# Effect of impurity and pressure on the topology of the Fermi surface of indium

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We study the dependences of the superconducting transition temperature $T_c$ and of the derivative of $T_c$ with respect to the pressure $P$ for ternary solid solutions of indium with lead and mercury impurities. By comparing these and the previously obtained data with the theory, two nonlinear mechanisms are discerned in the experimentally observed dependences of $T_c$ on the impurity concentration, one due to the smearing of the anisotropy of the energy gap in the electron spectrum, and the other to the peculiarities in the electron state density. It is shown that the nonlinear behavior of $T_c(c, P)$ and $\partial T_c/\partial P(c)$ is due to changes in the topology of the Fermi surface of indium. The values of the parameters that characterize the changes of the electron spectrum of indium under the influence of the impurity and of the pressure are obtained. The results are compared with the available data on the electronic properties of solid solutions of indium in the normal state.

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In earlier investigations of the superconducting characteristics of solid solutions of indium[1] it was observed that the derivative $\partial T_c/\partial P$ of the superconducting transition temperature $T_c$ with respect to the pressure P is a nonlinear function of the impurity concentration. It was shown that the nonlinear variation of $\partial T_c/\partial P$ in these systems is due to a change in the electronic properties. The two maxima in the dependence of $\partial T_c/\partial P$ on the concentration c, one observed when lead or tin impurity is added to the indium, and the other upon addition of cadmium, mercury, or thallium, were attributed to the appearance of two singularities in the density states of the indium electrons, caused by the changes in the Fermi-surface topology (FST) under the influence of the impurities.[1] These conclusions were confirmed by recent investigations of the electronic part of the heat capacity[2] and of the oscillations of the thermal conductivity in a magnetic field[3,4].

Further theoretical study of the effect of changes of the FST on the thermodynamic properties of superconductors has shown that a quantitative comparison of the experimental functions ($\partial T_c/\partial P(P, c)$ and $T_c(P, c)$) with the theoretical expressions can yield numerical values of the physical constants that characterize the change of the electronic spectrum under the influence of the impurity and of the pressure near the critical energy.[5]

This paper is devoted to further experimental study of the effect of impurities and pressure on the temperature of the superconducting transition of indium. These and the earlier data[1] are used to determine the parameters that characterize the change of the electronic spectrum of indium under the influence of impurities and pressure.

The electronic-spectrum characteristics obtained by investigating the superconducting properties of the metal are compared with data determined from the study of the de Haas-van Alphen effect, the electronic heat capacity, and the oscillations of the thermal conductivity in a magnetic field.

## SAMPLES AND MEASUREMENT METHOD

We investigated the variation of $T_c$ and $\partial T_c/\partial P$ in the ternary systems In–1.5 at.% Hg–Pb and In–3 at.% Hg–Pb with changing lead concentration from zero to 7 at.%, and in the binary In-Bi system with changing impurity concentration from[1)] zero to 2.5 at.%. The sample preparation procedure was described in detail earlier.[1] The investigated samples were single-phase. They were polycrystals with sufficiently uniform impurity distribution, as evidenced by the small widths of the transition curves from the normal to the superconducting state (Fig. 1) and by the linear dependence of the residual resistance on the impurity concentration. The superconducting transition temperature was determined by the vanishing of the electric resistivity of the samples, with accuracy $\pm 1 \times 10^{-3}$°K. The total error of $T_c$ as a function of the impurity concentration did not exceed $10 \times 10^{-3}$°K, and the average total error of $T_c$ was $\pm 7 \times 10^{-3}$°K.

The derivative of $T_c$ with respect to pressure was determined by the previously described method.[1] The accuracy of $\partial T_c/\partial P$ in the investigated systems, as well as in the previously studied solid solutions of indium, was $\pm 1 \times 10^{-6}$°K/atom.

## MEASUREMENT RESULTS

1. In–1.5% Hg–Pb solutions. The dependence of $\partial T_c/\partial P$ on the lead impurity concentration in these solutions has a clearly pronounced nonlinear character (Fig. 2). At a lead concentration c = 1.5%, a maximum equal to $-3.55 \times 10^{-5}$ deg/atm is observed. Further increase of the lead impurity concentration decreases the derivative, which reaches a minimum at c = 3.3%. The value of $\partial T_c/\partial P$ for the ternary system in this region of lead concentration is close within the limit of the ex-

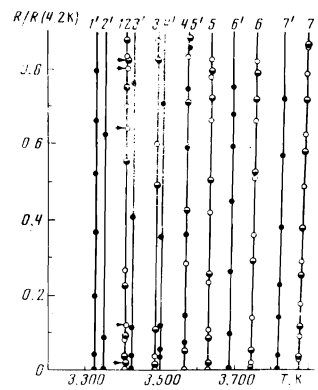


FIG. 1. Temperature dependence of R/R(4.2°K) for the following samples: 1, 1′–pure In; 2, 2′–In–1.5% Hg–1% Pb; 3, 3′–In–1.5% Hg–2% Pb; 4, 4′–In–1.5% Hg–3% Pb; 5, 5′–In–3% Hg–4% Pb; 6, 6′–In–3% Hg–5.5% Pb; 7, 7′–In–3% Hg–7% Pb. Transition curves 1–7 were plotted at P=0 (○–prior to application of pressure, ⊖–after the removal of the pressure), and 1′–7′ were plotted at P=1730 atm. The points with the arrows pertain to transition 2.

perimental accuracy to the value of $\partial T_c/\partial P$ corresponding to pure indium, namely $-4.62 \times 10^{-5}$ deg/atm. Further increase of the lead concentration increases the derivative to $-4 \times 10^{-5}$ deg/atm. The dependence of $T_c$ on the lead concentration in the ternary system In—1.5% Hg—Pb is in general linear. The deviation $\Delta T_c^*(c) = (T_c(c) - 0.08c - 3.348)°K$ of $T_c$ from linearity is shown in Fig. 2.

2. In—3% Hg—Pb solutions. The dependence of $\partial T_c/\partial P$ on the lead concentration in this system has a maximum at c = 5.3% (Fig. 3). This maximum coincides in magnitude with the maximum of $\partial T_c/\partial P$ for the In—1.5% Hg—Pb system. The superconducting transition temperature in the ternary system In—3% Hg—Pb increases generally linearly with increasing lead concentration, but the rate of change of $T_c$ in this system is smaller than in the In—1.5% Hg—Pb system. The nonlinear part of the $T_c(c)$ dependence $(\Delta T_c^*(c) = (T_c(c) - 0.07c - 3.374)K$ is shown in Fig. 3.

3. In-Bi solutions. Addition of bismuth to indium leads to a nonlinear variation of $\partial T_c/\partial P$ with a maximum at 0.55%. The variation of $\partial T_c/\partial P(c)$ in this system is similar to those obtained earlier by adding tin and lead impurities to indium[1], but is observed in a narrower concentration interval (Fig. 4a). The values of the maxima for these binary systems are the same, within the limits of experimental accuracy, and lower than for the ternary systems. The superconducting transition temperature of the indium is altered in nonlinear fashion by the bismuth impurity. Small amounts of bismuth decrease $T_c$. At high concentrations, a rapid increase of $T_c$ is observed. The nonlinear part of $T_c(c)$ $(\Delta T_c^*(c) = (T_c = 0.28c - 3.406)°K)$ is shown in Fig. 4b.

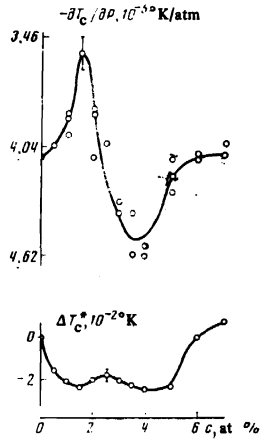


FIG. 2

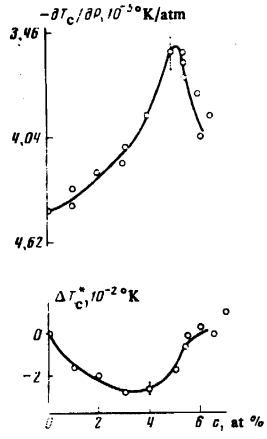


FIG. 3

FIG. 2. Variation of $\partial T_c/\partial P$ and $\Delta T_c^* = (T_c - 0.08c_{Pb} - 3.348)°K$ in the system In—1.5% Hg—Pb.

FIG. 3. Variation of $\partial T_c/\partial P$ and $\Delta T_c^* = (T_c - 0.07c_{Pb} - 3.374)°K$ in the system In—3% Hg—Pb.

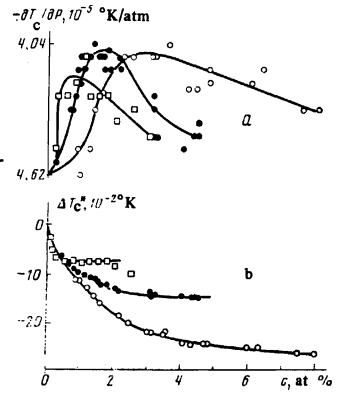


FIG. 4. Plots of $\partial T_c/\partial P$ and $\Delta T_c^* = (T_c - \varphi c - 3.406)°K$ of indium with the following impurities: □—Bi ($\varphi$=0.28 K/at.%), ○—Pb ($\varphi$=0.12 K/at.%), ●—Sn ($\varphi$=0.12 K/at.%).

## DISCUSSION OF RESULTS

The change of the superconducting transition temperature under the influence of the pressure and of the impurities is determined both by the changes in the electron and phonon spectra of the superconductor, and by the influence of the electron scattering by the impurities. A monotonic variation of the electron and phonon spectra leads to a smooth variation of $T_c$. The essentially nonlinear variation of $T_c$ can be caused by two mechanisms, first, the smearing of the anisotropy of the energy gap in the superconductor spectrum under the influence of the impurity, which leads to a nonlinear decrease of $T_c$,[6] and second a change in the FST under the influence of the impurity or the pressure, which can lead, depending on the type of topological transition, to either a nonlinear decrease or to an increase of $T_c$.[5]

Thus, the dependence of $T_c$ on the impurity concentration and on the pressure can be represented in the form

$$T_c(c, P) = T_c^0(c, P) + \sum_j \frac{1}{2} \tilde{\nu}_j T_c^0 J(\beta_j) - \langle a^2 \rangle T_c^0 I(\chi). \qquad (1)$$

The first term $T_c^0(c, P)$ is a smooth function of the impurity concentration and of the pressure. The second term describes the effect of the change of the FST on $T_c$. The summation is over all the singularities of the state density, which are connected with the possible changes of the FST. Here

$$\tilde{\nu}_j = \mp \delta\nu_j/\nu_0(\varepsilon_F) = \mp 2K_j^*(m_1^j m_2^j m_3^j T_c^0)^{1/2}/\pi^2 \nu_0(\varepsilon_F)$$

is the relative change of the state density in the topological transition, $\nu_0(\epsilon_F)$ is the smooth part of the density of states near the Fermi surface, $K_j^*$ is the number of equivalent points in the Brillouin zone, corresponding to a given singularity j of the density of states $\nu(\epsilon)$, and $T_c^0$ is the superconducting transition temperature of the pure metal.

The quantity $\tilde{\beta}_j = \pm(\epsilon_F - \epsilon_{cj})/2T_c^0$ is determined by the distance from the Fermi surface to the critical point $\epsilon_{cj}$. The signs + and − in the expressions for $\tilde{\nu}_j$ and $\tilde{\beta}_j$ determine the type of the topological transition. Thus, if $\tilde{\beta}_j$ increases, the result is either formation of a Fermi-surface cavity (if $\tilde{\nu}_j > 0$) or a breaking of the neck joining individual parts of the Fermi surface (if $\tilde{\nu}_j < 0$). If $\tilde{\beta}_j$ decreases, we get either a vanishing of a cavity of the surface ($\tilde{\nu}_j > 0$) or formation of a neck joining individual parts of the Fermi surface ($\tilde{\nu}_j < 0$).

The expression for $J(\beta)$ takes in the Fröhlich-Deby model the form[5]

$$J(\beta) = \int_{-\infty}^{\infty} F^2\left(\frac{T_c^0}{sk_F} y\right) (\beta + y) \frac{\operatorname{th} y}{y} dy.$$

where $F(x) = 1 - 2|x| + 2x^2 \ln(1 + 1/|x|)$, s is the speed of sound, and $k_F$ is the Fermi momentum.[2)]

The third term in (1) determines the change of $T_c$ due to the smearing of the anisotropy of the energy gap of the superconductor under the influence of the impurity. Here $\langle a^2 \rangle$ is the mean-squared anisotropy of the

energy gap in the pure superconductor. The quantity $\chi$ is connected with the cross section for electron scattering by the impurity and is proportional to the residual resistance. The function $I(\chi)$ is of the form[6]

$$I(\chi)=\int_0^{2\omega_D/T_c^0\pi}\frac{\mathrm{th}\,(^1/_4\chi y)}{1+y^2}\frac{dy}{y}$$

where $\omega_D$ is the Debye temperature.

The dependence of the anisotropic component of $T_c$ on the impurity concentration differs appreciably from the concentration dependence of the electronic component of $T_c$ due to the change of the FST. The electronic component depends essentially on the valence of the impurity, since it determines the sign of the change in the quantity $\beta \sim \epsilon_F - \epsilon_c$. The anisotropic component of $T_c$, on the other hand, is determined by the residual resistance and is not connected directly with the valence of the impurity.

The different dependences of the nonlinear components of $T_c$ on the type (valence) of the impurity makes it possible to separate these two nonlinear mechanisms in the concrete dependence of $T_c$ on c. To this end it is necessary to vary $\beta$ and $\chi$ independently. This cannot be done in binary systems. For an independent variation of $\beta$ and $\chi$ it is necessary to be able to vary the concentration of at least two sorts of impurities. The efficacy of such an approach was demonstrated in a study of thallium systems.[7]

The experimental data obtained by us on the variation of $T_c$ and of $\partial T_c/\partial P$ for ternary indium systems can be compared with expression (1) and each of the mechanisms can be independently separated. Earlier investigations of indium systems[1] have shown that the electronic spectrum of indium contains two critical energies $\epsilon_{c1}$ and $\epsilon_{c2}$ located on opposite sides of the Fermi energy. An analysis of the curves of Figs. 2, 3, and 4 leads to the conclusion that the observed nonlinear variation of $\partial T_c/\partial P$ in these systems is due to the same singularities in the density of the electronic states.

We can therefore attempt to describe the entire aggregate of the experimental data on the dependences of the superconducting transition on the impurity concentration and on the pressure by means of formula (1), assuming that in indium there are only two critical energies in the immediate vicinity of the Fermi energy:

$$T_c(c_1, c_2, P)=T_c^0(c_1, c_2, P)+{}^1/_2T_c^0\tilde{\nu}_1J(\beta_1)+{}^1/_2T_c^0\tilde{\nu}_2J(\beta_2)-\langle a^2\rangle T_c^0I(\chi), \quad (2)$$

where $c_1$ is the concentration of the Pb impurity and $c_2$ is the Hg concentration. The quantities $\tilde{\beta}_1$ and $\tilde{\beta}_2$ in (2) are generally speaking functions of the three variables $c_1$, $c_2$, and P. We shall assume, however, that the electronic nonlinear components of $T_c$ are functions of a single variable, the effective electron density $c_{eff}$, which can be either positive or negative:

$$c_{eff}=c_1+\gamma_2c_2+\zeta P. \quad (3)$$

The expressions for $\tilde{\beta}_1$ and $\tilde{\beta}_2$ can then be written in the form

$$\beta_1=\tilde{a}_1(c_{eff}-c_{cI}), \quad \beta_2=\tilde{a}_2(c_{eff}-c_{cII}), \quad (4)$$

where $c_{cI}$ and $c_{cII}$ are the critical values of the effective electron densities at which the change of the FST takes place.

The quantity $\chi$ in (2) is given by[6]

$$\chi=140\sum_i\frac{\partial\rho}{\partial c_i}\lambda_ic_i, \quad (5)$$

where the summation is over all i sorts of the impurities, and $\lambda_i$ are quantities on the order of unity and are connected with the anisotropy of the cross sections for the scattering of the electrons by the impurities. The derivatives of the residual resistivity $\rho$ with respect to the impurity concentration are, in accord with our data,

$$\partial\rho/\partial c_{Hg}=1.7\cdot10^{-2}\,1/\text{at.\%}, \quad \partial\rho/\partial c_{Pb}=7.2\cdot10^{-2}\,1/\text{at.\%}.$$

It is convenient to start the comparison of the theory with experiment by reducing the functions $\partial T_c/\partial P(c)$, since the anisotropic component of $T_c$ is practically independent of the pressure.

## DEPENDENCE OF $\partial T_c/\partial P$ ON THE IMPURITY CONCENTRATION

Differentiating (2) with respect to pressure and taking (3) and (4) into account, we obtain

$$\partial T_c/\partial P(c_1, c_2)=\partial T_c^0/\partial P+{}^1/_2T_c^0\tilde{\nu}_1\tilde{a}_1\zeta J'\times[\tilde{a}_1(c_{eff}-c_{cI})]+{}^1/_2T_c^0\tilde{\nu}_2\tilde{a}_2\zeta J'[\tilde{a}_2(c_{eff}-c_{cII})]. \quad (6)$$

We determine the parameters in (6) by comparing this expression with the experimental data for the binary and ternary systems investigated here and in earlier studies.[1] The least-squares calculations were performed with an M-20 computer. The obtained parameters are listed in Table I. The first column contains the results on systems with lead and mercury impurities, the third the results for lead and cadmium impurities, and the third the results of simultaneous reduction of both sets of experimental data. In this case it was assumed that

$$c_{eff}=c_1+\gamma_2c_2+\gamma_3c_3+\zeta P, \quad (7)$$

where $c_3 = c_{Cd}$. The first line of Table I gives the number N of the investigated samples, and the last line the values of the ratio $\chi^2/N$. The values of the parameters obtained in the reduction of the three sets of the experimental data are close to each other, and the values of $\chi^2/N$ in all cases are of the order of unity. This indicates that formula (6) describes well the entire set of the experimental data. Figure 5 shows a plot of $\Delta\partial T_c/\partial P = \partial T_c/\partial P - \partial T_c^0/\partial P$ against $c_{eff}$, based on formula (6) and the parameter values given in the third column of Table I. The figure shows also the experimental data, with $c_{eff}$ determined from (7). As seen from Fig. 5, all the experimental points fit quite well a single curve. From Table I and formula (7) it follows that whereas an impurity with a larger valence (compared to indium) increases the effective electron density, impurities with smaller valence (mercury, cad-

TABLE I.

| Parameters | In—Pb, In—Hg, In — 1.5% Hg—Pb, In — 3% Hg—Pb | In—Pb, In—Cd, In—2%Pb—Cd | In—Pb, In—Hg, In—Cd, In — 1.5% Hg—Pb, In — 3% Hg—Pb, In—2%Pb—Cd |
|---|---|---|---|
| $N$ | 48 | 48 | 95 |
| $\tilde{\nu}_1\tilde{a}_1\zeta$ [K/atm] | $(11\pm0.4)\cdot10^{-6}$ | $(13\pm0.9)\cdot10^{-6}$ | $(11\pm0.4)\cdot10^{-6}$ |
| $\tilde{\nu}_2\tilde{a}_2\zeta$ [K/atm] | $(8.6\pm0.5)\cdot10^{-6}$ | $(11\pm1.3)\cdot10^{-6}$ | $(8.8\pm0.5)\cdot10^{-6}$ |
| $\tilde{a}_1$ | $-2.2\pm0.25$ | $-2.2\pm0.3$ | $-2.2\pm0.2$ |
| $\tilde{a}_2$ | $1.5\pm0.2$ | $0.8\pm0.5$ | $1.5\pm0.15$ |
| $c_{cI}$ | $-1.6\pm0.3$ | $-1.8\pm0.5$ | $-1.6\pm0.3$ |
| $c_{cII}$ | $2.2\pm0.2$ | $2.2\pm0.2$ | $2.2\pm0.2$ |
| $\gamma_2$ | $-2.48\pm0.03$ | – | $-2.49\pm0.03$ |
| $\gamma_3$ | – | $-1.64\pm0.07$ | $-1.56\pm0.04$ |
| $(\partial T_c^0/\partial P)\cdot10^5$ [K/atm] | $-5.28\pm0.08$ | $-5.7\pm0.2$ | $-5.3\pm0.07$ |
| $\chi^2/N$ | 2.2 | 0.56 | 1.3 |

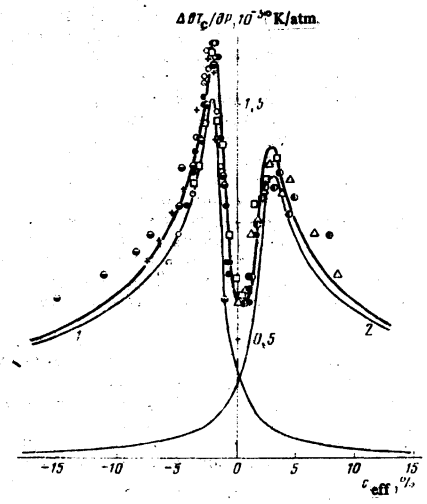


FIG. 5. Dependence of $\Delta\partial T_c/\partial P$ of indium on the effective impurity concentration: 1, 2—variation of $\partial T_c/\partial P$ with changing distance between the Fermi energy and the critical energies $\epsilon_{c1}$ and $\epsilon_{c2}$, respectively. Points—experimental data for the following systems: ◒—In–Hg, ◑—In–Pb, △—In–Sn, □—In–1.5% Hg–Pb, +—In–3% Hg–Pb, ○—In–Cd, ●—In–2% Pb–Cd.

TABLE II.

| Parameters | Pb | Hg | Cd | Tl | Sn | Bi |
|---|---|---|---|---|---|---|
| $c_{c1}$ [at. %] | – | 0.65±0.06 | 1.1±0.1<br>1 [4] | 1.9±0.04 | – | – |
| $c_{c2}$ [at. %] | 2.2±0.2 | – | – | – | 1.1±0.1<br>1 [2] | 0.55±0.05 |
| $\gamma$ | 1 | −2.48±0.03 | −1.6±0.04 | −0.9±0.02 | 2±0.02<br>2 [4] | 4±0.4 |

mium) decrease it ($\gamma_2 < 0$, $\gamma_3 < 0$). In the region $c_{eff} < 0$ (the systems In-Hg and In-Cd) the change of $\partial T_c/\partial P$ is determined mainly by the first singularity of the electron density of states, which is connected with the change of the FST at $\epsilon_F = \epsilon_{c1}$. In the region $c_{eff} > 0$ (the system In-Pb), the second singularity of the state density is principally involved. The contribution of each singularity to the nonlinear dependence of $\partial T_c/\partial P$ on $c_{eff}$ is shown in Fig. 5 (curves 1 and 2). At $c_{eff} = 0$ (pure indium), the contributions of the two nonlinear components are approximately equal and add up to about 13% of $\partial T_c^0/\partial P$.

Using the obtained values of the paramcters, we can reduce the previously obtained experimental values of $\partial T_c/\partial P(c)$ in the systems In-Sn,[1] In-Tl,[1] and In-Bi. Table II lists the critical concentrations $c_{c1}$ of the cadmium, mercury, and thallium impurities at which a topological transition takes place, and the concentration $c_{c2}$ of the lead, tin, and bismuth impurities that cause the change of the FST at $\epsilon_F = \epsilon_{c2}$. It lists also the values of the effectiveness of these impurities relative to lead.

For comparison, Table II gives also the values of the corresponding parameters obtained in an investigation of the electron spectrum of solid solutions of indium in the normal state (the electronic part of the heat capacity,[2] the de Haas-van Alphen effect,[8] calculation based on the study of the oscillations of the thermal conductivity in a magnetic field[4]). It is seen from the table that the impurity critical concentrations and effectiveness values obtained in the normal and superconducting states are in agreement.

Assuming that the equal-energy surfaces near the critical point $\epsilon_{c2}$ are surfaces of the second kind, we can determine from the data of[8] the effective critical concentration of the lead impurity $c_{c1}$. Its value is −1.6% and agrees with the value obtained on superconductivity data (see Table I).

Using the data of Tables I and II we can determine the values of $|\epsilon_F - \epsilon_{c1}|_0$ and $|\epsilon_F - \epsilon_{c2}|_0$ in pure indium, and also the values of the derivatives $\partial|\epsilon_F - \epsilon_{cj}/\partial c$:

$$|\varepsilon_F-\varepsilon_{c1}|_0=2T_c^0|\tilde{a}_1c_{c1}|\approx 2.1\cdot 10^{-2}\ \text{eV},$$
$$|\varepsilon_F-\varepsilon_{c2}|_0=2T_c^0|\tilde{a}_2c_{c2}|\approx 2\cdot 10^{-3}\ \text{eV},$$
$$\partial|\varepsilon_F-\varepsilon_{c1}|/\partial c_{Pb}\approx 1.3\cdot 10^{-3}\ \text{eV/at.\%}.$$

The signs of the presented quantities determined from the superconducting properties cannot be determined. It can be stated, however, that $\epsilon_F - \epsilon_{c1}$ and $\epsilon_F - \epsilon_{c2}$ have opposite signs.

## DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE ON THE IMPURITY CONCENTRATION

As seen from (6), and investigation of the dependence of $\partial T_c/\partial P$ on the impurity concentration makes possible to determine only the product

$$\tilde{v}\tilde{a}_j\zeta_b=\pm\frac{1}{2T_c^0}\frac{\delta\nu_j}{\nu_0}\frac{\partial(\varepsilon_F-\varepsilon_{cj})}{\partial P}.$$

The values of each of the factors can be obtained by reducing the experimental data on the dependence of $T_c$ on c for the systems In—Pb, In—Hg, In—1.5% Hg—Pb, and In—3% Hg—Pb. We shall carry out the calculations in accord with formulas (2)—(5), in which we put P = 0. We use here the previously obtained parameters $\tilde{\alpha}_1$, $\tilde{\alpha}_2$, $c_{cI}$, $c_{cII}$, and $\gamma_2$, and represent the smooth function $T_c^0(c_1, c_2)$ in the form

$$T_c^0(c_1c_2)=T_c^0+\frac{\partial T_c^0}{\partial c_1}c_1+\frac{\partial T_c^0}{\partial c_2}c_2+A_1c_1^2+A_2c_2^2+A_3c_1c_2. \qquad (8)$$

We note that the dependence of $T_c$ on the impurity concentration in each of the binary and ternary systems can be described by taking into account in (8) only terms that are linear in the concentration.

The parameters obtained by comparing the theoretical expression with the complete set of experimental data on $T_c$ in the binary and ternary indium systems are listed in Table III (first column).

The value $\chi^2/N \approx 1$ indicates that the difference between the theoretical curve and the experimental data lies within the limits of the accuracy of $T_c$. The concentration dependences of $T_c$ for the systems In—Hg and In—3% Hg—Pb, plotted using the obtained parameters, are shown in Fig. 6. The figure gives also the experimental data and shows the resolution of the theoretical curve into individual components corresponding to the terms in formulas (2) and (8). Curves 1 and 2 represent the change of $T_c$ due to singularities in the density of states of the electrons at $\epsilon = \epsilon_{c1}$ and $\epsilon = \epsilon_{c2}$. The superconducting transition temperature decreases in the presence of the first singularity and increases in the presence of the second. Besides the electronic nonlinear components, a large contribution to the dependence of $T_c$ on c of indium is made by the anisotropic mechanism brought about by the smearing of the anisotropy of the energy gap under the influence of the impurity (curve 3). The value of the anisotropic component does not depend on the valence of the impur-

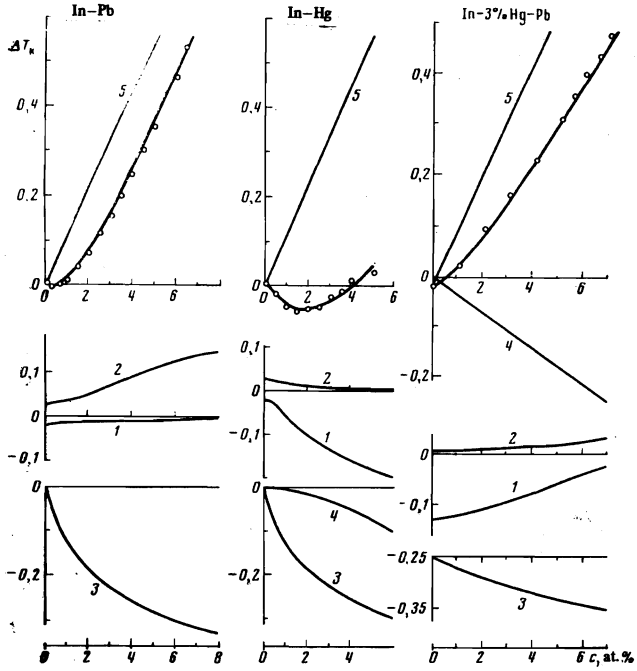


FIG. 6. Variation of $T_c$ in the systems In–Pb, In–Hg, and In–3% Hg–Pb. Curves 1 and 2–nonlinear components due to change in the distances between the Fermi energy and the critical energies $\epsilon_{c1}$ and $\epsilon_{c2}$; curve 3–nonlinear component due to smearing of the anisotropy of the energy gap; curve 4–quadratic component; curve 5–linear component.

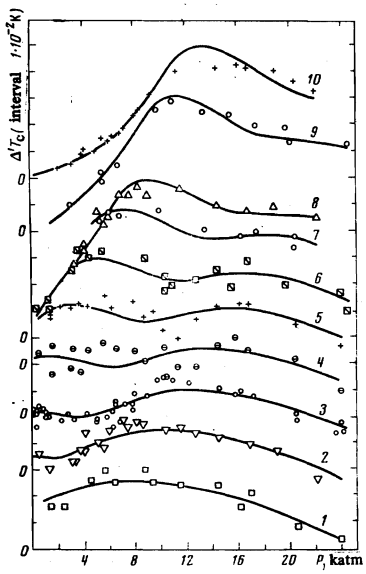


FIG. 7. Plot of $\Delta' T_c$ against the pressure for In with the following impurities: Pb–2%, 1% (curves 1 and 2), Cd–0.5%, 1%, 1.5%, 2%, 2.5%, 3%–3.5% (curves 4–10, respectively), and pure indium (curve 3).

ity, and leads only to a decrease of $T_c$. As seen from Fig. 6, in binary systems the nonlinear change of $T_c$ is determined mainly by the anisotropic mechanism. In ternary systems, the nonlinear change of $T_c$ due to this mechanism is much smaller than in binary systems. The electronic mechanism manifests itself therefore more pronouncedly in the experimental $T_c(c)$ dependence of ternary systems (see Figs. 2 and 3). This shows that an investigation of ternary systems is essential for a reliable separation of the electronic nonlinear mechanism in the dependence of $T_c$ on c (formula (2)) is essential for a correct determination of the magnitude of the anisotropic mechanism. If we disregard in expression (1) for $T_c(c)$ the terms that describe the contribution of the change of the FST, then when the theory is compared with experiments it is impossible to determine uniquely the parameters $\langle a^2 \rangle$ and $\lambda_i$, which describe the anisotropic component. In this case we can determine only the product of these parameters.

TABLE III.

| Parameters | First calculation | Second calculation |
|---|---|---|
| $\tilde{c}_1 \cdot 10^3$ | −3.7±0.7 | −3±0.6 |
| $\tilde{c}_2 \cdot 10^3$ | 5.2±1.6 | 3±1 |
| $(\partial T_c^0/\partial c_1) \cdot 10^3$ [K/at.%] | 110±10 | 110±6 |
| $(\partial T_c^0/\partial c_2) \cdot 10^3$ [K/at.%] | 110±20 | 90±7 |
| $T_c^0$ [K] | 3.396±0.006 | 3.406±0.003 |
| $\langle a^2 \rangle$ | 0.03±0.01 | 0.03±0.0004 |
| $\lambda_{Pb}$ | 0.4±0.1 | 0.5±0.1 |
| $\lambda_{Hg}$ | 2.3±0.5 | 1.6±0.3 |
| $A_3 \cdot 10^3$ [K/(at.%)$^2$] | −12±1 | −12±1 |
| $A_1 \cdot 10^3$[K/(at.%)$^2$] | 0±1 | 0 |
| $A_2 \cdot 10^3$ [K/(at.%)$^2$] | −6±3.6 | 0 |
| $\chi^2/N$ | 1 | 1.08 |
| $N$ | 48 | 48 |

TABLE IV.

| Parameters | Their values | Parameters | Their values |
|---|---|---|---|
| $\tilde{v}_1 \cdot 10^3$ | −11±1.6 | $\gamma_3$ | −1.9±0.2 |
| $\tilde{v}_2 \cdot 10^3$ | 3±1.4 | $\zeta \cdot 10^3$ | 0.4±0.05 |
| $\tilde{\alpha}_1$ | −1±0.2 | $(\partial T_K^0/\partial P) \cdot 10^5$ [K/atm] | −4.5±0.1 |
| $\tilde{\alpha}_2$ | 1.8±0.6 | $B \cdot 10^6$ [K/atm-at.%] | 0.8±0.06 |
| $c_{cI}$ | −2±0.2 | $N$ | 200 |
| $c_{cII}$ | 2.5±1 | $\chi^2/N$ | 9.9 |

In addition to the nonlinear terms, a decisive role in the variation of $T_c$ of the considered system is played by the linear components. Usually the linear variation of $T_c$ following addition of the impurity is attributed to the monotonic variation of the phonon and electron spectra, due to the differences between the valences and masses of the impurity and solvent-metal atoms. In the investigated systems, the impurity atom masses are double the indium-atom masses, the valence of mercury is lower than that of indium, and that of lead is higher. The fact that the coefficients of the linear terms (Table III) for the lead and mercury impurities have the same sign and even the same numerical value indicates that the main contribution to the linear component of $T_c$ is made not by the change of the electron density, but by the increase in the density of the low-frequency phonon, owing to the indium-spectrum deformation caused by the introduction of the heavy impurity. The mercury impurity deforms the low-frequency part of the phonon spectrum more strongly than the lead impurity, since the decrease of $T_c$ due to the decrease of the electron density is compensated in the In–Hg system. This may be due to the more substantial weakening of the interatomic bonds in the In–Hg system in comparison with pure indium and with the In-Pb system.[9,10]

The differences between the low-frequency part in the phonon spectrum of indium and in the In–Hg system can lead to different changes of $T_c$ following addition of the lead impurity. This appears to be the reason why it is necessary to take into account the quadratic terms in (8), the most essential of which is the bilinear term proportional to $c_1 c_2$. If we put in (8) $A_1 = A_2 = 0$, then the agreement between theory and experiment is hardly worse ($\chi^2/N = 1.08$, Table III, column 2). It will be

shown in the next section that the bilinear term must be taken into account also when describing the dependence of $T_c$ on the pressure in indium with cadmium impurity.

## PRESSURE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE OF INDIUM SOLID SOLUTIONS

Smith[11] has investigated the variation of $\Delta T_c(P, c) = T_c(P, c) - T_c(0, c)$ for pure indium and for indium with lead and cadmium impurities. The experimental data corresponding to low impurity concentrations are shown in Fig. 7, where $\Delta' T_c(P) = \Delta T_c(P) - 3.88 \times 10^{-2} P$ (°K/atm). Let us analyze the results on the basis of formulas (2), (4), and (7), assuming that the anisotropic component of $T_c$ makes no contribution to the function $T_c(P)$. We express the smooth function $T_c^0(P, c_1, c_3)$ in the form

$$T_c^0(P, c_1, c_3) = T_c^0(0, c_1, c_3) + \frac{\partial T_c^0}{\partial P} P + BPc_3. \qquad (9)$$

We note that the $T_c(P)$ dependences of individual systems can be described by taking into account in (9) only the linear term. The bilinear term is necessary in order to describe with a single expression the joint action of the pressure and of the impurity on the smooth component of $T_c^0$ in In–Cd systems.

The results of a simultaneous reduction of the experimental data of Fig. 7 are given in Table IV. A comparison of the parameters in Table IV with the corresponding values from Tables I and III shows that the parameters determined from $T_c(P)$, $\partial T_c/\partial P(c)$ and $T_c(c)$ agree both in sign and in order of magnitude.

The theoretical curves corresponding to these values of the parameters are shown in Fig. 7. It is seen from the figure that formula (2) describes quite well the entire set of experimental data. Smith's conclusion[11] that to explain the presented experimental data it is necessary to assume the existence of a third singularity in the density of states of the indium electrons is therefore incorrect.

Figure 8a shows a plot of $\Delta' T_c$ of indium against $P_{eff} = c_{eff}/\zeta$ in a wide range of $P_{eff}$. The curves of Fig. 7 correspond to individual sections of this curve and differ only in the linear components. The nonlinear $T_c(P_{eff})$ component is shown in Fig. 8b (curve 3). The figure shows also the individual contributions made to $T_c(P_{eff})$ by the first and second singularities of the density of states (curves 1 and 2), corresponding to two topological transitions at $P_{eff}$ equal to −5 katm and +6 katm, respectively. The region of negative values of $P_{eff}$ is reached by adding cadmium, while addition of lead extends the investigated region of positive $P_{eff}$. The nonlinear change of $T_c$ of indium and its solution under pressure takes place against the background of a strong linear decrease of $T_c$. The linear component in the In–Pb system is the same as in pure In. In the In–Cd system, $T_c$ decreases more rapidly. The difference between the values of $\partial T_c/\partial P$ in indium and in indium with cadmium is described by the bilinear term in (9). The bilinear term in $T_c^0(c, P)$, just as in $T_c^0(c_1, c_2)$ can be attributed to deformation of the phonon spectrum by the impurity, a deformation due to weakening of the interatomic bonds in the lattice. In this case the compressibility of the lattice becomes larger than in the pure metal, and this leads to a stronger decrease of $T_c$ under pressure.[9]

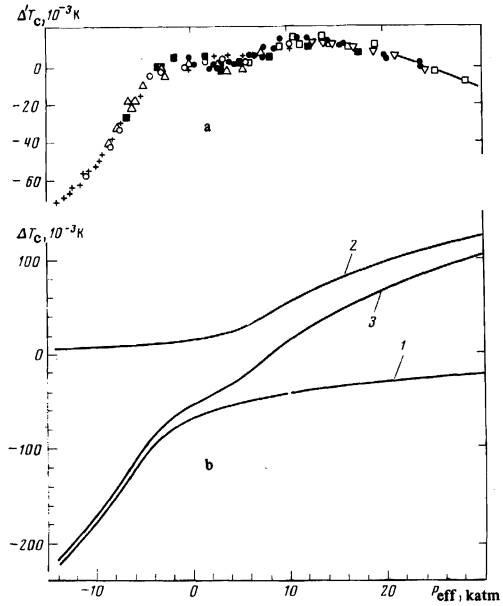


FIG. 8. a) Dependence of $\Delta' T_c$ on the effective pressure $P_{eff}$ for pure indium. Points—experimental data of Fig. 7: ●—pure In, +—In with 3.5% Cd; ○—3% Cd, △—2.5% Cd; ■—1.5% Cd; ▽—In with 1% Pb; □—2% Pb. b) Nonlinear component of $\Delta' T_c$ vs. the effective pressure (curve 3) and its resolution into two components (curves 1 and 2), due to the change of the distance between the Fermi energy and the critical energies $\epsilon_{c1}$ and $\epsilon_{c2}$, respectively.

## EFFECT OF IMPURITY AND PRESSURE ON THE ENERGY SPECTRUM OF INDIUM

As shown in the preceding section, the superconducting data make it possible to determine most reliably the signs of the parameters and the values of the critical concentrations (pressures). This makes it possible to determine the type of the topological transition (formula (1)). In indium with mercury, cadmium, or thallium impurity, where $\tilde{\nu}_1 < 0$ and $\partial\tilde{\beta}_1/\partial c = \alpha_1\gamma > 0$ (Tables I–IV), the neck joining the individual cavities of the Fermi surface is broken. When an impurity of higher valence is added to the indium (lead, tin, bismuth) and under hydrostatic compression we get $\tilde{\nu}_2 > 0$, $\partial\tilde{\beta}_2/\partial c = \tilde{\alpha}_2\gamma > 0$ and $\partial\tilde{\beta}_2/\partial c = \tilde{\alpha}\gamma > 0$ (see the tables). In this case a new cavity of the Fermi surface is produced.

The relatively simple shape of the Fermi surface of indium makes it possible to compare our results with the Fermi-surface model. The Fermi surface of pure indium is located in the second (hole group) and third (electron group) Brillouin zones. The electron group is much smaller than the hole group and comprises a torus in the planes (001), made up of β-tubes joined by narrow necks at the corners of the third Brillouin zone (Fig. 9a). The Fermi surface of pure indium has no other singularities.

An impurity of lower valence (cadmium) decreases the cross sections of the β-tubes.[3] It was shown in[4] that a topological transition connected with breaking of the necks joining the β-tubes should take place at a Cd concentration 1%. This transition obviously corresponds to the singularities of the behavior of $\partial T_c/\partial P(c)$ and $T_c(P, c)$ observed in indium with 1.1% Cd, 0.66% Hg, and 1.9% Tl. The Fermi surface for this case is illustrated in Fig. 9b.

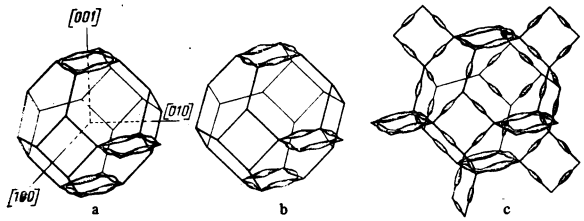


FIG. 9. Fermi surface of indium and of its solid solutions in the third Brillouin zone: a—pure indium, b—indium with cadmium, mercury, or thallium impurity, c—indium with lead, tin, or bismuth impurity.

According to the Fermi-surface model of[12], higher-valence impurities or pressure can result in production of $\alpha$-tubes on the edges of the third Brillouin zone (Fig. 9c). This topological transition seems to be the cause of the singularities of the behavior of the superconducting properties of indium following addition of 1.1% Sn, 2.2% Pb, and 0.55% Bi, or under a pressure of 6 katm. A similar singularity in the behavior of the electronic part of the heat capacity was observed when 1% Sn was added to indium.[2]

When the Pb concentration is increased to 8%, a new topological transition takes place and causes a nonlinear variation of $T_c$ as a function of pressure[11] and of uniaxial tension.[13] This transition in pure indium should occur at 20 katm if the relation between the effectivenesses of the pressure of the lead impurity, which was established above ($\zeta \cdot 10^3 = 0.4$) is correct. We note that the change of the linear dependence of $T_c(P)$ of pure indium, which was observed in the region 25—30 katm,[14] may be due to this topological transition.

We note in conclusion that an investigation of $T_c$ and $\partial T_c/\partial P$ of indium as a function of the impurity concentration and of the pressure has shown that a study of the superconducting characteristics reveals reliably changes in the topology of the Fermi surface. Comparison of the theory with various independent experimental data shows that even when a highly simplified model is used it is possible to determine reliably from the superconducting data the values of the critical concentrations and pressures.

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[1)]The concentration was determined from the residual resistance with accuracy 0.1 at.%. The impurity concentrations are cited henceforth in atomic per cent.

[2)]For indium, $s=1.2\times10^5$ cm/sec and $k_F=1.51\text{Å}^{-1}$.

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