Electron-phonon interaction and topological features in the thermal emf of metals

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Anomalies in the thermal emf of indium associated with a change in the topology of the Fermi surface have been studied as functions of the temperature and the concentration of mercury and cadmium impurities at pressures up to 12 kbar. The results reveal that the anomalous component of the thermal emf, $\delta\alpha$, changes sign as the impurity concentration is reduced. For high-purity samples, the absolute value of $|\delta\alpha|$ increases with increasing temperature. The experimental data do not conform to the existing theoretical interpretation {V. G. Vaks *et al.*, Zh. Eksp. Teor. Fiz. **80**, 1613 (1981) [Sov. Phys. JETP **53**, 830 (1981); A. A. Varlamov and A. V. Pantsulaya, Zh. Eksp. Teor. Fiz. **89**, 2188 (1985) [Sov. Phys. JETP **62**, 1263 (1985)]; A. A. Abrikosov and A. V. Pantsulaya, Fiz. Tverd. Tela (Leningrad) **28**, 2140 (1986) [Sov. Phys. Solid State **28**, 1195 (1986)]}. It has thus been necessary to develop the theory further. It is shown that the entire set of experimental data can be explained by considering the umklapp processes by which electrons are scattered by phonons from large parts of the Fermi surface to a small region of states which has appeared as a result of a topological transition.

INTRODUCTION

In 1960, I. M. Lifshitz[1] predicted electron topological transitions in metals. Such transitions occur when the Fermi energy of the electrons, ε_F, is equal to the critical energy ε_c. A constant-energy surface $\varepsilon(\mathbf{p}) = \varepsilon_c$ contains a singular point $\mathbf{p} = \mathbf{p}_c$, at which the electron group velocity $v = \nabla\varepsilon(\mathbf{p})$ vanishes. As we know, topological changes in constant-energy surfaces $\varepsilon(\mathbf{p})$ near the point $\mathbf{p}_c$ lead to singularities in the electron state density $\nu(\varepsilon)$, Van Hove singularities.[2] Topological changes in the Fermi surface can be induced through hydrostatic compression of a substance, through uniaxial extension, and by adding impurities with a different valence. In several metals the difference $\varepsilon_F - \varepsilon_c$ is small ($\ll\varepsilon_F$), and it may be reduced by some external agent, e.g., hydrostatic compression, becoming equal to zero at some critical pressure P_c.

Topological transitions have been observed experimentally in a study of the de Haas-van Alphen effect in cadmium under pressure,[3] during uniaxial extension of aluminum whiskers,[4] and in several superconductors in studies of how their critical superconducting transition temperature T_c and the derivative $\partial T_c/\partial P$ depend on the concentrations of various impurities whose addition leads to a change in $|\varepsilon_c - \varepsilon_F|$ (Refs. 5 and 6).

It has now been established that a topological transition is also accompanied by singularities in the kinetic characteristics of metals, which are sharpest in the diffusive part of the thermal emf α. The theoretical and experimental work on this question has usually been restricted to the region in which the impurity scattering of electrons is predominant.[7–12] Only in the work of Abrikosov and Pantsulaya[13] was it noted that additional scattering of electrons by phonons can substantially reduce the magnitude of the singularity $|\delta\alpha|$. We have studied this question experimentally in the case of indium.[14] It turns out that as the ratio of the resistances at room temperature and liquid-helium temperature (RRR) increases, the absolute value $|\delta\alpha|$ falls off with the temperature, in qualitative agreement with Ref. 13. For extremely pure samples (RRR = 11 000), however, the value of $|\delta\alpha|$ increases with increasing temperature.

Unfortunately, only the absolute value of the change in the thermal emf was studied in Ref. 14. Further experiments showed that in samples with a small impurity concentration the anomalous component $\delta\alpha$ may actually change sign as the temperature is raised, and in extremely pure samples (RRR $\gtrsim$ 7500) the change is $\delta\alpha < 0$ over the entire temperature interval (3–7 K). These results cannot be explained on the sole basis of the existing theory,[7,8,13] according to which the quantity $\delta\alpha$ has a strictly fixed sign, and $|\delta\alpha|$ falls off with increasing temperature. When the electron-phonon interaction is taken into account, the singular part $\delta\alpha$ becomes[13]

$$\delta\alpha \sim \frac{1}{e}\frac{\tau_i^{-1}(\tau_p^{-1}+\tau_i^{-1})}{(\tau_i^{-1}+\tau_\varepsilon^{-1})^2} J(\xi, T), \tag{1}$$

where $\tau_i^{-1} \sim C$ is the rate at which electrons collide with impurities of concentration C, and $\tau_p^{-1} \sim T^5$ and $\tau_\varepsilon^{-1} \sim T^3$ are the electron-phonon collision frequencies which correspond to the relaxation of the electron momentum $\mathbf{p}$ and the electron energy ε. (We recall that we have $\tau_\varepsilon^{-1} \gg \tau_p^{-1}$.) The function $J(\xi,T)$ depends on the difference $\xi \equiv \mu - \varepsilon_c$ and has its standard form,[12,14] where μ is the chemical potential.

It follows from expression (1) that the amplitude of the singular part of the thermal emf can depend on the temperature T in different ways, depending on the relations among relaxation times τ (Ref. 13):

$$A_1(T) = \tau_i^{-1}(\tau_i^{-1}+\tau_p^{-1})/(\tau_i^{-1}+\tau_\varepsilon^{-1})^2.$$

Specifically,

$$A_1(T) = \begin{cases} 1, & \tau_i^{-1} \gg \tau_p^{-1}, \tau_\varepsilon^{-1} \\ \sim T^{-6}, & \tau_\varepsilon^{-1} \gg \tau_i^{-1} \gg \tau_p^{-1}. \\ \sim T^{-1}, & \tau_\varepsilon^{-1} \gg \tau_p^{-1} \gg \tau_i^{-1}. \end{cases} \tag{2}$$

According to (2), in extremely pure samples the amplitude of the singular part of the thermal emf should tend toward zero in the limit $C \to 0$ and should fall off monotonically with increasing temperature, not changing sign in the process.

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For a detailed study of the reasons for the difference between the theory and the experimental results, we have now measured the singularities in the thermal emf in a series of indium samples of different impurity levels. We have also carried out a theoretical analysis of this phenomenon. We find as a result that the entire set of experimental data can be described by introducing some electron processes involving umklapp scattering from large areas of the Fermi surface near the point of the topological transition in which phonons participate.

A quantitative comparison of theory and experiment yields the characteristic energy of the phonons which participate in processes in which electrons are scattered between a new cavity which forms in the third zone and the hole surface in the second.

TEST SAMPLES AND MEASUREMENT PROCEDURE

Samples of pure indium and of indium containing small impurities of mercury and cadmium were synthesized by extruding the substance through a window 1.5–4 mm in diameter and then annealing for a day at 100 °C. Table I shows the approximate composition and the values of RRR of the test samples.

For the measurements of the thermal emf under a pressure up to 12–13 kbar, we used a pressure chamber[15] with a channel 8 mm in diameter. The temperature gradient along the sample was $\Delta T \sim 0.02$ K, and the average temperature T (up to 7 K) measured with a gold-iron superconducting thermocouple (made of GDI, gold doped with a small amount of iron impurity), whose characteristics do not change up to 12 kbar (Ref. 6). The potential differences which arise at the sample and the thermocouple when there is a temperature gradient along the sample are found by a bridge method, in which a SKIMP instrument is used as a null indicator (the sensitivity is 10^{-14}–10^{-15} V).[17] The pressure is applied at room temperature by a manual press (up to 10 metric tons) and is monitored by measuring the change in the resistance of an alloy equivalent to Manganin [*Translator's note*: we will say simply "Manganin"]. After cooling to liquid-helium temperature, the pressure is remeasured, on the basis of the shift of T_c of a tin wire. The error of the pressure measurements is 0.1 kbar. At a given pressure we measure the temperature dependence at the resistance, $R(T)$, the thermal emf $\alpha(T)$, and the critical temperature T_c.

A study of the thermal emf in a pressure chamber has certain features which distinguish it from measurements in a vacuum chamber. Since temperature gradients up to 3 K/mm may occur between the channel wall and the sample when the latter is heated to 7 K, the thermocouple must make good thermal contact with the sample.

In the present experiments we use a thermocouple which is soldered to the sample. The second ends of the thermocouple are led out of the chamber through a hole 1 mm in diameter in a baffle 3 in the liquid-helium bath. These second ends are accordingly at an identical temperature (Fig. 1). When this method is used to measure the gradient, the thermal emf of the sample, α_{samp}, also contributes to the resultant value of ΔT. The thermal emf of the GDI, α_{GDI}, is usually some two or three orders of magnitude larger than α_{samp}, so the latter can be ignored in the measurements of ΔT.

A significant temperature gradient arises in the pressure chamber because of the parasitic heat fluxes (the high density of mounting wires, the heat-conducting medium, and the small working volume) when power is dissipated in heater $H2$. This gradient has the sign opposite that which arises when a current is passed through $H1$. Some simple automatic-control apparatus made it possible to raise the average temperature of the sample (to 7 K) while keeping the gradient fixed (0–10^{-2} K/cm).

To test this procedure for studying the thermal emf under pressure, we compared the results of the measurements in vacuum with those of measurements in the pressure chamber at $P \approx 0$ kbar. The results agreed within 5–10%, demonstrating the validity of this new procedure. To measure the thermal emf of a substance with a high thermal conductivity (pure indium and indium with a minimal impurity concentration) we used long samples (~ 10 cm) of small diameter (1.5 mm). This choice made it possible to establish a measurable temperature gradient. This sample, in the form of a wire, was wound tightly without glue on a

TABLE I.

№	Impurity	Approximate atomic percentage	RRR
1	Mercury	0.8	74
2	»	0.08	648
3	»	0.03	2 240
4	»	0.009	6 500
5	Cadmium	2.5	14
6	»	0.07	470
7	»	0.01	3 300
8	»	0.005	7 500
9	No impurity	0	11 000
10	»	0	11 000

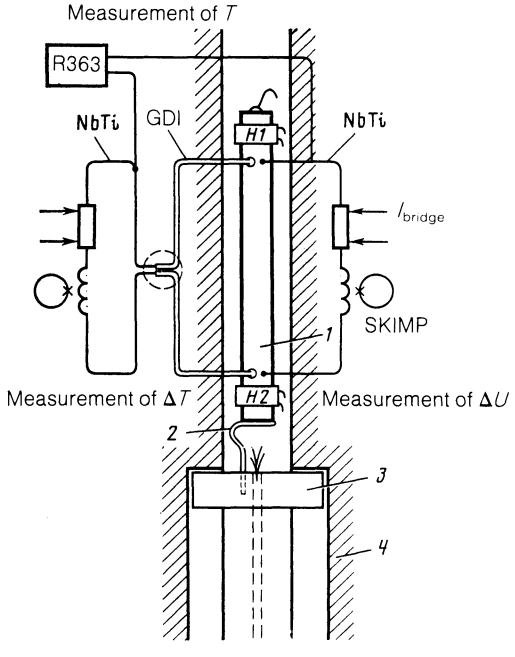

FIG. 1. Layout of the measurements in the pressure chamber. 1—Sample; 2—heat conductor; 3—baffle; 4—wall of pressure chamber; $H1$, $H2$—heaters.

paper-covered "Manganin" rod 2 mm in diameter and ~30 mm long. The paper provided electrical insulation. Heaters were wound at the end of the rod. Thermal contact of the sample with the heaters was arranged in the following way: With heater H 1 by means of an adhesive and GKZh oil; with H 2 by soldering to the "Manganin" rod in the immediate vicinity of the heater. After all the operations involving mechanical deformation, the samples were annealed at $T = 100$ °C for about a day in order to remove residual stresses. Sample No. 9, for which data were reported in Ref. 14, was annealed only 3 h. The effect was to round off the structural features somewhat.

RESULTS

The Fermi surface of indium is known quite well. It is similar to the Fermi surface of aluminum, but there are probably no electron α tubes in the third Brillouin zone of indium because of a slight tetragonal distortion of the fcc lattice.[19] The electron β tubes are connected to the right by narrow necks (the transverse dimension in reciprocal space is ~0.01 a.u.; Ref. 20).

A detailed study of the Fermi surface of the third zone in dilute alloys of InTl and InPb was carried out in Ref. 20 on the basis of the de Haas-van Alphen effect. It was shown that a lead impurity increases the dimensions of all the cross sections, while a Tl impurity reduces them.

A study[6] of binary and ternary alloys of indium with Pb, Sn, Cd, Tl, and Hg revealed two extrema on the curve of the derivative of the superconducting transition temperature T_c with respect to the pressure P ($\partial T_c/\partial P$) versus the impurity concentration. These extrema are evidence of topological transitions.

The dimensions of the necks between the β tubes are small, and their cross section is shrunk by an acceptor impurity.[20] One of the transitions (the first) was accordingly associated with a rupture of the necks. The other transition (the second) is believed by Volynskiĭ *et al.*[6] to be a consequence of the appearance of α tubes at the edges of the Brillouin zone. The nonlinear $T_c(P)$ dependence indicates that this topological transition of the Fermi surface may be possible in pure indium subjected to pressure.[21]

An acceptor impurity, mercury or cadmium, reduces the cross section of the necks between the β tubes. At a mercury concentration of about 1%, or a cadmium concentration of about 2%, the connectedness of the rings is disrupted. Hydrostatic compression makes it possible to gradually restore the necks between the β tubes while measuring the thermal emf.

a) To study the thermal emf under the conditions corresponding to the first topological transition we used samples Nos. 1 and 5, in which the β rings were ruptured by a relatively high impurity of mercury and cadmium.

The results of these measurements are shown in Fig. 2. Shown at the left is the temperature dependence of the thermal emf of sample No. 1 (at the top) and that of sample No. 5 (at the bottom) at several pressures. Shown at the right is a plot of the thermal emf of these samples versus the pressure at the temperature marked by the dashed line in the left part of the figure.

The anomalous behavior of the thermal emf at pressures below 5 kbar is evidence of topological changes in the Fermi surface. It can be concluded from the asymmetry of the $\alpha(P)$ curves and the sign $\delta\alpha > 0$ that the transition occurs in the electron parts of the Fermi surface and consists of a decrease in the connectedness of the Fermi surface. This conclusion supports the suggestion regarding the nature of the transition (based on the band structure) as consisting of a restoration by pressure of the necks which were removed by the addition of an acceptor impurity.

The solid lines in the figures correspond to calculations from the expression[14]

$$\alpha(P)=\alpha(0)+A\int_{-\infty}^{+\infty} y\,\mathrm{ch}^{-2}\frac{y}{2}\left\{\xi+yT+[(\xi+yT)^2+(\Gamma/2)^2]^{1/2}\right\}^{1/2}dy,$$

$$\xi=(\varepsilon_F-\varepsilon_{c1})\,|_{P=0}+\frac{\partial(\varepsilon_F-\varepsilon_{c1})}{\partial P}P,\qquad \Gamma\equiv\frac{\hbar}{\tau}. \tag{3}$$

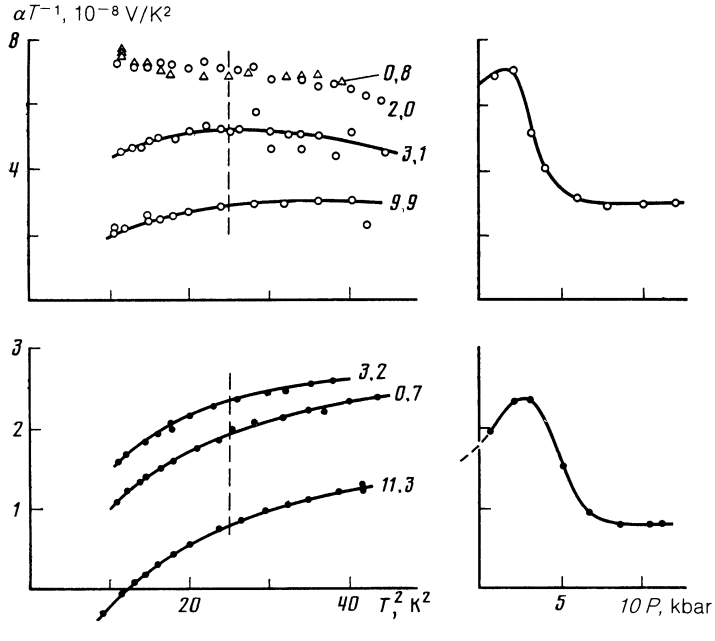

FIG. 2. Left—Temperature dependence at αT^{-1} (the curve labels are the pressures, in kilobars); right—dependence on the pressure ($T = 5$ K), for samples No. 1 (top) and No. 5 (bottom).

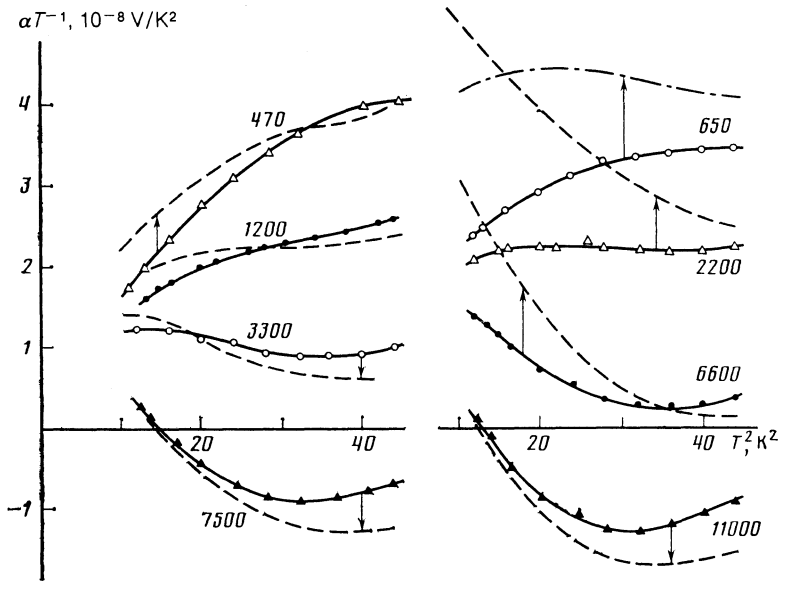

FIG. 3. Plots of $\alpha T^{-1}(T^2)$ for various indium samples with impurities of cadmium (at the left) and mercury (right) for $P \approx 0$ kbar and $P \approx 7$ kbar (the dashed curves), corresponding to the maximum of $|\delta\alpha(P)|$. The curves are labeled with the values of RRR of the samples.

The values of the parameters $\varepsilon_F - \varepsilon_{c1}$ and $\partial(\varepsilon_F - \varepsilon_{c1})/\partial P$ found from the best (least-squares) fit of the experimental values by this expression are not very reliable because there are no points on the left slope of the anomaly at $P = 0$ kbar.

b) To study the thermal emf under the conditions corresponding to the second transition we used indium samples with a small impurity concentration ($\lesssim 0.1\%$). This concentration caused only a slight change in the cross section of the necks and a slight shift of the second transition up the pressure scale.

Figure 3 shows the temperature dependence of the thermal emf of samples Nos. 2–4 and 6–10 in the coordinates α/T, T^2 for two pressures: approximately zero and ≈ 7 kbar (the dashed lines correspond to the maximum value of the singular part of the thermal emf). It can be seen from this figure that the diffusive part of the thermal emf is positive for all of the samples and has a magnitude of about $2 \cdot 10^{-8}$ V/K^2. The part of the thermal emf associated with the phonon drag (the low-temperature slope of the curves), however, differs from sample to sample not only in magnitude but also in sign. For the purest indium sample (RRR = 11 000) the phonon part of the thermal emf, α_{ph}, is negative.

Figure 4 shows the pressure dependence of the thermal emf for several samples. The asymmetry of the $\alpha(P)$ curves, which is typical of the thermal emf under conditions corresponding to topological changes in the Fermi surface,[7–14] and the fact that $\delta\alpha > 0$ holds (for the samples whose resistance is determined primarily by scattering by impurities) are evidence that the pressure induces an increase in the connectedness of the electron parts of the Fermi surface in indium. For samples Nos. 2–4 the shape of the $\alpha(P)$ curves is so "classical" that one can reliably subject the experimental data to mathematical analysis.[14] A least-squares fit of the experimental points by the theoretical curve yields the following values for the parameters characterizing the second topological transition[14]:

$$\varepsilon_F - \varepsilon_{c2} \approx -110 \text{ K}, \quad \frac{\partial(\varepsilon_F - \varepsilon_{c2})}{\partial P} \approx (15 \pm 1) \text{ K/kbar},$$

$$\Gamma \sim 10^{-(2-4)} \text{ K}.$$

The $\alpha(P)$ curves for samples with a cadmium impurity were not compared with expression (3) since in this case the topological singularity in the thermal emf is superposed on a pressure-dependent regular part of the thermal emf. For several samples with a low impurity concentration, $\delta\alpha$ changes sign as we go to higher temperatures. This effect can be seen well in Figs. 3 and 4.

The intersection of the curves in Fig. 3 which correspond to zero pressure and to the pressure at which $\alpha(P)$ reaches its maximum implies a change in the sign of the anomalous component of the thermal emf. The temperature at which this intersection occurs decreases with increasing RRR, falling below T_c at RRR $\gtrsim 7500$. A comparison of the results of measurements of the thermal emf (Fig. 3) shows that in the samples containing a Hg impurity (the mass of the mercury atom is much larger than that of the Cd or In atom) and in samples with a Cd impurity the changes in the sign of $\delta\alpha$ occur at quite different temperatures.

Figure 4 shows $\alpha(P)$ for several samples at various temperatures. The curves for sample No. 7 (top left) clearly

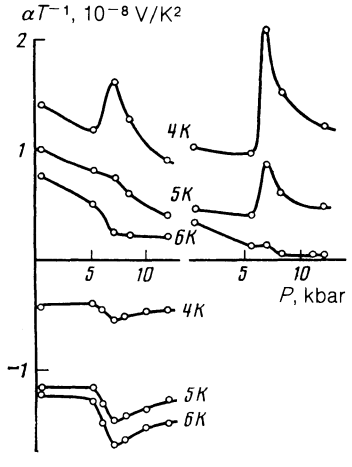

FIG. 4. αT^{-1} versus the pressure for samples No. 7 (top left), No. 4 (right), and No. 10 (bottom) at various temperatures (the curve labels) (the curves are drawn by hand).

demonstrate the change in the sign of the anomalous component of the thermal emf as the temperature is raised. At $T = 4$ K, the singularity in $\delta\alpha$ is seen as a well-defined maximum in $\alpha(P)$, which subsequently decreases with the temperature and becomes almost imperceptible at $T = 5$ K. With a further increase in the temperature, this singularity on the $\alpha(P)$ curve is instead seen as a minimum ($T = 6$ K), which corresponds to a negative sign of the anomalous component $\delta\alpha$. For the purest samples, Nos. 9 and 10 (bottom left), the singularity is seen only as a minimum over the entire working temperature range. As the temperature is raised, This minimum deepens, i.e., the absolute value $|\delta\alpha|$ increases.

A significant part of the resistance of these samples is due to scattering of electrons by phonons. For example, in the temperature interval 3.5–6.5 K the resistance of samples Nos. 10 and 11 changes by a factor of six, that of samples Nos. 4 and 8 by a factor of three, and that of samples Nos. 2 and 6 by only 20%.

THEORY

The experimental results obtained here (Figs. 3 and 4) and also those which have been found previously[14] for pure indium require further development of the theory derived in Refs. 7, 8, 12, and 13. Those earlier papers dealt with the topological singularities of the electron-impurity collision integral (e–i scattering) which stemmed from the transition of electrons from large parts of the Fermi surface to an electron-state region near the point $\mathbf{p}_c$, where a small cavity appears in the Fermi surface. We know that the diffusive part of the thermal emf is due to a difference between the mobilities of "hot" ($\varepsilon > 0$) and "cold" ($\varepsilon < 0$) electrons (the Fermi energy is adopted as the origin for the scale of the energy ε here). For elastic collisions of electrons with impurities, their energy is conserved:

$$\varepsilon(\mathbf{p}) = \varepsilon(\mathbf{p}') \tag{4}$$

($\mathbf{p}$ and $\mathbf{p}'$ are the momenta of the electron before and after the collision). In such collisions, the hot (cold) electrons from large cavities on the Fermi surface thus undergo transitions to a region of hot (cold) electrons on a small cavity of the Fermi surface near the point $\mathbf{p}_c$ (Fig. 5, transitiions 1–2 and 1′–2′). Since for the small electron cavity, for example, the state density increases substantially with energy, hot electrons from the large cavity are less mobile than the cold electrons. In other words, the sign of the singular part of the thermal emf is determined by the expression

$$\operatorname{sign}\delta\alpha_{ei} = \operatorname{sign}\left[\delta\nu(\mu+|\varepsilon|) - \delta\nu(\mu-|\varepsilon|)\right], \quad |\varepsilon| \lesssim T, \tag{5}$$

where $\delta\nu(\eta)$ is the irregular part of the electron-state density, which has the standard form[2]:

$$\delta\nu(\eta) = (2m_1m_2m_3)^{1/2}(4\pi)^{-1}\begin{cases} \pm(\varepsilon_c-\eta)^{1/2}\theta(\varepsilon_c-\eta) \\ \pm(\eta-\varepsilon_c)^{1/2}\theta(\eta-\varepsilon_c) \end{cases} \tag{6}$$

Here m_i are the principal values of the electron mass tensor $\partial^2\varepsilon(\mathbf{p})/\partial p_i^2$ at the point $\mathbf{p} = \mathbf{p}_c$, ε_c is the critical energy, and the $\pm$ specify different types of topological transitions. In a case in which electrons are scattered primarily by impurities, the sign of the singular part of the thermal emf is thus determined exclusively by the type of topological transition of the Fermi surface.

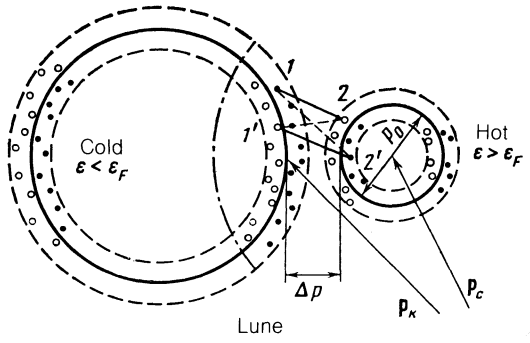

FIG. 5. Electron scattering processes which occur in ei transitions (1–2, 1′–2′ and in ep transitions (1–2′, 1′–2).

We find a different situation when we consider the singularity in the electron-phonon collision integral at a topological transition of the Fermi surface. It is this question which we wish to analyze in the present section of this paper.

From the quasimomentum balance equation of a nonuniformly heated electron-phonon system in an external field,[22] we can show that there is no essentially singular part of the thermal emf, $\delta\alpha$, associated with the electron-phonon collisions (e–p transitions) if we ignore processes involving scattering: e–p transitions between different cavities of the Fermi surface. This approximation is justified at temperatures $T \ll \omega_0$, where these transitions are extremely improbable (ω_0 is the typical phonon frequency, given in order of magnitude by $\omega_0 \approx s\Delta p$; s is the sound velocity; and Δp is the shortest distance between cavities of the Fermi surface in $\mathbf{p}$ space).

We can show, however, that even for $T \lesssim \omega_0$ the singular contribution of e–p transitions to the thermal emf is comparable to the contribution of e–i collisions, even for relatively dirty samples, with energy relaxation times τ_e and τ_i which are on the same order of magnitude. Specifically, under the conditions $\tau_\varepsilon \approx \tau_i$ and $T \approx \omega_0$ the frequencies of e–p and e–i transitions from states near $\mathbf{p}_c$ to the nearby large cavity in the Fermi surface are approximately identical, so the numbers of inverse transitions per unit time are also identical. These inverse transitions are transitions from a "lune" with dimensions on the order of the thermal momentum of a phonon, $q \approx T/s$, to the large cavity on the Fermi surface in the region near $\mathbf{p}_c$ in e–p collisions and from the entire large cavity into this region in the case of scattering by impurities. For the purer samples, the electron nonequilibrium associated with the topological singularity of the electron-phonon collision integral manages to propagate (diffuse) out of the lune to a significant part of the large cavity in the Fermi surface before it undergoes relaxation. This makes a significant contribution to the singular part of the thermal emf.

The most interesting question is that of the sign of $\delta\alpha_{ep}$: the singular part of the thermal emf associated with scattering processes in e–p collisions. In contrast with e–i transitions, e–p collisions are inelastic; the energy conservation law takes the form

$$\varepsilon(\mathbf{p}) - \varepsilon(\mathbf{p}') = \pm\omega_\lambda(\mathbf{p}-\mathbf{p}'), \tag{7}$$

where $\omega_\lambda(\mathbf{q})$ is the phonon dispersion law corresponding to the λ branch of lattice vibrations. For transitions accompa-

nied by the emission of phonons with an energy $\omega \gg T$, a hot electron ($\varepsilon > 0$) goes into a region of cold electrons ($\varepsilon < 0$; transition 1–2′ in Fig. 5), so it is more mobile than a cold electron which absorbs a phonon of energy $\omega \gg T$ (transition 1′–2) in the case in which an electron cavity is produced.[1)] In other words, such transitions change the relation between the number of transitions out of the regions $\varepsilon > 0$ and $\varepsilon < 0$ in comparison with e–i transitions, so their contribution to the singular part of the emf, $\delta\alpha_{ep}$, has the opposite sign:

$$\operatorname{sign} \delta\alpha_{ep}' = \operatorname{sign} [\delta\nu(\mu-\omega) - \delta\nu(\mu+\omega)]. \tag{8}$$

In the case $\omega \ll T$, the transitions are nearly elastic since the energy transfer is significantly smaller than the typical thermal energy of an electron. Consequently, the sign of the contribution of such transitions is the same as that of e–i collisions. It follows from no more than these qualitative considerations that for $T \lesssim \omega_0$ the signs of $\delta\alpha_{ep}$ and $\delta\alpha_{ei}$ are opposite, since only phonons with an energy $\omega \geqslant \omega_0$ participate in electron-phonon scattering processes.

For a quantitative analysis of that topological singularity in the thermal emf which stems from electron-phonon collisions, we start from the kinetic equation for electrons:

$$-\frac{(\varepsilon-\mu)}{T}(\mathbf{v}_p \nabla T)\frac{\partial n_0}{\partial \varepsilon} = \mathrm{St}_{e,ph} n_p \tag{9}$$

(ε is the energy of the electrons). We restrict the analysis to the diffusive part of the thermal emf, and we ignore phonon-drag effects. In the kinetic equation for the phonons we can thus omit the term which contains the temperature gradient ∇T:

$$\mathrm{St}_{ph,\,e} N_k = 0. \tag{10}$$

The collision integrals in (9) and (10) which correspond to collisions of an electron with phonons, $\mathrm{St}_{e,\mathrm{ph}}\, n_p$ and to collisions of a phonon with electrons, $\mathrm{St}_{\mathrm{ph},e} N_k$, are of standard form.[23] We write the nonequilibrium distribution functions of the electrons (n_p) and of the phonons (N_k) as follows:

$$\begin{aligned} n_p &= n_0 - \varphi_p \partial n_0/\partial\varepsilon, \\ N_k &= N_0 - \chi_k \partial N_0/\partial\omega, \end{aligned} \tag{11}$$

where n_0 and N_0 are the equilibrium Fermi-Dirac and Bose-Einstein distributions, respectively, for electrons and phonons, and φ_p and χ_k are their nonequilibrium increments.

Substituting the solution of Eq. (10) for the phonon function χ_k into Eq. (9), we find, in the linear approximation, the following inhomogeneous integral equation for φ_p:

$$-\frac{(\varepsilon-\mu)}{T}(\mathbf{v}_p \nabla T)\frac{\partial n_0}{\partial \varepsilon} = I_{e,ph}\{\varphi_p; \chi_k(\varphi_p)\}. \tag{12}$$

We restrict the analysis to the situation in which the frequency of transitions of an electron from the lune to the vicinity of the point $\mathbf{p}_c$ is significantly lower than the frequency of the energy relaxation of the electron in the large cavity on the Fermi surface, τ_ε^{-1} (a necessary condition here is $\Delta p^2 v_0 / p_0^2 v_F = \sigma \ll 1$, where p_0 and v_0 are the dimension in momentum space and the velocity of the electrons of the cavity which forms, and v_F is a typical velocity of the electrons on the large part of the Fermi surface).

In solving Eq. (12) we can use a method similar to that discussed in Ref. 22. To first order in the parameter σ, we find from (12) the following equation for the function $\varphi_p^{(1)} \equiv \psi$, which is related to the singular component of the thermal emf:

$$\int \frac{d\varepsilon}{|v_p|} I_{e,ph}\{\psi, \chi_k(\psi)\} = X_{1p} + X_{2p}. \tag{13}$$

The quantity X_{1p} determines the number of transitions per unit time of electrons with momentum $\mathbf{p}$ in the lune region to the vicinity of point $\mathbf{p}_c$:

$$X_{1p} = \int \frac{d\varepsilon}{|v_p|} \varphi_p^{(0)}(\varepsilon) F_p(\varepsilon). \tag{14}$$

Here the function

$$\varphi_p^{(0)} \approx T^{-1}(\varepsilon-\mu)\mathbf{v}_p \nabla T \tau_\varepsilon$$

is the solution of Eq. (12) in the zeroth approximation. The function $\varphi_p^{(0)}$ is, to within quantities $\sim T/\varepsilon_F$, odd in the energy $\varepsilon - \mu$ (Ref. 22). The function $F_p(\varepsilon)$ in (14) is given by

$$F_p(\varepsilon) = \sum_{\varkappa,\lambda} \frac{g_{pp_c}^2}{8T} \frac{[\delta\nu(\varepsilon(\mathbf{p}) - \varkappa\omega_\lambda(\mathbf{p}-\mathbf{p}_c))]}{\operatorname{sh}[\omega_\lambda(\mathbf{p}-\mathbf{p}_c)/2T] \operatorname{ch}[(\varepsilon(\mathbf{p})-\mu)/2T]} \cdot \{\operatorname{ch}[(\varepsilon(\mathbf{p}) - \mu - \varkappa\omega_\lambda(\mathbf{p}-\mathbf{p}_c))/2T]\}^{-1}, \tag{15}$$

where g_{pp_c} is the matrix element for the interaction of electrons with phonons, and we have $\varkappa = +1$ if a phonon is emitted by an electron or $\varkappa = -1$ if an electron absorbs a phonon. The quantity F_p has been calculated under the assumption that the thermal momentum of the phonons satisfies $q \gg p_0$. In this case the phonon energy can be assumed to remain constant for all transitions from a fixed point $\mathbf{p}$ to the vicinity of the point $\mathbf{p}_c$. The function X_{2p} in (13), whose particular form is unimportant to the analysis below, describes collisions of electrons with nonequilibrium phonons produced in transitions of electrons to the vicinity of the point $\mathbf{p}_c$.

There is an important point to be considered in the process of solving Eq. (13). This equation describes not an energy relaxation but a "transport" relaxation similar to momentum relaxation in the problem of electrical conductivity. The situation is that transitions to the vicinity of the point $\mathbf{p}_c$ alter the total number of particles in a thermal layer near a certain point $\mathbf{p}$ in the large cavity (the integrand in the expression for X_{1p} is not an even function of $\varepsilon - \mu$), so the relaxation requires movement of the electrons along the Fermi surface. Under the assumption that the primary relaxation mechanism is electron diffusion over the Fermi surface driven by collisions with phonons and directed away from the given lune toward the large cavity on the opposite part, where the sign of the nonequilibrium increment is different (Fig. 5), we find the following expression for the singular part of the thermal emf:

$$\delta\alpha = A_2(T) \sum_{\varkappa,\lambda} \int_{\omega_{0\lambda}}^{\infty} \frac{dy}{\operatorname{ch}(y/2T)} \cdot \int_{-\infty}^{\infty} \frac{x\delta\nu(\mu + x - \varkappa y)\,dx}{D(x/2T)\operatorname{ch}(x/2T)\operatorname{ch}((x-\varkappa y)/2T)}, \tag{16}$$

where $\omega_{0\lambda}$ is the minimum frequency of a phonon of branch λ which is participating in this umklapp process [this frequency is found from the condition for tangency of the

$\varepsilon(\mathbf{p}) = \varepsilon_F$ and ω_λ $(\mathbf{p} - \mathbf{p}_c) = \omega_{0\lambda}$) surfaces]. The functions

$$D(x) = \int_0^\infty \frac{z^2\,dz}{\mathrm{sh}(2z)\,(1 - \mathrm{th}^2 x\,\mathrm{th}^2 z)}$$

incorporate the dependence of the relaxation time τ_ε on the electron energy. The amplitude $A_2(T)$ is given by

$$A_2(T) \propto \frac{\rho(T)\tau_\varepsilon\tau_p}{T^2}, \tag{17}$$

where $\rho \sim T^5$ is the resistivity of the metal, $\tau_\varepsilon \propto T^{-3}$ and $\tau_p \propto T^{-5}$.

In conclusion, having transformed (16), we can write the final equation with which we will compare the experimental data:

$$\delta\alpha T^{-1} \approx BT^{-n}\,\mathrm{ch}^{-2}\frac{\omega_0}{2T} f(\xi, \omega_0, T), \tag{18}$$

$$f(\xi, \omega_0, T) = \frac{1}{T^n}\int_0^\infty \frac{dy}{\mathrm{ch}^2 y\,(\mathrm{th}(\omega_0/2T) + \mathrm{th}\, y)}$$

$$\cdot\int_{-\infty}^{+\infty} \frac{x\,dx\{\delta\nu(\mu+\omega_0+2Tx+2Ty) - \delta\nu(\mu-\omega_0-2Tx-2Ty)\}}{D(x)\,\mathrm{ch}^2 x[1 + \mathrm{th}\, y\,\mathrm{th}(\omega_0/2T) + \mathrm{th}\, x(\mathrm{th}(\omega_0/2T) + \mathrm{th}\, y)]}. \tag{19}$$

Here $\delta\nu(\eta)$ is given by (6); the quantity BT^{-n} is equal to $ev_F^2\omega_0^2\tau_p\rho T^{-2.5}$; in order of magnitude (i.e., $n = 2.5$); $\xi = \mu - \varepsilon_c$; and $\xi(P) = \xi(0) + (\partial\xi/\partial P)P$.

The value of the exponent, $n = 2.5$, is intimately related to the two-step relaxation which is characteristic of the effect under consideration here. First there is energy relaxation, in the stage in which the nonequilibrium increment $\xi^{(0)}$ is formed, and then there is transport relaxation, dscribed by Eq. (13). A relaxation of this nature is implied by the comparison with experiment, which we make below.

DISCUSSION OF RESULTS

Let us analyze the form of the integral $f(\xi,\omega_0,T)$ as a function of the parameters $\xi/2T$ and $\omega_0/2T$. The function $f(\xi,\omega_0,T)$ is plotted versus the ratio $\xi/2T$ for various values of the parameter $\omega_0/2T$ (the curve label) at the left in Fig. 6. It can be seen from this figure that at small values $\omega_0/2T \sim 10^{-1}$ the integral is positive, while as $\omega_0/2T$ increases to 2.5 the integral becomes negative, acquiring an absolute value comparable to $f(\xi/2T;\omega_0/2T = 0.1)$.

In a first approximation, the anomalous component found experimentally is $\delta\alpha = \delta\alpha_{ei} + \delta\alpha_{ep}$, where $\delta\alpha_{ei}$ is the contribution from *ei* transitions and $\delta\alpha_{ep}$ is the contribution from *ep* transitions. It is the competition between these contributions which ultimately determines the sign of $\delta\alpha$.

Let us take a qualitative look at how $\delta\alpha$ changes as the temperature is raised in the case in which a new electron cavity appears. At the lowest temperatures, we have a pa-

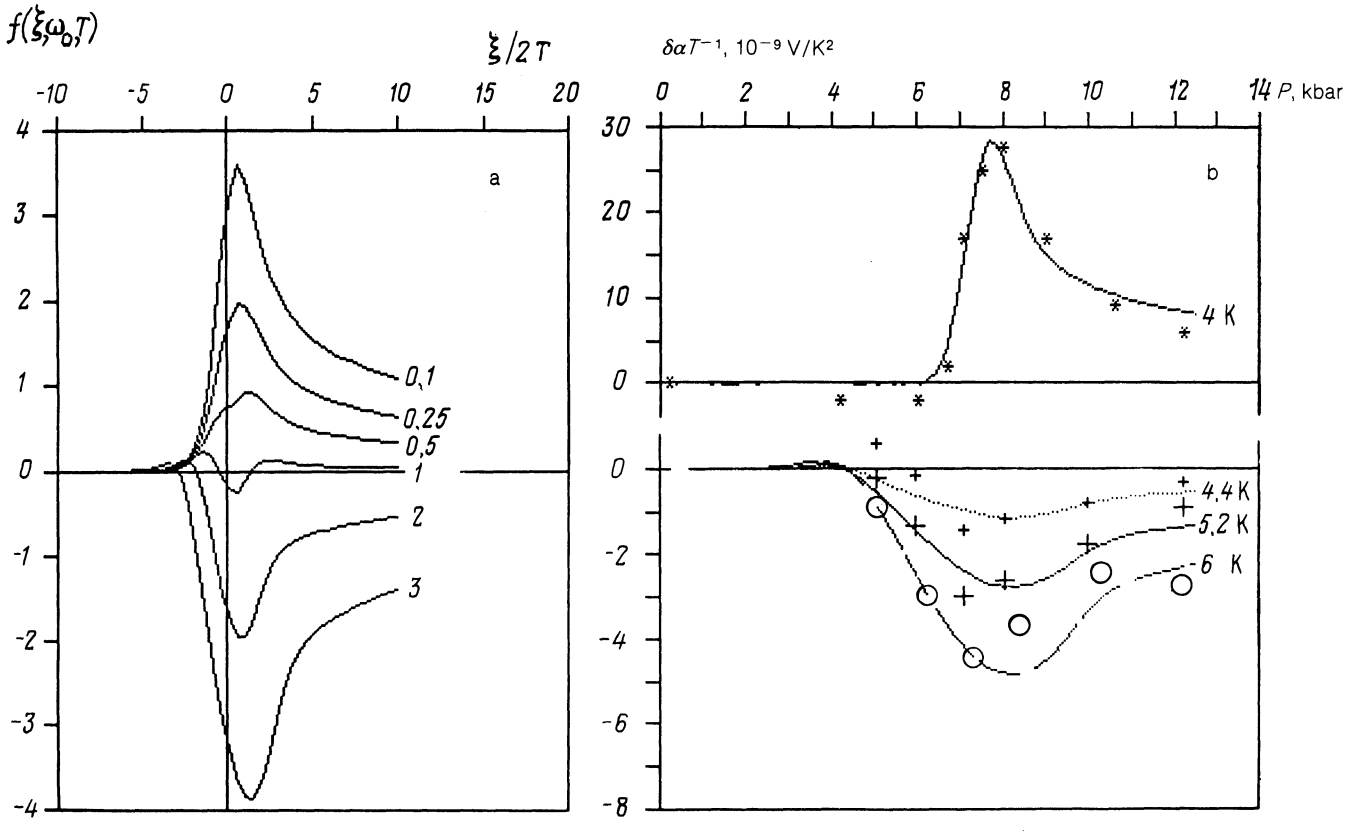

FIG. 6. a—Plot of $f(\xi,\omega_0,T) = f(\xi/2T;\ \omega_0/2T)$ versus $\xi/2T$ (the curves are labeled with the value of the ratio $\omega_0/2T$); b—(bottom) fit of the experimental points on $\delta\alpha(p)T^{-1}$ for sample No. 10 by expression (18) and (top) the same, for sample No. 2, fitted by expression (3) (Ref. 14).

rameter value $\omega_0/2T \gg 1$ ($\omega_0 = s|p_k - p_c|$); the signs of $\delta\alpha_{ei}$ and $\delta\alpha_{ep}$ are different, but impurities play the leading role in the electron scattering; and the contribution $HgI_2 da_{ep}$ is exponentially small [the coefficient of the integral in (18) is $\sim\cosh^{-2}(\omega_0/2T)$], so we have sign $\delta\alpha$ = sign $\delta\alpha_{ei} > 0$. As the temperature is raised, $|\delta\alpha_{ei} T^{-1}|$ decreases, while $|\delta\alpha_{ep} T^{-1}|$ increases, and at a certain temperature the sum $\delta\alpha_{ei} + \delta\alpha_{ep}$ may change sign: $\delta\alpha < 0$. As the temperature increases further, ($\omega_0/2T \lesssim 1$), however, $\delta\alpha_{ep}$ changes sign, and the anomalous component $\delta\alpha$ should again become positive. Consequently, over a wide temperature range we can expect the sign of $\delta\alpha_{ep}$ to change twice: first when the contributions of *ei* and *ep* transitions to $\delta\alpha$ are comparable and then when the sign of $\delta\alpha_{ep}$ changes.

Experimental data for sample No. 10 were compared with theoretical expression (18). It was assumed for this comparison that the contribution $\delta\alpha_{ei}$ is insignificant for this particular sample, as follows from an estimate of $\delta\alpha_{ei}$ from (1). We assumed that ω_0 in (18) was independent of the pressure. Our adjustable parameters were the general scale factor B, the exponent n on the temperature in the coefficient of the integral, and the typical phonon energy ω_0. Using the values found previously[14] for $\xi(0)$ and $\partial\xi/\partial P$, we find that the values $\omega_0 = 35$–40 K and $n = 2$–2.5 result in the best least-squares fit of expression (18) to the experimental data. When we include $\xi(0)$ and $\partial\xi/\partial P$ in the list of adjustable parameters, we find no substantial changes in the results of the calculations.

With which topological transition can we associate the anomaly in the thermal emf of pure indium? We have already mentioned that Volynskiĭ *et al.*[6] regarded the topological change induced by pressure in the Fermi surface of indium to be the appearance of α tubes at the edges of the Brillouin zone. However, a-theoretical derivation[24] of possible changes in the third zone caused by pressure has shown that when the spin-orbit interaction is taken into account the first event should be the appearance not of α tubes, as was suggested, but of electron cavities at points W. The value $\omega_0 = 40$ K found for the typical energy of the phonons participating in electron umklapp processes corresponds to specifically this point of view, as we will now show.

The maximum velocity s od L phonons in indium[25] is 9.6 Thz/a.u. $\approx$ 460 K/a.u. Using the value found for ω_0, we can estimate the typical distance between the point W and the nearest part of the remainder of the Fermi surface—a projection of the hole surface of the second zone:

$$\Delta p \sim \frac{\omega_0}{s} \sim \frac{(35\text{–}40)\,\text{K}}{460\ \text{K/a.u.}} \sim (0.07\text{–}0.1)\ \text{a.u.} \qquad (20)$$

This result agrees with the data of Ref. 20.

It can be seen from Fig. 6 and these estimates that the agreement between the experimental data and the theoretical expressions is completely satisfactory, in view of the assumptions made above.

In summary, all the data show that the sign of $\delta\alpha$ is determined not only by the type of topological transition, as has been assumed, but also by the particular mechanism by which electrons are scattered by phonons. The fact that there is a quantitative difference between the relations between $\delta\alpha_{ei}$ and $\delta\alpha_{ep}$ in the cases of the mercury and cadmium impurities, at approximately the same values of RRR (of the electron mean free path), remains unexplained. There is the possibility that this result is a consequence of an effect of the singular part of the phonon drag,[26] which we have not discussed.

[1)]The absorption of a phonon by an electron at point 1 and the emission of a phonon by an electron at point 1′ are less probable than the processes which we are considering.

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