Increase of the Anisotropy of the Energy Gap in Superconducting Thallium under Pressure*

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A study has been made of the dependence of the superconducting transition temperature of thallium on the density of lattice defects due to plastic deformation, as a function of hydrostatic pressures up to 4 kbar. The change in critical temperature with resistivity ratio is found to be pressure-dependent. It can be accounted for by a theory of gap anisotropy given by Markowitz and Kadanoff and yields a strongly pressure-dependent anisotropy parameter $\lambda\langle a^2\rangle$ which varies from 0.0008 at zero pressure to 0.007 at $p=4$ kbar. Only a little change in the "valence" effect with pressure is observed. The well-known anomalous enhancement of the transition temperature of thallium at pressures up to 2 kbar can be explained quantitatively by this increase of the gap anisotropy under pressure.

INTRODUCTION

IN this paper we will try to explain an irregularity of an effect which itself has not yet been explained satisfactorily. This situation occurs in the pressure dependence of the superconducting transition temperature T_c of thallium. In contradiction to the behavior of the majority of superconductors, in which the transition temperatures decrease nearly linearly with pressure[1]—an effect which itself is not understood at present[2]—the transition temperature of thallium increases by about 0.01°K at lower pressures up to 2 kbar, passes through a maximum, and then decreases.[3] It is this enhancement which we will try to explain.

In the last year several papers have presented new data on this subject.[4–7] By studying the influence of dilute alloying of bismuth, antimony, and particularly mercury on the pressure dependence of T_c of thallium, these authors concluded that the $T_c(p)$ behavior of thallium can be expressed as the sum of a regular, linearly decreasing term and a nonlinear term for which changes in the topology of the Fermi surface are responsible. In an earlier paper[8] we suggested that the observed disappearance of the enhancement of T_c upon introduction of lattice defects supported the assumption that this effect is due to smoothing out of a pressure-dependent anisotropy of the energy gap as the electronic mean free path is reduced. In the present paper we offer a detailed investigation. The data are now precise and reproducible enough to be susceptible to a treatment in terms of the special theory of Markowitz and Kadanoff,[9] and in fact confirm our earlier conclusion.

EXPERIMENTAL TECHNIQUES AND DATA ANALYSIS

We have studied the effects of lattice imperfections, as measured by the resistivity ratio, on the pressure-

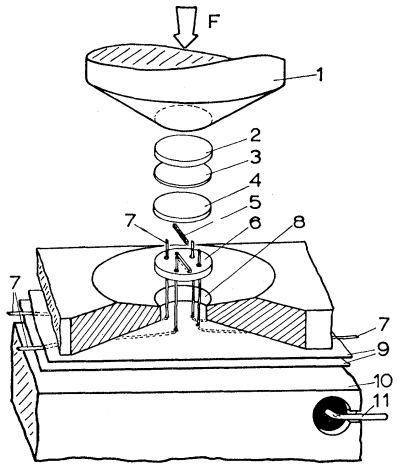

FIG. 1. Exploded view of the pressure cell showing mounting of the sample. 1. Carboloy truncated-cone piston. 2. Hardened tool-steel piston, 0.5 mm thick, 3.0-mm o.d. 3. Nickel gasket, 0.13 mm thick. 4. Steatite disk 0.20 mm thick, 3.0-mm o.d. 5. Specimen, 2.5×0.04×0.04 mm. 6. Steatite disk, 0.25 mm thick with groove for specimen and four holes for platinum ribbons. 7. Platinum ribbons, cross section 0.1×0.02 mm: The ends that stick out though part 6 are just bent down over the sample. 8. Pressure cylinder, height 0.75 mm, o.d. 3.0 mm. 9. Cigarette-paper insulating sheets. 10. Countersupport. 11. Thermoresistor.

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[1] See review articles: M. Levy and T. L. Olsen, in *Physics of High Pressures*, edited by A. van Itterbeek (North-Holland Publishing Company, Amsterdam, 1965); N. B. Brandt and N. I. Ginzburg, Usp. Fiz. Nauk **85**, 485 (1965) [English transl.: Soviet Phys.—Usp. **8**, 202 (1965)].

[2] James W. Garland, Jr., Phys. Rev. Letters **11**, 114 (1963).

[3] L. D. Jennings and C. A. Swenson, Phys. Rev. **112**, 31 (1958).

[4] B. G. Lazarev, L. S. Lazareva, V. I. Makarov, and T. A. Ignat'eva, Zh. Eksperim. i Teor. Fiz. **48**, 1065 (1965) [English transl.: Soviet Phys.—JETP **21**, 711 (1965)].

[5] V. I. Makarov and V. G. Bar'yakhtar, Zh. Eksperim. i Teor. Fiz. **48**, 1717 (1965) [English transl.: Soviet Phys.—JETP **21** 1151 (1965)].

[6] N. B. Brandt, N. I. Ginzburg, T. A. Ignat'eva, B. G. Lazarev, and V. I. Makarov, Zh. Eksperim. i Teor. Fiz. **49**, 85 (1965) [English transl.: Soviet Phys.—JETP **22**, 61 (1966)].

[7] B. G. Lazarev, L. S. Lazareva, T. A. Ignat'eva, and V. I. Makarov, Dokl. Akad. Nauk SSSR **165**, 74 (1965) [English transl.: Soviet Phys.—Doklady **10**, 620 (1966)].

[8] W. Gey, Solid State Commun. **4**, 403 (1966).

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

induced shift of the superconducting transition temperature of thallium. A pressure device which is similar to that described earlier[10] was used for generation of suitable hydrostatic pressure up to 4 kbar. The polycrystalline sample[11] is embedded in a groove in a soft steatite disk and covered by another steatite disk, both of which provide the pressure medium (Fig. 1) and are surrounded by a short pressure cylinder. This type of mounting of the sample is essential to obtain hydrostatic pressure. That the strain is fairly hydrostatic in the low-pressure region can be checked in various ways: If the pressure were partly uniaxial, then an analogous experiment with well-known superconductors would yield smaller values for dT_c/dp than are known from the literature.[3] Indeed, dT_c/dp is found to be reduced 4–6% when tin and indium samples with a thickness-to-width ratio of 10 are simply squeezed between two steatite disks. However, a sample with nearly square cross section, placed in an appropriate groove in the lower disk, yields good agreement of the measured data with those of Jennings and Swenson.[12] A second proof

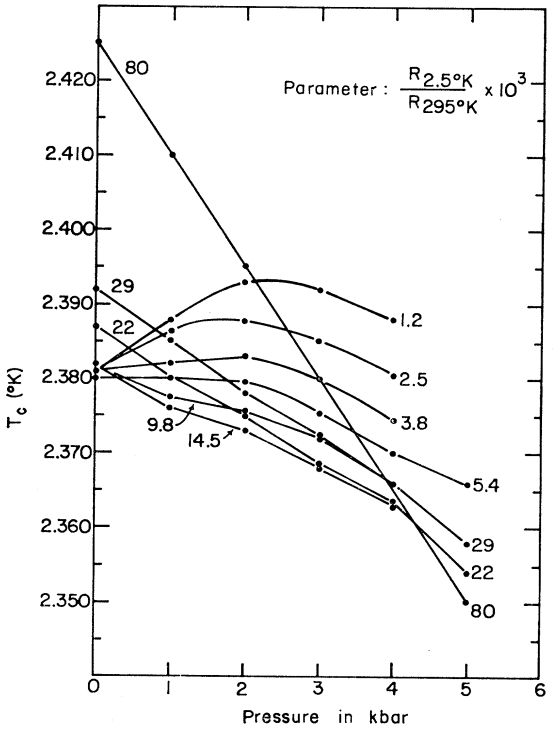

FIG. 2. Pressure dependence of the superconducting transition temperature of thallium with various resistivity ratios ($R_{2.5°K}/R_{295°K}$)$\times 10^3$ as a parameter, showing the disappearance of the pressure-induced maximum in T_c upon increasing resistivity ratio.

[10] W. Buckel and W. Gey, Z. Physik **176**, 336 (1963). Brief descriptions of the device in English are given in the review articles of Ref. 1.

[11] Asarco thallium of 99.999+% purity.

[12] Although the agreement in the low-pressure region is excellent, our described calibration shows slight deviations from that of Jennings and Swenson near 10 kbar; our T_c-p dependence for both Sn and In is more nearly linear.

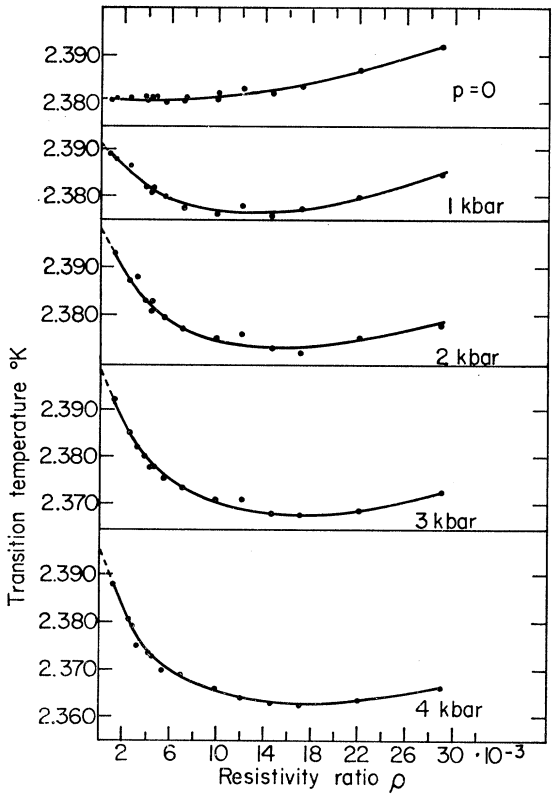

FIG. 3. Data of Fig. 2 replotted. Transition temperature of thallium as a function of resistivity ratio with pressure as a parameter, showing the drop in T_c characteristic for mean-free-path effects on gap anisotropy. Dashed lines: extrapolation to $\rho=0$.

that the pressure so obtained is fairly hydrostatic is seen in the agreement of our data on the undeformed pure Tl sample itself with those of Jennings and Swenson, who undoubtedly had highly hydrostatic conditions.

Lattice defects have been generated by repeated application of much higher pressures (up to 32 kbar) in the same apparatus at 2.5°K and subsequent removal of pressure at the same temperature. Pure hydrostatic pressure applied to a single crystal would yield no lattice imperfections. However, our samples are polycrystalline. Therefore, upon compression, shear at grain boundaries may occur in the elastically anisotropic hexagonal material—presumably in large part by the migration of dislocations from the boundaries into the bulk. Some support for this model is given by the observation that a sample which consisted of about 20 crystallites (sample 1) was much easier to load with imperfections than a sample with only 4–5 crystallites (sample 2). This grain growth was obtained by annealing the sample for 24 h just below the transformation temperature from the hcp to a bcc structure (at 234°C). As a measure of the degree of internal deformation, in accordance with common practice we use the residual resistivity ratio, which, however, we define, following

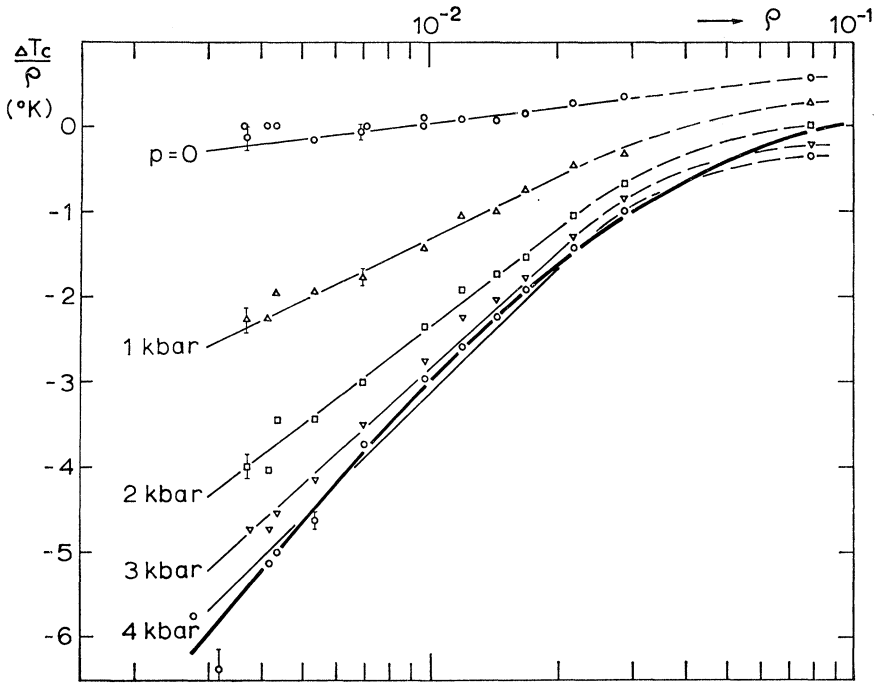

FIG. 4. $\Delta T_c/\rho$ versus ρ plot for various pressures up to 4 kbar. The slope of the linear parts of the curves are measures of the anisotropy parameter $\langle a^2 \rangle$. The data points at $\rho = 80 \times 10^{-3}$ were obtained by forcing the sample through a high-pressure phase transformation. Bars at several points indicate an uncertainty of determination of T_c of ± 0.5 mdeg. The heavy solid line represents the exact function $I_c'(\rho)$ of Markowitz and Kadanoff's theory for $p = 4$ kbar.

Markowitz and Kadanoff, as $\rho = R_{2.5°K}/R_{295°K}$, the reciprocal of the usual quantity.

Measurements of the changes of ρ produced by excursions of applied pressure to various values showed that detectable plastic deformation began to appear only above pressures of 4 kbar. Thus it was possible to use the same apparatus to produce plastic deformation by applying very high pressures and to obtain virtually hydrostatic stress by confining pressure to a low-pressure regime below 4 kbar.

For measurement of the resistance of the sample, it is connected to four platinum ribbons (cross section 0.1 mm$\times$0.02 mm) which serve as current and potential leads (see Fig. 1). That even during the application of high pressure, no appreciable geometrical deformation of the sample occurs was confirmed by the observation that the room-temperature value of the resistance of the sample changed less than 0.2% during repeated (10–15 times) application of pressure up to 32 kbar. The transition to superconductivity was observed by continuously recording the resistance of the sample during temperature changes. For the unstrained sample just above the critical temperature, measuring currents of 1 mA yielded voltages of the order of 0.2 μV. It was shown that currents smaller than 2 mA did not shift or broaden the transition noticeably. The width of the transition, taken between 10% and 90% of normal resistivity, varied between 8×10^{-3} and 12×10^{-3} °K for all pressures and degrees of deformation. These small widths were only obtained after carefully de-Gaussing the ferromagnetic Carboloy pressure piston. The temperature at which half of the normal resistance occurs was taken as the transition temperature T_c. Without changing the pressure or the defect concentration, the reproducibility of the measured T_c was better than 0.5×10^{-3} °K.

In Fig. 2 we show the observed pressure dependence of T_c with the resistivity ratio ρ as parameter. As already mentioned, the curve for the unstrained sample with $\rho = 1.2 \times 10^{-3}$ agrees very well with Jennings and Swenson's data, thus indicating that our pressure is hydrostatic. Upon gradually raising the number of imperfections by cold-working, the enhancement in T_c disappears and the pressure dependence of transition temperature becomes linear with a negative slope $dT_c/dp = -1.50 \times 10^{-5}$ °K/bar when a comparatively high resistivity ratio $\rho = 80 \times 10^{-3}$ is reached. Actually this highest ρ value was not obtained in the described manner but by forcing the sample through a phase transformation at 37 kbar and subsequently removing the pressure at 2°K, which results in the reappearance of the low-pressure phase with an obviously much more heavily distorted lattice.[8]

In Fig. 3, the data are replotted with the pressure as parameter. The characteristic depression of T_c and the curvature of the T_c–p plot suggest that an anisotropy of the energy gap is smoothed out as the electronic mean free path is reduced by imperfections. The theoretical foundation of this concept has been given by Markowitz and Kadanoff[9] and successfully applied to various experimental results. In order to evaluate the governing parameters, we follow the standard treatment and show log ρ vs $\Delta T_c/\rho$ in Fig. 4, where the data plot nearly linearly for $\rho < 0.03$ and the slopes of the straight

lines are a direct measure of the anisotropy parameter $\langle a^2\rangle$ of Markowitz and Kadanoff. We immediately notice that $\langle a^2\rangle$ is pressure-dependent, rising monotonically from a small value at zero pressure to a value larger by a factor of 8 at 4 kbar. Data for a different sample (consisting of a smaller number of crystallites) show the same increase of $\langle a^2\rangle$ under pressure. Numerical values for the anisotropy parameter can be obtained by use of Eq. (50) of Ref. 9. This requires the knowledge of a characteristic number in the theory which is proportional to ρ:

$$\chi=\lambda\hbar[\bar{v}_f/(bkT_c)]\rho.$$

$\bar{v}_F$ is the average value of the Fermi velocity, $b=\rho l$ is the constant which relates the resistivity ratio to the electronic mean free path l at the measuring temperature, and λ is a constant which depends on scattering anisotropy and is unity for isotropic impurity scattering. Since in our case the scattering centers are mainly dislocations, λ may differ from unity. We account for this by keeping λ explicitly in the anisotropy parameter as $\lambda\langle a^2\rangle$. The values of $\bar{v}_F$ and b are properties of the host which are unfortunately not known experimentally for thallium. We therefore relate the unknown quantities to those which can be estimated. By setting $b=l_{2.5°K}\times(\sigma_{295°K}/\sigma_{2.5°K})$ and using the expression for the conductivity

$$\sigma=(Ne^2/m^*)\tau,$$

we obtain

$$\frac{\chi}{\rho\lambda}=\frac{\hbar Ne^2}{\sigma_{295°K}m^*kT_c}$$

where $\sigma_{295°K}=5.52\times10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ is the conductivity at 295°K.[13] The unknowns are here the effective number of electrons per unit volume, N, and the effective electron mass m^*. Soven[14] suggests that the Fermi surface of thallium is fairly close to that obtained from a free-electron model for a trivalent hexagonal close-packed metal. By way of trial, we therefore set $m^*=m_0$, and choose for the effective number of electrons per atom $n=3$; we obtain

$$\chi/\rho\lambda=1700.$$

Compared with the experimental data on tin and indium,[9] this number seems high. A check of it would be desirable. Thus, before presenting numerical values for the anisotropy parameter under pressure—the quantity we are most interested in—, we separate the accompanying effects that are independent of anisotropy. From analogous experiments done with doped superconductors we know that these effects, which are sometimes lumped into the term "valence effect," are linear in impurity concentration, at least for lower concentrations. It is this feature, of course, which permits the separation of anisotropy and "valence effect."[15] We shall see later that there is evidence that the linearity of the "valence effect" holds also for our lattice imperfections up to a resistivity ratio $\rho\sim30\times10^{-3}$. We are, therefore, justified in separating out the linear term, which we call $(\partial T_c/\partial\rho)_p$ as a function of pressure. It turns out that $(\partial T_c/\partial\rho)_p$ is rather sensitive to the choice of the quantity $\chi/\rho\lambda$, and we will use this to check the validity of our calculated number. In Fig. 5 the pressure dependence of $(\partial T_c/\partial\rho)_p$ is plotted for several values of $\chi/\rho\lambda$ near our calculated value 1700. Physically, we would expect $(\partial T_c/\partial\rho)_p$ not to change markedly with pressure: $(\partial T_c/\partial\rho)_p$ probably depends mainly on such parameters as ω_D, $N(0)$, and V, all of which determine the transition temperature in the BCS theory. Since pressures up to 4 kbar change T_c only about 3% at most, we can consider the pressure dependence of any combination of the above parameters to be negligible and are led to the assumption that $(\partial T_c/\partial\rho)_p$ is almost pressure-independent. Figure 5

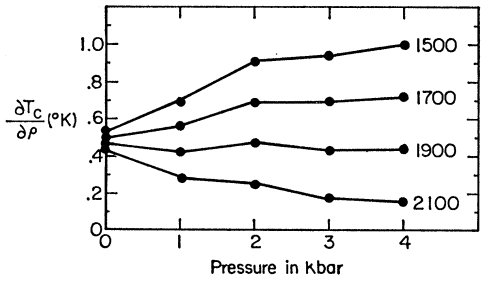

FIG. 5. Pressure dependence of the "valence effect" $\partial T_c/\partial\rho$ as obtained from the experimental data for different values of $\chi/\rho\lambda$.

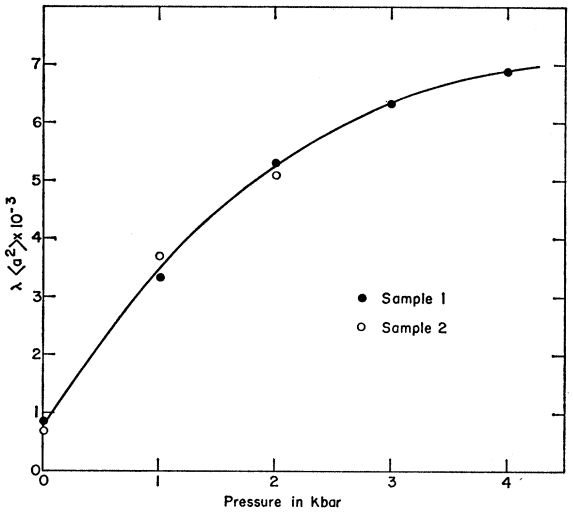

FIG. 6. Pressure dependence of the anisotropy parameter $\lambda\langle a^2\rangle$ in thallium as evaluated from the experimental data. The nonlinear rise of this quantity provides an explanation of the anomalous pressure-induced increase of T_c.

[13] *Landolt-Börnstein Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1959), 6th ed., Chap. II/6, p. 1.

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

[15] Although actually no valence differences are involved in our case, we follow Markowitz and Kadanoff in adopting the term "valence effect," meaning all effects linear in ρ.

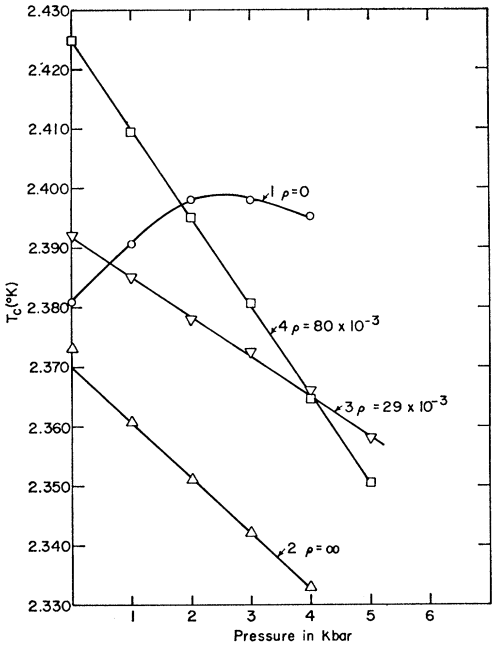

FIG. 7. Analysis of the pressure-induced enhancement of T_c of thallium in terms of pressure-dependent gap anisotropy. Description in the text.

tells us that the best choice is $\chi/\rho\lambda=1900$, which differs by only about 10% from our calculated value and thus confirms it.

We are not ready to present numerical data for the anisotropy parameter $\lambda\langle a^2\rangle$. From the straight-line fits of Fig. 4 and with $\chi/\rho\lambda=1700$, we obtain the curve shown in Fig. 6, which is our main result. In this plot, data on a second sample are included. The interesting physical feature is the monotonic rise of the anisotropy of the energy gap from a rather small value of $\lambda\langle a^2\rangle=0.0008$ at zero pressure up to $\lambda\langle a^2\rangle=0.0069$ at 4 kbar, with an indication of a saturation at higher pressures. This result is the basis for our explanation of the enhancement of the transition temperature in thallium in the lower pressure region. We wish to point out that since $\lambda\langle a^2\rangle$ is inversely proportional to $\chi/(\rho\lambda)$, changes in the choice of $\chi/(\rho\lambda)$ affect only the absolute values of $\lambda\langle a^2\rangle$ for the various pressures, but not the fact that the gap anisotropy increases markedly with pressure.

Before discussing the results we wish to draw attention also to the detailed agreement over a wide range of ρ between our data at 4 kbar, where they provide the most sensitive test, and the exact function $I_c(\chi)$ of the theory of Markowitz and Kadanoff. Allowance for the fact that thallium is a stronger coupling superconductor has been made in calculating $I_c(\chi)$. With $\chi/(\rho\lambda)-1700$, $\lambda\langle a^2\rangle=0.0069$, and $\partial T_c/\partial\rho=0.72$, we have good agreement of the function $I_c'(\rho)$, shown as a heavy solid line in Fig. 4, and the experimental data, except for one point at the upper end where the high resistivity ratio $\rho=80\times10^{-3}$ was obtained in a different way.

The fact that our experimental data seem to follow the theory in such detail leads us to believe that the effects of the generation of lattice imperfections by cold-working due to the application of high pressure are appropriately represented as effects on the gap anisotropy of shortening the electronic mean free path. It also shows that the valence effect is linear for $\rho<30\times10^{-3}$.

Although it seems already evident from Fig. 2, we now try to analyze more quantitatively how the anomalous enhancement of T_c under pressures up to 2 kbar can be explained by the observed dependence of the anisotropy of the energy gap in thallium. In Fig. 7, curve 1 represents the pressure dependence of T_c for the limit $\rho\to0$ as obtained from the extrapolation in Fig. 3. From this curve we subtract the maximal depression of T_c due to complete smoothing out of the gap anisotropy by going to the limit $\rho\to\infty$, which is given by Eq. (44c) of Ref. 9:

$$(\Delta T_c)_{\max}=T_c\frac{1}{VN(0)}\langle a^2\rangle.$$

We then arrive at curve 2 of Fig. 7, which shows the linear decrease common for soft superconductors. This curve shows what we would have for the anisotropy effect alone as $\rho\to\infty$. We obtain an average slope

$$(dT_c/dp)_{\rho\to\infty}=-1.0\times10^{-5}\ ^\circ\text{K/kbar}.$$

For a quantitative check of our anisotropy concept we would like to have the slope dT_c/dp for $\rho\to\infty$ measured. This condition cannot be verified experimentally, and in fact in this limit the theory also should fail.[9] We therefore compare our calculated slope $(dT_c/dp)_{\rho\to\infty}$ with the slope for the two highest resistivity ratios obtained, $\rho=29\times10^{-3}$ and 80×10^{-3}. The data for these are included in the figure as curves 3 and 4. We see that the calculated $\rho\to\infty$ slope is already approached by the slope of the lower experimental ρ, but the higher experimental-ρ slope differs by a factor of 1.5. It must be borne in mind, however, that experimentally the highest resistivity ratio was obtained by forcing the sample through a phase transformation which certainly affected at least the valence effect, as already indicated in Fig. 4, so that this datum probably should be disregarded.[16]

We therefore conclude that the concept of pressure-dependent gap anisotropy discussed above quantitatively explains the anomalous enhancement of the transition temperature of thallium at pressures up to 2 kbar.

An interesting question remains of how this large pressure dependence of the gap anisotropy can be

[16] In fact, there is indication from the data that the valence effect becomes pressure-dependent at this high imperfection concentration. This dependence cannot be isolated, however, if it is due to the different scattering centers introduced by the different procedure or if at higher concentrations $\partial T_c/\partial\rho$ becomes intrinsically pressure-dependent.

explained. Gap anisotropy as treated above contains, by definition, anisotropy in the phonon spectrum, in the electron-phonon interaction, and in the electronic density of states. Which of these factors is affected most by pressure cannot be decided without further investigation. It may very well be that the anisotropy in the density of states dominates. Associated variation of the energy dependence of the density of states was assumed by Lazarev and co-workers[4–7] to explain their data in a qualitative way.

COMPARISON WITH OTHER RESULTS

It is easy to see that our results are not in contradiction with the data of Quinn and Budnick,[17] who did not observe a decrease of T_c in thallium upon decreasing the electronic mean free path by dilute alloying of indium, bismuth, and lead, but observed an immediate increase of T_c. In Fig. 8 we have plotted the dependence of the transition temperature on the residual resistivity ratio as obtained in our experiments on plastically deformed pure thallium at zero pressure, together with Quinn and Budnick's results on dilute alloys of In, Pb, and Bi. In spite of the paucity of the experimental points for the alloys, it seems obvious that the large valence effect in the alloys obscures the very small anisotropy effect in thallium. In our results on plastically deformed thallium, the valence effect is just strong enough to eliminate any decrease in T_c as ρ decreases, leaving only a weakly curved region at small ρ. At zero pressure, the gap anisotropy is known to be small from an investigation of Weil and Lawson, who determined the value of the energy gap for several directions by ultrasonic methods.[18] From their data, we roughly estimate $\langle a^2 \rangle$ to be around 0.0007 compared with our value of 0.0008.

Hasse and Lüders[19] and Hasse and Seifritz[20] have obtained varying resistivity ratios and accompanying changes in T_c by deforming Tl plastically by twisting wires at cryogenic temperatures. There is strong disagreement between our results and theirs, though they used methods which at first sight seem closely related to ours. The discrepancies are most easily demonstrated by replotting their data together with ours, Fig. 9. Curves 1–6 represent the twisted-wire data on various samples. Since they were obtained at zero pressure, these data are to be compared with our zero-pressure curve (open circles), which was identical on two samples. Besides the large differences between different samples, the curvature and the enormous decrease in T_c are most striking. Although we do not think that substantial residual stresses in the twisted wires can be held responsible for these discrepancies, we include our data obtained under a pressure of 4 kbar for comparison. Without further information, we can only give a guess about the source of the differences: Since Hasse and Seifritz find good agreement of their twisted-wire data with alloy data on indium,[20] the suspicion arises that thallium is anomalous for some reason. It is conceivable that there is an influence of a phase transformation.[8]

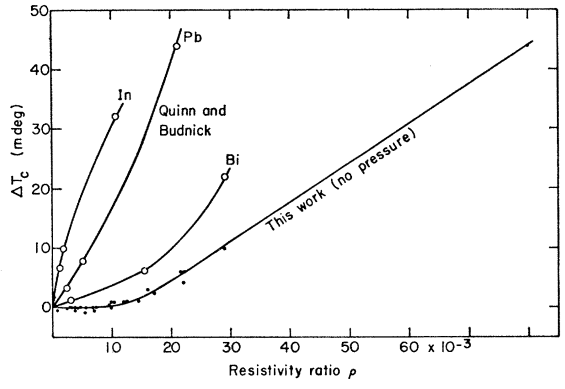

FIG. 8. Comparison of our data, obtained by plastic deformation on two samples at zero pressure, with data of Quinn and Budnick (Ref. 8) obtained by dilute alloying of In, Pb, and Bi.

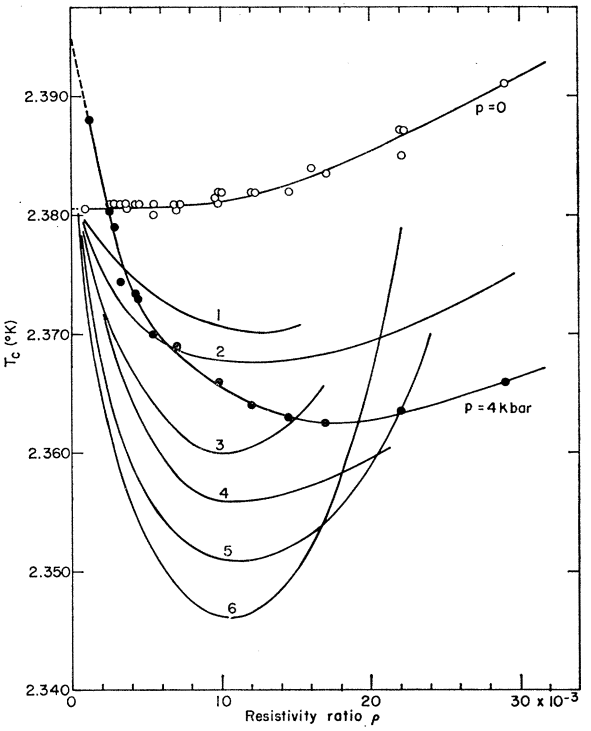

FIG. 9. Comparison of the data obtained by different methods of plastic deformation on the change of T_c in thallium with resistivity ratio. Curves 1–6: different samples, twisted-wire technique (Refs. 19, 20). Open circles: data on two samples, present work, no pressure, lattice imperfections introduced by repeated application of high pressure. Full circles: the same, measuring pressure 4 kbar.

SUMMARY

We conclude that the picture of suppression of gap anisotropy, as the electron mean free path is decreased,

[17] D. J. Quinn and J. I. Budnick, Phys. Rev. **123**, 466 (1961).
[18] R. Weil and A. W. Lawson, Phys. Rev. **141**, 452 (1966).
[19] J. Hasse and K. Lüders, Z. Physik **173**, 413 (1963).
[20] J. Hasse and W. Seifritz, Z. Physik **193**, 52 (1966).

can be applied successfully to "physical impurities," e.g., lattice defects in thallium, when they are introduced by virtually hydrostatic compression at 2.5°K.

At zero pressure, we find an extremely small gap-anisotropy parameter $\lambda\langle a^2\rangle=0.0008$ (compared with $\lambda\langle a^2\rangle\approx0.02$ for Sn and In). We also find that the anisotropy parameter of Tl increases strongly with pressure, reaching $\lambda\langle a^2\rangle=0.007$ at 4 kbar, which explains quantitatively the anomalous pressure dependence of T_c in thallium.

ACKNOWLEDGMENTS

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Anomalous Scattering by Magnetic Impurities in Superconductors*

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The effect of magnetic impurities in superconductors is studied by using the dispersion equations, which are simple extensions of those introduced by Suhl. In the case of a single impurity, we find that, if $T_{c0}>T_r$ (where T_{c0} is the superconducting transition temperature and T_r is the Suhl-Abrikosov resonance temperature), a pair of bound states appear in the energy gap, while if $T_{c0}<T_r$, resonances appear at low temperatures. Also, self-consistent equations are constructed to treat the case of dilute concentration of impurity atoms. In the gapless region it is established that the Abrikosov-Gor'kov expressions are valid, except that τ_s in their theory must be replaced by the exact frequency-dependent spin-flip lifetime $\tau_s(\omega)$ in the normal state.

I. INTRODUCTION

As Kondo[1] has recently pointed out, the spin-exchange scattering from magnetic impurities gives rise to an electron scattering amplitude in normal metals, which diverges logarithmically at low temperatures. Since Kondo's calculation is perturbational, his approach is valid only within two approximations. The impurity concentration must be small so that the spin correlation among impurity atoms is negligible, and the temperature must be relatively high, so that the logarithmic term (which comes from the second-order Born term) is still a small correction to the first-order Born term. Therefore there naturally arises a question concerning the convergence of the perturbation series at low temperatures, even if one still confines oneself to the dilute-concentration limit of magnetic impurities.[2–5]

Recently, Suhl[2] and Abrikosov[4] were able to show that, if one sums up a certain class of the higher order effects [which essentially consist of diagrams containing only single-particle (or hole) states as intermediate states] than the second-order term, the logarithmic divergence in the scattering amplitude disappears, but the scattering amplitude develops a pair of poles at temperatures lower than T_r, the resonance temperature. T_r corresponds roughly to the temperature at which the second-order Born term becomes comparable with the first-order term and thus a simple perturbation calculation breaks down. In spite of the apparent success of Suhl and Abrikosov's theory [which not only gives a formal answer to the convergence problem of the perturbation series, but also allows one to calculate various equilibrium as well as inequilibrium properties of a dilute impurity system at low temperature ($T\lesssim T_r$)], a detailed study of the analytical behaviors of the scattering amplitude as a function of energy reveals a serious drawback: The poles are in the physical sheet (i.e., the first plane) of the complex energy plane, which is inconsistent with the principle of causality.[2,3] Fortunately, in a recent work Suhl and Wong[6] have succeeded in removing this difficulty in the framework of his dispersion theory.

It is well known that the spin-exchange scattering drastically modifies the electronic properties of super-

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