of the original metal, ϵ_F is the Fermi energy, and ϵ_c is the critical energy at which the change in the topology of the Fermi surface takes place. The quantity v characterizes the relative change in the density of the electronic states associated with the change in the topology of the Fermi surface, when $\epsilon_F = \epsilon_c + 2T_c^0$;[5] the λ_i take into account the transverse anisotropy of the scattering of the i-th impurity[2]; $\langle a^2\rangle$ denotes the root-mean-square deviation of the gap anisotropy; and the K_i are the coefficients associated with the linear terms. The quantities $J(\beta)$ and $J_c(\chi)$ in expression (1) have the following form:[2, 7]

$$J(\beta)=\int_{-\beta}^{\infty}|K(0,t_c^0y)|^2(\beta+y)^{1/2}\frac{\operatorname{th} y}{y}dy,$$

$$t_c^0=\frac{2T_{\text{к}}{}^0}{\omega_D}, \quad J_c(\chi)=\int_0^{2\omega_D/T_c\chi}\frac{dy}{y}\frac{\operatorname{th}(\chi y/4)}{1+y^2},$$

where K(0, x) is the kernel of the effective electron-electron interaction, which in the Fröhlich-Debye model[20] is determined by the formula

$$K(0, x)=1-2x+2x^2\ln(1+1/|x|).$$

The tabulated values of the functions $J(\beta)$ and $J_c(\chi)$ are presented in Figs. 4 and 5.

In the subsequent comparison of the experimental data with the theory we shall assume that the quantity $\tilde{B}$ depends linearly on the impurity concentration and on the pressure, that is,

$$\tilde{\beta}(P,C)=\tilde{\beta}_0+\frac{\partial\tilde{\beta}}{\partial C}C+\frac{\partial\tilde{\beta}}{\partial P}P$$

or

$$\tilde{\beta}(P)=\tilde{Z}(P-P_c), \quad \tilde{\beta}(C_i)=\tilde{Z}_i(C_i-C_c^i), \\ \tilde{\beta}(P, C_i)=\tilde{Z}(P-(P_c-\alpha_iC_i)), \quad \tilde{Z}=\pm Z, \quad \tilde{Z}_i=\pm Z_i, \tag{2}$$

where

$$Z=\frac{\partial(\varepsilon_F-\varepsilon_c)}{\partial P}, \quad Z_i=\frac{\partial(\varepsilon_F-\varepsilon_c)}{\partial C_i}=\alpha_iZ, \\ P_c=-\beta_0/Z, \quad C_c^i=-\beta_0/Z_i,$$

P_c denotes the critical pressure at which the topology of the Fermi surface is changed; C_c^i are the critical concentrations at which the topology of the Fermi surface changes; Z denotes the rate of change of the energy difference $(\epsilon_F-\epsilon_c)$ under the influence of pressure; Z_i denotes the rate of change of the energy difference $(\epsilon_F-\epsilon_c)$ under the influence of the i-th impurity. The ± signs associated with the quantities $\tilde{v}$ and $\tilde{\beta}$ take the four types of topological transitions into account. If $\tilde{Z} > 0$, either the formation of a new cavity of the Fermi surface ($\tilde{v} > 0$) or the transformation of an open surface into a closed one ($\tilde{v} < 0$) occurs upon an increase of ϵ_F. If $\tilde{Z} < 0$, either the vanishing of a small cavity of the Fermi surface ($\tilde{v} > 0$) or the transformation of a closed surface into an open one ($\tilde{v} < 0$) occurs upon increase of the Fermi energy.

The first term in expression (1) takes the effect of impurities and pressure on the electronic spectrum of the metal into account–that is, the change of the quantity $\epsilon_F-\epsilon_c$ under the influence of impurities or pressure[5, 7] –and may be expressed as a nonlinear decrease or a nonlinear increase in T_c. An important role is played here by how the Fermi energy of the metal varies under the influence of impurities or pressure–whether it increases (positive effective valence[2] of the impurity or hydrostatic pressure) or decreases (negative effective valence of the impurity). This must correlate with the sign of the variation of T_c as a function of P or C. The nonlinearity in the region of small concentrations or pressures with an inflection point and a smooth variation in the region of large concentrations or pressures is characteristic for such dependences.

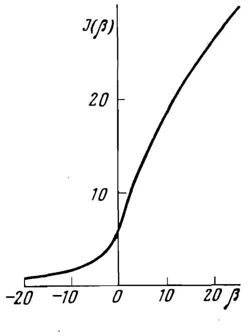

FIG. 4

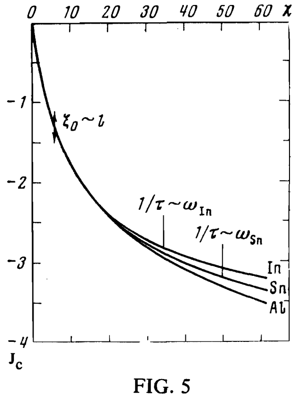

FIG. 5

FIG. 4. Theoretical $J(\beta)$ dependence in the Fröhlich-Debye model.
FIG. 5. Theoretical $J_c(\chi)$ dependence.

The second term in expression (1) takes the impurity into account only as a scattering center, and this leads to a nonlinear decrease of T_c, associated with the decrease in the anisotropy of the electron-electron interaction upon scattering of the electrons by impurities. For this mechanism the value of the nonlinear component of T_c is determined by the total residual resistance of the solution and does not depend on the valence of the doping impurities.[2]

Let us first discuss the experimental data, attesting to the appearance of only one nonlinear mechanism in T_c related to a change in the topology of the Fermi surface–this is the dependence $T_c(P)$ in solid solutions of Tl.

A. The $T_c(P)$ dependence for solid solutions of Tl-Hg, Tl-In, and Tl-Hg-In. It is not difficult to see from expression (1) that the experimentally observed difference $\Delta T_c(P, C) = T_c(P, C) - T_c(0, C)$ is, just like the relation $\Delta T_c(P) = T_c(P) - T_c(0)$, determined by only one nonlinear mechanism. In fact, by taking expression (2) into account, from expression (1) we obtain

$$\begin{aligned}\Delta T_c(P, C) = {}&{}^1/_2 T_c{}^0 \tilde{v} J\{\tilde{Z}[P-(P_c-\alpha C)]/2T_c{}^0\}\\ &-{}^1/_2 T_c{}^0 \tilde{v} J\{-\tilde{Z}(P_c-\alpha C)/2T_c{}^0\} - KP.\end{aligned} \tag{3}$$

If a function of a single variable, $\Delta T_c'(P^*)$, is introduced such that

$$\begin{aligned}\Delta T'(P^*) = {}&{}^1/_2 T_c{}^0 \tilde{v} J\{\tilde{Z}(P^*-P_c)/2T_c^0\}\\ &-{}^1/_2 T_c{}^0 \tilde{v} J\{-\tilde{Z}P_c/2T_c^0\} + KP^*,\end{aligned} \tag{4}$$

expression (3) can be represented in the form

$$\Delta T_c(P, C) = \Delta T_c'(P+\alpha C) - \Delta T_c'(\alpha C).$$

Thus, the function of two variables, $\Delta T_c(P, C)$, is expressed in terms of a function of a single variable, $\Delta T_c'(P^*)$. The argument P^* of this function may take either positive or negative values.

Thus, the plots $\Delta T_c(P)$ for different impurity concentrations correspond to separate segments of a single curve $\Delta T_c'(P^*)$ which are displaced along the pressure axis by the amount αC, and displaced along the temperature axis by $\Delta T_c(\alpha C)$. Therefore, the impurity plays the role of a certain effective pressure, changing the position of the energy ϵ_F with reference to the critical value ϵ_c.

Thus, the experimental $\Delta T_c(P, C)$ dependences for thallium containing different impurities (Fig. 3) can be represented as a single curve $\Delta T_c'(P^*)$. To do this it is necessary, by comparing the experimental data with theory, to determine the values of the parameters appearing in formula (3). The values of these parameters found by the method of least squares on an ÉVM-220 computer are as follows: $\tilde{v} = (13.5 \pm 3) \times 10^{-3}$, $K = (-24.5 \pm 0.05) \times 10^{-3}$ deg/katm, $P_c = -2.6 \pm 0.3$ katm, $C_c = 0.43 \pm 0.02$ at.% Hg, $\tilde{Z} = (5.4 \pm 0.6) \times 10^{-4}$ eV/katm, $\tilde{Z}_{Hg} = -(3.3 \pm 0.4) \times 10^{-3}$ eV/at.%, and $\tilde{Z}_{In} = (2.7 \pm 0.5) \times 10^{-3}$ eV/at.%.

The theoretical dependence $\Delta T_c'(P^*)$, corresponding to the found values of the parameters, is depicted in Fig. 6. The experimental points pertaining to Fig. 3 and previously published data[12] are presented in this figure. As is clear from Fig. 6, good agreement is observed between theory[7, 8] and experiment.

From the data presented above (the values of the parameters $\tilde{Z}$ and $\tilde{Z}_i$) it follows that the impurity In and the pressure change the difference $(\epsilon_F - \epsilon_c)$ in one direction, and the impurity Hg changes it in the opposite direction. This corresponds to the experimental data in Fig. 3. The signs of the parameters $\tilde{v}$ and $\tilde{Z}$ enable us to conclude that, for pure thallium there exists a small cavity in the Fermi surface which grows under pressure and vanishes under the influence of an impurity of small valence (Hg). For each metal the quantity $\epsilon_F - \epsilon_c$ is determined by its electronic structure. In order to change the topology of the Fermi surface it is necessary that the difference $\epsilon_F - \epsilon_c$ tends to zero.

However, it may be found that this difference increases under the influence of pressure, which is realized in the case of Tl. Then, for the observation of a change in the topology of the Fermi surface under pressure it is necessary to introduce into the metal an impurity for which the sign of the derivative $\partial(\epsilon_F - \epsilon_c)/\partial C$ will be opposite to the sign of the derivative $\partial(\epsilon_F - \epsilon_c)/\partial P$. Hg is such an impurity for Tl. Under the influence of Hg impurities, the value of ϵ_F for Tl may become smaller than ϵ_c (for Tl-Hg (0.9 at.%) and Tl-Hg (1.2 at.%) solutions), and the existing small cavity in the Fermi surface disappears. Then, if pressure is applied to such a solid solution, the difference $\epsilon_F - \epsilon_c$ passes through zero, and the appearance of a small cavity in the Fermi surface is observed. This corresponds to the nonlinear dependence $\Delta T_c(P, C)$ with the inflection point $\epsilon_F \approx \epsilon_c$ (Fig. 3, curves 4, 5, 6) and the maximum of the derivative $\partial T_c/\partial P(P)$ at $\epsilon_F \cong \epsilon_c$.

The experimentally observed $\Delta T_c(P, C)$ dependences for the investigated solutions (Fig. 3) are determined by the ratio of the magnitudes of the linear and nonlinear components. The contribution of the nonlinear component is determined by the difference $\epsilon_F - \epsilon_c$, which is different in different solutions. Therefore, the nonlinear $\Delta T_c(P, C)$ dependences have a different shape (Fig. 3.) for different solutions, appearing, however, as part of the overall $\Delta T_c(P^*)$ dependence (Fig. 6). Thus, in order to observe changes in the topology of the Fermi surface in regard to nonlinear superconducting characteristics, it is necessary to have two parameters, which change ϵ_F in opposite directions. In the investigation of the $\Delta T_c(P, C)$ dependences these were the pressure (hydrostatic stress) and the impurity Hg of smaller valence. However, as the two parameters which change ϵ_F of the metal in opposite directions, one can use two impurities of different effective valences (for example, In and Hg,

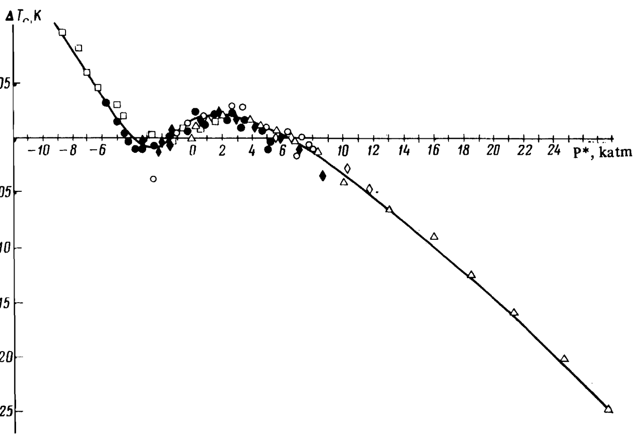

FIG. 6. The $T_c(P^*)$ dependence for thallium. The solid curve represents the theory, the points correspond to experiment: ○, ◇, ◆, ●, □ correspond to curves 1, 3, 4, 5, 6 of Fig. 3; △ corresponds to the results of article [12].

Sb and Hg) and observe the change in the topology of the Fermi surface according to the nonlinear $\Delta T_c(C)$ dependences in ternary solid solutions.

B. The dependence $T_c(C)$ for solid solutions of Tl. Let us examine how the nonlinear mechanisms for the effect of impurities on T_c[2, 5] manifest themselves in Tl. In order to compare the experimental data of Figs. 1 and 2 with theory, we shall utilize expression (1) for P = 0, that is,

$$\Delta T_c(C_1,C_2)=\frac{1}{2}\tilde{v}T_c{}^0\Big\{J\Big[\tilde{Z}_1\Big(C_1+\frac{\tilde{Z}_2}{\tilde{Z}_1}C_2-C_c{}^1\Big)\frac{1}{2T_c{}^0}\Big]$$

$$-J\Big[-\frac{\tilde{Z}_1C_c{}^1}{2T_c{}^0}\Big]\Big\}-\langle a^2\rangle T_c{}^0J_c(\lambda_1C_1+\lambda_2C_2)+T_c{}^0(K_1C_1+K_2C_2). \qquad (5)$$

The results of a theoretical treatment of the $\Delta T_c(C_1, C_2)$ dependences for solutions of Tl-Hg and Tl-Hg(1 at.%)-In_x are given in Fig. 7. The $\Delta T_c(C_1, C_2)$ dependence has three terms, each of which is characterized by the appropriate parameters. The values and signs of all the parameters appearing in the first term of expression (5) are determined in the previous section (A) from the $\Delta T_c(P, C)$ dependences. Theoretical curves for the first term in $\Delta T_c(C_1, C_2)$, corresponding to the values of the parameters found for the solutions Tl-Hg and Tl-Hg-In_x, are presented in Fig. 7 (curves 2).

Having fixed the parameters in the first term, one can determine the values of the remaining parameters appearing in expression (5) by the method of least squares. These parameters have the following values:

$$\langle a^2\rangle=(8\pm1)\cdot10^{-3},\quad K_{Hg}=21.5\pm2\ \text{mK/at.\%},$$
$$K_{In}=12.8\pm1.5\ \text{mK/at.\%},\quad \lambda_1=\lambda_2=0.9\pm0{,}2.$$

The theoretical dependences of the second and third terms for the solutions Tl-Hg and Tl-Hg-In_x, corresponding to these parameters, are depicted in Fig. 7—by curves 3 and 4, respectively. Thus, the two nonlinear mechanisms for the effect of impurities on T_c, having a different nature, are separated from the $\Delta T_c(C_1, C_2)$ dependences.

From the data presented in Fig. 7 it is seen that the experimental $\Delta T_c(C)$ dependences of thallium (Fig. 7, curves 1) are practically completely described by the first term of expression (5) (Fig. 7, curves 2), that is, they are determined by the nonlinear mechanism connected with the change in the topology of the Fermi surface.

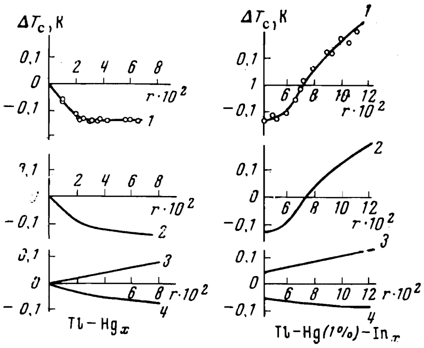

FIG. 7. The dependence of ΔT_c on r for solid solutions of Tl-Hg_x and Tl-Hg (1 at.%)-In_x: 1—the total theoretical curve $\Delta T_c(r)$, the points represent experimental results; 2—the nonlinear component of the dependence $\Delta T_c(r)$ due to the change in the topology of the Fermi surface; 3—the linear component of the dependence $\Delta T_c(r)$; 4—the nonlinear component of the dependence $\Delta T_c(r)$ determined by the reduction in the anisotropy of the gap.

From expression (5) and the cited Fig. 7 it is seen that the first term may lead to a nonlinear increase of the superconducting transition temperature if the difference $\epsilon_F-\epsilon_c$ increases, i.e.,

$$\Big\{J\Big(\tilde{Z}_1\Big(C_1+\frac{\tilde{Z}_2}{\tilde{Z}_1}C_2-C_c{}^1\Big)\frac{1}{2T_c{}^0}\Big)-J\Big(-\frac{\tilde{Z}_1C_c{}^1}{2T_c{}^0}\Big)\Big\}>0,$$

and to a nonlinear decrease of T_c if $\epsilon_F-\epsilon_c$ decreases, i.e.

$$\Big\{J\Big(\tilde{Z}_1\Big(C_1+\frac{\tilde{Z}_2}{\tilde{Z}_1}C_2-C_c{}^1\Big)\frac{1}{2T_c{}^0}\Big)-J\Big(-\frac{\tilde{Z}_1C_c{}^1}{2T_c{}^0}\Big)\Big\}<0$$

(see the experimental $\Delta T_c(C)$ dependences given in Figs. 1 and 2).

From the cited data it is clear that, by using two impurity components which change $\epsilon_F-\epsilon_c$ in opposite directions in ternary solid solutions (for example, Hg and In), one can realize both possibilities in regard to changes in the topology of the Fermi surface—the disappearance of the small cavity (for example, solid solutions of Tl-In-Hg_x, Fig. 1) and its reestablishment (solid solutions of Tl-Hg-In_x, Fig. 1b). In one case the variable is the concentration of the impurity of smaller effective valence, and in the other case—the impurity of larger effective valence. We note that the investigation of $T_c(C)$ for ternary solid solutions enables us to actually experimentally isolate the nonlinear mechanism associated with the change in the topology of the Fermi surface. This is related to the fact that the nonlinear mechanism due to the decrease in the anisotropy of the effective electron-electron interaction parameter depends on the concentration much more weakly in ternary solutions than it does in binary solutions (Fig. 7, curves 4). The preliminary introduction of impurities (for example, Hg) increases the residual resistance of the original metal, which also leads to a decrease in the role of this nonlinear mechanism in the overall $\Delta T_c(C)$ dependence associated with the introduction of a different impurity (for example, In) into the solution Tl-Hg-In_x.

In addition, the presence in a solution of two impurities with different valencies gives the possibility to change $\epsilon_F-\epsilon_c$ by the introduction of one of the impurities in such a way as to be able, by changing the concentration of the other impurity, to observe the total nonlinearity in $T_c(C)$ due to a topological transition in the metal, whereas only the individual parts of the overall dependence are observed in binary solutions.

C. The topology of the Fermi surface of Tl. From an analysis of the experimental data it follows that for Tl $\bar{v} > 0$, $\tilde{Z} > 0$, and $P_c = -2.6$ katm. This allows us to conclude that closed regions of the Fermi surface exist for Tl, which pertain either to "electrons" ($Z = \tilde{Z}$) or to "holes" ($Z = -\tilde{Z}$). Moreover, under the influence of In impurities and pressure these parts of the Fermi surface increase, but under the influence of Hg impurities they decrease, and they vanish ($\epsilon_F-\epsilon_c = 0$) for $C_c = 0.43\%$.

Let us compare these results with existing models of the Fermi surface. Theoretical models of the Fermi surface of Tl[15, 16] describe the larger portions of the Fermi surface well and strongly differ in the description of small parts of the surface. Certain refinements are made for small portions of the Fermi surface in the fourth and fifth Brillouin zones in the recent theoretical work by Holtham,[16] by taking into consideration the experimentally observed small cross sections of the

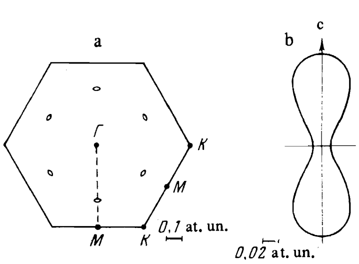

FIG. 8. The small electron pockets in the fourth Brillouin zone (a) and the Fermi surface of the fifth Brillouin zone (b) according to the theoretical calculations [16].

Fermi surface according to the de Haas–van Alphen effect,[17] cyclotron resonance,[18] and also the effect of pressure on the de Haas–van Alphen effect.[19] According to this theoretical model, Tl has a dumb-bell shaped electron surface with a narrow neck of the order of 10^{-2} eV in the fifth zone, and small electron pockets of the order of 4×10^{-3} eV in the fourth zone (Fig. 8). Using our data one can determine the value of $\epsilon_F - \epsilon_c = \tilde{Z}P_c = 1.4 \times 10^{-3}$ eV for those portions of the Fermi surface which are responsible for the change in the topology of the Fermi surface. By comparing this value with the calculated data[16] for the small electron pockets in the fourth zone, one can conclude that the changes of these smallest portions of the Fermi surface of Tl under the influence of pressure and impurities not only lead to a nonlinear dependence $T_c(P)$ for pure Tl and its solutions, but also give a contribution to the nonlinear changes in the dependences $T_c(C)$ for ternary and binary solutions of Tl.

The authors regard it as their duty to express their gratitude to Academician B. G. Lazarev,(Ukrainian Academy of Sciences), Corresponding Member V. G. Bar'yakhtar (Ukrainian Academy of Sciences) and V. V. Gann for a discussion of the results.

[1)] The $\Delta T_c(P)$ dependence of this very solution, obtained in previous investigations, [12] is not accurate in the region of small pressures due to the difficulty of correctly taking the effect of the plunger's residual magnetic moment on T_c into account.

[2)] The effective valence takes into consideration the change in the concentration of electrons in the metal, the change in the potential of the positive ion core, and the change in the volume of the unit cell of the matrix under the influence of the impurity.

---

[1]E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957); R. I. Gayley, Jr., E. A. Lynton, and B. Serin, Phys. Rev. **126**, 43 (1962); G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. **114**, 719 (1959).

[2]D. Markowitz and L. P. Kadanov, Phys. Rev. **131**, 563 (1963).

[3]T. A. Ignat'eva, V. I. Makarov, and N. S. Tereshina, Zh. Eksp. Teor. Fiz. **54**, 1617 (1968) [Sov. Phys.-JETP **27**, 865 (1968)].

[4]J. Hasse and V. Reichert, Z. Phys. **221**, 471 (1969).

[5]V. G. Bar'yakhtar, I. I. Fal'ko, and V. I. Makarov, Zh. Eksp. Teor. Fiz. **49**, 1858 (1965) [Sov. Phys.-JETP **22**, 1270 (1966)].

[6]B. G. Lazarev, L. S. Lazareva, V. I. Makarov, and T. A. Ignat'eva, Zh. Eksp. Teor. Fiz. **48**, 1065 (1965) [Sov. Phys.-JETP 21, 711 (1965)].

[7]V. I. Makarov and V. G. Bar'yakhtar, Zh. Eksp. Teor. Fiz. **48**, 1717 (1965) [Sov. Phys.-JETP **21**, 1151 (1965)].

[8]V. G. Bar'yakhtar, V. V. Gann, V. I. Makarov, and T. A. Ignat'eva, Zh. Eksp. Teor. Fiz. **62**, 1118 (1972) [Sov. Phys.-JETP **35**, 591 (1972)].

[9]B. G. Lazarev, L. S. Lazareva, V. I. Makarov, and T. A. Ignat'eva, Zh. Eksp. Teor. Fiz. **46**, 829 (1964) [Sov. Phys.-JETP **19**, 566 (1964)].

[10]N. B. Brandt and Ya. G. Ponomarev, Zh. Eksp. Teor. Fiz. **55**, 1215 (1968) [Sov. Phys.-JETP **28**, 635 (1969)].

[11]E. S. Itskevich, Prib. Tekh. Eksp. **4**, 148 (1963).

[12]N. B. Brandt, N. I. Ginzburg, T. A. Ignat'eva, B. G. Lazarev, L. S. Lazareva, and V. I. Makarov, Zh. Eksp. Teor. Fiz. **49**, 85 (1965) [Sov. Phys.-JETP **22**, 61 (1966)].

[13]B. G. Lazarev, L. S. Lazareva, and V. I. Makarov, Zh. Eksp. Teor. Fiz. **43**, 2311 (1962) [Sov. Phys.-JETP **16**, 1632 (1963)].

[14]V. G. Bar'yakhtar and V. I. Makarov, Zh. Eksp. Teor. Fiz. **49**, 1934 (1965) [Sov. Phys.-JETP **22**, 1320 (1966)].

[15]P. Soven, Phys. Rev. **137**, A1706, A1717 (1965).

[16]P. M. Holtham, J. Phys. **F3**, 1361 (1973).

[17]Y. Ishizawa and W. R. Datars, Phys. Lett. 30A, 463 (1969).

[18]J. C. Shaw and G. E. Everett, Phys. Rev. **B1**, 537 (1970).

[19]J. R. Anderson, J. C. Schirber, and D.R. Stone, Colloq. Int. INRS **188**, 131 (1970).

[20]G. J. Culler, B. D. Fried, R. W. Huff, and J. R. Schreiffer, Phys. Rev. Lett. **8**, 399 (1962).

Translated by H. H. Nickle
112