Properties of Indium and Thallium at Low Temperatures*

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The pressure-volume relationships for superconductors near absolute zero are of potential interest for comparison with theories which attempt to explain the variation of the superconducting transition temperature with pressure. Such data for thallium are of special interest since the variation of transition temperature with pressure is different for thallium than for any other known pure metal. In these experiments, measurements on indium of the total compression to 10 000 atmos for various temperatures down to 4.2°K served as a check of similar measurements on thallium. No unusual behavior was found for either metal. These results were combined with the measurement of the total thermal expansions for both metals to give isobars at both zero pressure and at 10 000 atmos pressure over the range from 4.2° to 300°K. The results of some low-temperature compressive testing experiments on both metals are also given, together with some indirect evidence as to the vanishing of work hardening effects at low temperature and moderate hydrostatic pressures. Finally, measurements on the electrical resistance of indium show an unexplained kink in the R *vs* T curve at about 210°K. The effect on the electrical resistance of indium due to tensile (plastic) deformation at 4.2°K was also measured.

INTRODUCTION

THE measurement of the effects of high hydrostatic pressures on superconducting transition points has currently become a fairly important branch of low-temperature research.[1] While the general field has been surveyed and data exist for various substances, probably the only generalization which can be made is that the superconducting transition point *usually* decreases as the applied pressure is increased. Little is known about the basic theory behind this effect, and as yet there exist no bases for correlating these pressure effects and others, such as the changes in volume or electrical resistance with pressure. If the superconducting transition is very sensitive to volume changes, as it seems to be, then measurements of $P-V$ isotherms at low temperature for superconducting elements can be of considerable interest. The measurement of these is not too difficult, since a number of the superconductors (indium and thallium in particular, and probably pure tin, lead, mercury, and cadmium)[2] retain sufficient plasticity at their transition points so that variations of volume with pressure can be obtained at liquid helium temperatures by using a method which has been described elsewhere.[3-5]

The work on indium and thallium which is given below was undertaken to provide such $P-V$ data for these substances. There are two considerations which govern the choice of materials; first, and foremost, they must be plastic, and, secondly, they must be of specific interest. Indium was chosen initially because of its plasticity, and the original work done on it was an attempt to discover the relationship between the extrusion experiments performed by Stewart[2] and the shear yield strength and work hardening of a substance. Both extrusion pressures and compressive stress-strain curves were measured, and very unusual results were obtained which indicated a shear sensitive transition at very low temperatures. As a result of this, several different low-temperature properties of indium were measured in the hope that they would shed some light on this suspected transition. These experiments included: (a) the electrical resistance as a function of temperature from 300° to 4.2°K; (b) the electrical resistance of a wire as a function of strain (plastic) at 4.2°K; (c) an x-ray Laue pattern taken before and after deformation at 4.2°K; (d) the total volume change at 10 000 atmos pressure between 300° and 4.2°K.

Outside of a kink in the electrical resistance about 210°K (a discontinuity in the temperature coefficient of resistance), no unusual effects were found. Attempts to reproduce the yield strength and extrusion phenomena a year later were not successful, and as the original effects remain unexplained, only the second set of stress-strain curves (of normal behavior) are given below. The total linear thermal expansion of indium was also roughly measured to 4.2°K so that it would be possible to convert the compressibility measurements into actual molar volumes at 10 000 atmos pressure from 4.2°K to room temperature.

Thallium also satisfies the plasticity criterion at low temperature, and, whereas there was no reason to suspect abnormal behavior for indium, thallium represents an exception among pure metallic superconductors in that it initially shows an increase of superconducting

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[1] See the article by C. F. Squire in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1955), p. 151.
[2] J. W. Stewart, doctoral thesis, Harvard University, submitted May, 1954 (unpublished).
[3] C. A. Swenson, "The application of high hydrostatic pressures at liquid helium temperatures," Paper No. 54-33-3, delivered before the Instrument Society of America Meeting, Philadelphia, 1954 (to be published in the Proceedings); also reported in slightly revised and corrected form under the same title as U. S. Army Office of Ordnance Research Technical Memorandum, TM-55-1 (unpublished).
[4] J. W. Stewart, Phys. Rev. **97**, 578 (1955).
[5] C. A. Swenson, Phys. Rev. **99**, 423 (1955).

transition point with pressure, although for quite high pressures (several thousand atmospheres) the effect is normal.[6] Chester has suggested the possibility of a phase transition in thallium to explain this result,[7] and it was with the object of testing this hypothesis that the work on the $P-V$ curves of thallium was undertaken. Indium, presumably having a normal behavior, was useful as a comparison sample, to verify that any unusual effects observed were solely a function of the sample being tested, and not due to the apparatus. Thermal expansion data also were taken for thallium, so that, again, it would be possible to have two isobars, one at zero pressure and one at 10 000 atmos. As was the case for the similar measurements on indium, no unexpected behavior was found.

Neither indium nor thallium are "nice" substances to work with from a physical viewpoint, since they both have anisotropic crystal structures. Indium has a slightly distorted face-centered cubic lattice (face-centered tetragonal with $c/a=1.07$ at room temperature),[8] while thallium is hexagonal with an axial ratio of 1.598.[9] Thus, every effort was made to assure that the abovementioned thermal expansion and electrical resistance data were taken on finely polycrystalline samples with no preferred orientation, so that the true average effects were being observed. The object, fortunately, was to look for anomalous behavior or transitions, and not to try to present data of theoretical interest.

No anomalies were expected in the zero-pressure range, since the heat capacities of both indium and thallium have been measured, the former between 2°K and room temperature,[10,11] and the latter from 1.5° to 4.2°K, and from 15° to 300°K.[12,13] The gap existing for thallium is very tantalizing, since the data obtained on the two sides of it seem inconsistent. Both metals have rather low melting points, as is characterized by their low Debye θ's, about 130° for indium and 94° for thallium.

Finally, thallium has the disadvantage that it oxidizes very rapidly at room temperature, so that detailed electrical resistance measurements were not attempted.

MATERIALS USED

The indium and thallium used were both obtained from A. D. Mackay, Inc., and were specified as 99.9% pure. Fortunately, the actual purity should not be too important for either the compression or the rather qualitative thermal expansion data which were taken. The purities were probably much better, since the residual resistances were about $10^{-3}R_{273}$ for indium and $3\times10^{-3}R_{273}$ for thallium. Both wires were extruded and not annealed. The indium was cast under vacuum from ingots into rods from which samples were machined or formed by pressure at room temperature. The thallium was furnished in the form of a rod from which the samples were machined on a lathe and then stored under water which had been boiled. It was never possible to keep all traces of the oxide from the surface of the thallium samples. The residual resistances quoted above refer to samples taken from the metals after processing.

TEMPERATURE MEASUREMENT

All temperatures recorded in these experiments were measured with Leeds-Northrup copper-constantan thermocouple wire (No. 30 B. and S. gauge, enamel and glass insulation), which had been calibrated in this laboratory between 4.2° and 300°K, using a constant volume gas thermometer. The accuracy is estimated to be of the order of 0.1 degree down to 50°K, and about 0.5° from 50° to 15°K. This was not a limiting factor in any of the measurements.

COMPRESSION MEASUREMENTS

The apparatus and techniques used in measuring the total compressions of indium and thallium to 10 000 atmos are identical with those described elsewhere,[3,5,14] and will not be given here in detail. The sample (0.375 in. long by 0.253 in. diam) was placed in a cylinder of hardened tool steel of the same diameter, and was compressed in an elongated press by two hardened steel pistons. The low-temperature end of this press could be placed in a Dewar, or in a special cryostat where it could be kept at any desired temperature between 4.2°K and room temperature to a constancy of about 0.1°. As will be described later, both indium and thallium are quite plastic at the lowest temperatures, so the resulting pressure (force applied/area) is hydrostatic to a good approximation, and the motion of the pistons is a measure of the volume change of the sample. Several cycles were necessary to season the sample initially at each temperature so as to obtain reproducible data.

Basically, three corrections must be applied to any data taken; these are concerned with friction (both in the sample and in the hydraulic press), background stretch of the apparatus with no sample present, and expansion of the sample holder cylinder due to the internal hydrostatic pressures up to 10 000 atmos. The first correction is obtained by taking data at both increasing and decreasing pressure and the second by doing blank runs at all temperatures in both the cryostats used. The third correction is determined by comparing the room temperature compression of a

[6] M. D. Fiske, Phys. Rev. 94, 495 (1954).
[7] P. F. Chester (private communication).
[8] W. A. Betteridge, Proc. Phys. Soc. (London) **A50**, 519 (1938).
[9] H. Lipson and A. R. Stokes, Nature **148**, 437 (1941).
[10] K. Clusius and L. Schachinger, Z. angew. Physik 4, 442 (1952).
[11] J. R. Clement and E. H. Quinnell, Phys. Rev. **92**, 258 (1953).
[12] W. H. Keesom and J. A. Kok, Physica 1, 175, 503, 595 (1933–1934); Leiden Comm. 230c, 230e, and 232a.
[13] J. F. Hicks, Jr., J. Am. Chem. Soc. **60**, 1000 (1938).
[14] C. A. Swenson and R. H. Stahl, Rev. Sci. Instr. **25**, 608 (1954).

substance, obtained using the two above corrections, with the true value which is known quite accurately from other measurements. This correction must be extrapolated to low temperature by the assumption that it is inversely proportional to the elastic (or Young's) modulus of the steel used in making the sample holder cylinder.[15]

The last two corrections are quite large, and introduce a basic uncertainty of about five percent into any volume change obtained in the present experiments. However, the correction data, while showing considerable scatter, could be represented by smoothed curves which were taken as being correct and which were used consistently. The philosophy was that if the sample holder and sample were placed in the press, and then in the cryostat, the relative accuracies would be much better if the setup were not disturbed during a series of runs at various temperatures. Thus, for any series the data should be consistent (and were) to about one percent, while if the sample holder were removed and then replaced in the press, the answer could vary by about 5%.

In practice, the cylinder expansion correction was determined for each sample and for each loading of the sample holder in the press by doing a room-temperature run, since Bridgman's work gives fairly accurate room temperature compression data for both indium and thallium.[16] The series of experiments on thallium shown in Fig. 1 lasted over a period of a week, with the sample holder remaining undisturbed in the press during this time, and the scatter of four room-temperature runs made at different times is shown about an average correction figure. There is an added advantage to making a final correction in this way since it automatically takes into account any small effects which might have been otherwise overlooked. It does, of course, make any results relative to those of Bridgman, and subject to any correction which may be later made in his data.

The actual procedure which was used to calculate the results shown in Fig. 1 is given below, and was necessitated by the small total compressions observed. The change in length of the sample was measured for small pressure increments from 1500 to 10 000 atmos for both increasing and decreasing pressures, and the total apparent change in volume (measured as a change in length, δl) between 1500 and 10 000 atmos was obtained by applying the friction and background stretch corrections. The curves showed no signs of abrupt volume changes, so only the total ΔV was measured. The lower limit of 1500 atmos was due to apparatus limitations,[5] and also uneven friction. The total compression was assumed to be linear (the deviations are small), and this change in length was converted into a total change in length in 10 000 atmos. The same experiment gave a measurement of the length, l_0, and the final $\delta l/l_0$ obtained in this way was corrected to a true $\Delta V/V_0$ in 10 000 atmos by subtracting the cylinder expansion correction. V_0 here is the volume at zero pressure at the temperature of the experiment. The cylinder expansion correction was calculated using the linear assumption also, so unless the small curvature which is observed by Bridgman changes radically with temperature, it should result in fairly accurate values for the true $\Delta V/V_0$ in 10 000 atmos, even though the curvature has presumably been ignored.

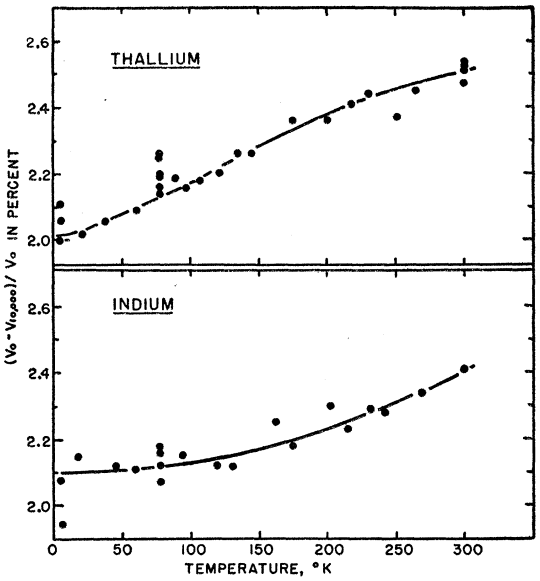

FIG. 1. The total hydrostatic compressions in 10 000 atmos of indium and thallium as a function of temperature. V_0 refers to the volume of the sample at zero pressure and the temperature of the test.

The final results for indium and thallium are given in Fig. 1, with the smooth curve being drawn through the points (not indicated) which were most consistent. The smoothed curves are summarized in Table I. There is some arbitrariness about drawing the indium curve, but since occasional points do seem to lie off the smooth curve for no known reason, little weight was given to the two points which lie high at about 160° and 200°K. The scatter at 77°K is common to both metals, and although it is presumably an apparatus effect, it is not understood. The 77°K points shown represent a variety of cooling rates in both the Dewar and cryostat, ranging from six to eight hours to ten minutes, done with both zero pressure on the sample and also with a pressure of 10 000 atmos. No consistent trend could be observed, although the calibration runs, done under similar conditions, showed no such scatter. The slowest cooling rate gave the lowest point for thallium, and this

[15] The elastic modulus of a piece of the same steel as used in the cylinder (Omega, Rockwell "C", 656) was measured directly as a function of temperature in this laboratory, using the same press and cryostat. These measurements showed a linear variation of the Young's modulus from 24.5×10^6 psi at room temperature to 27.6×10^6 psi at 60°K, with a rapid leveling off from this value to 28.0×10^6 psi at 4.2°K.

[16] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1945).

TABLE I. The smoothed total thermal expansions, compressions in 10 000 atmos, and molar volumes of indium and thallium at low temperature.

	Indium				Thallium			
	$\frac{l-l_{273}}{l_{273}}$	$\frac{V_0-V_{10\,000}}{V_0}$			$\frac{l-l_{273}}{l_{273}}$	$\frac{V_0-V_{10\,000}}{V_0}$		
T(°K)	in percent		$V_{p=0}$	$V_{p=10\,000}$	in percent		$V_{p=0}$	$V_{p=10\,000}$
			cc/mole				cc/mole	
300	+0.085	2.41	15.712	15.333	+0.061	2.51	17.124	16.694
275	+0.006	2.36	15.673	15.305	+0.003	2.48	17.094	16.670
250	−0.072	2.31	15.638	15.276	−0.055	2.45	17.065	16.647
225	−0.147	2.27	15.602	15.250	−0.113	2.42	17.036	16.624
200	−0.220	2.23	15.568	15.222	−0.168	2.38	17.007	16.603
175	−0.290	2.20	15.534	15.196	−0.222	2.33	16.980	16.585
150	−0.357	2.17	15.503	15.169	−0.274	2.28	16.954	16.568
125	−0.424	2.15	15.472	15.143	−0.324	2.23	16.929	16.551
100	−0.485	2.13	15.442	15.117	−0.373	2.17	16.904	16.536
75	−0.543	2.12	15.413	15.092	−0.420	2.12	16.880	16.522
50	−0.596	2.11	15.390	15.067	−0.461	2.08	16.858	16.508
25	−0.634	2.10	15.375	15.051	−0.494	2.04	16.842	16.498
0	−0.643	2.10	15.370	15.048	−0.507	2.02	16.836	16.496

agreed well with the continuation into the low-temperature region, so it was taken as the correct value. It is gratifying that the curves above and below 77° join up so well, since the background stretch correction is discontinuous at this point, with the temperature gradients along the press supports changing as the refrigerating fluid is changed from liquid nitrogen to liquid helium, and liquid nitrogen is added to the outer jacket. The scatter at 4.2° is due to, roughly, the same reasons. In all cases, the scatter is about the five percent which was expected.

The curves of Fig. 1 show no sign of discontinuities in the total compression to 10 000 atmos, at least none greater than $5\times10^{-4}V_0$. Thus, one must conclude that the possibility of a first-order transition in the region from room temperature to liquid helium temperatures, and from zero to 10 000 atmos, is quite small for either substance.

THERMAL EXPANSIONS OF INDIUM AND THALLIUM

The total compression measurements are more useful when expressed as a change in molar volume at a pressure of 10 000 atmos, since the data of Fig. 1 come out in terms of the volume at zero pressure at the temperature of the experiment. In order to make these calculations, the change in molar volume at zero pressure must be measured as a function of temperature for each substance. In principle, it would be possible to obtain this from the observed changes in length of the samples in the press, but any answer so obtained would be with respect to stainless steel. Unfortunately, these figures showed considerable scatter, so that it was thought worth while to check them with an independent setup. The accuracy required is not high, and it was quite sufficient to know the ratio $V_{4.2}/V_{273}$ to 0.01%.

A simple setup was built which used a specimen three inches long and 0.25 in. in diameter, held freely in a copper jacket at low temperature, and with fixed quartz feeler rods connected to its top and bottom and also to a dial gauge at room temperature. The dial gauge was calibrated against a micrometer screw, so that changes in length could be measured reliably to better than 10^{-4} inch. The whole setup was placed with its low temperature section in the cryostat, and changes in length were measured as a function of temperature over the temperature region from room temperature to 4.2°K. In order to check the accuracy of the setup, and to allow a correction to be made for the thermal expansion of the quartz and any temperature inhomogeneities, a piece of very pure (99.999%) copper was also run, and the results compared with the more accurate ones of Bijl and Pullan. The correction so determined amounted to about one percent of the values for $\delta l/l_{273}$ shown in Fig. 2 and also listed in Table I.

These data were then used to calculate the total volume changes, and finally the variation of molar volume with temperature at both zero pressure and, by using the compression measurements, at 10 000 atmos. The volumes at zero pressure were taken as 15.71 cc for indium, at 25°C, based on a density of 7.303,[17] and 17.114 cc at 18°C for thallium, based on x-ray data.[9] The number of significant figures carried in the tables does not reflect the inaccuracies in these starting points, but they are used only as a convenience to show the variations of molar volume. These molar volumes are also listed in Table I for both indium and thallium.

The heat capacity results can be used in conjunction with these data to obtain a value for the Grueneisen constant, γ, which is defined in the equation,

$$dV/dT=\gamma K_0 C_v,$$

where V is the molar volume, K_0 is the initial compressibility, and C_v is the specific heat at constant volume. While the thermal expansions are not accurate enough to give a reliable value for γ in the region below 77°, above this temperature the data can be represented quite closely by a γ of 2.35 for indium and 1.80 for

[17] D. D. Williams and R. R. Miller, J. Am. Chem. Soc. 72, 3821 (1950).

thallium. One must not take these results too seriously, since there is no assurance that the thermal expansion measured is for a genuinely polycrystalline sample of either substance.

The volume expansion coefficient calculated for indium for the region near the ice point (95×10^{-6}/degree) agrees well, however, with the figure of Williams and Miller (97.5×10^{-6}/degree),[17] which is an average for the region from 25°C to the melting point. Since they measured a volume expansion directly, this gives some confidence that the assumption that this sample was a true polycrystal of random orientation is justified.

MECHANICAL PROPERTIES OF INDIUM AND THALLIUM AT LOW TEMPERATURE

One of the limiting factors in the use of these techniques for compression measurements at low temperatures is that the substances used must remain quite plastic at the lowest temperatures reached—that is, they must have a low shear yield strength and very small work-hardening so that pressure differences cannot be set up between the sides and ends of the samples. Earlier extrusion measurements by Stewart[2] listed both of these substances as of doubtful plasticity, but the criterion used was very rigid, and the extrusion pressures which he measured were of the order of hundreds of times the yield strengths as found in these experiments. The extrusion experiments were also repeated in this work, but are not of sufficient interest to be described in detail.[18]

In order to investigate these mechanical properties, the same hydraulic press which was used for the compression measurements was used to measure the stress-strain curves, in compression, for cylinders of both materials (0.40 in. long and 0.353 in. in diameter). The samples were annealed in boiling water for two hours after machining or forming. This annealing seemed to be quite important for reproducible results at 77°K (the stress-strain curve for indium at 77°K actually resembled the 4.2°K curve if the only annealing given was to leave it at room temperature for a week), but had little or no effect on the 20°K or 4.2°K curves. These measurements, typical results of which are shown in Figs. 3(a) and (b), were made with the sides of the cylinders unsupported, and the departure from linearity shown corresponds to plastic deformation of the samples.

In another identical experiment, the results of which are not illustrated, the stress-strain curve for indium at 4.2°K was found to increase linearly to a strength

[18] The extrusion experiments at 4.2°K (see reference 3 for experimental details) usually behaved as follows: As the pressure on the sample was increased, the material began to flow through the hole at about the yield strength, tending to form a button, but, due to work-hardening effects, the button merely increased slightly in length with each pressure application until at about 400 times the yield strength an explosive, irreproducible, extrusion was found. This was quite different from the case at 77°K where, at slightly smaller pressures, free flow was observed, the rate of flow depending very markedly on the applied pressure.

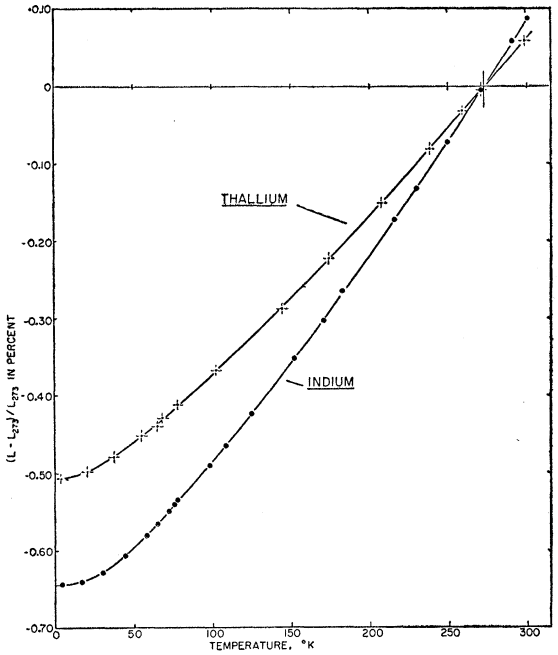

FIG. 2. The total linear thermal expansions of indium and thallium at zero pressure, after apparatus corrections have been applied.

of about 15 kg/mm² (or 1500 atmos) when the length of the sample was decreased by 15%. This represents an increase by work-hardening of a factor of thirty in yield strength, and should be compared with room temperature where a maximum increase of about two or three is possible before free flow sets in. It must be emphasized that these experiments give a compressive yield strength, which is roughly twice the shear yield strength which applies above.

This work-hardening can be quite serious, since because of the geometry of the experiments on total compression, the samples undergo considerable plastic deformation during the course of a single cycle of the pressure from zero to 10 000 atmos, and then back to zero. The sources of this plastic deformation are twofold. First, the area of the sample holder increases elastically by about one percent because of the hydrostatic pressure exerted by the sample, and the sample must first flow outwards to fill this extra volume, and then flow back as the pressure is relieved. This results in a two percent plastic deformation. The second effect is more basic, and is due to the fact that the sample material must flow even in the absence of any change in area of the holder in order for the one-sided compression to be transformed into a uniform change in density.

This latter effect can be estimated by considering an "equivalent" path through which the sample must pass to get from zero pressure and volume, V_0, to 10 000 atmos pressure and the volume $V_0-\Delta V$. One first applies a pure hydrostatic pressure of 10 000 atmos

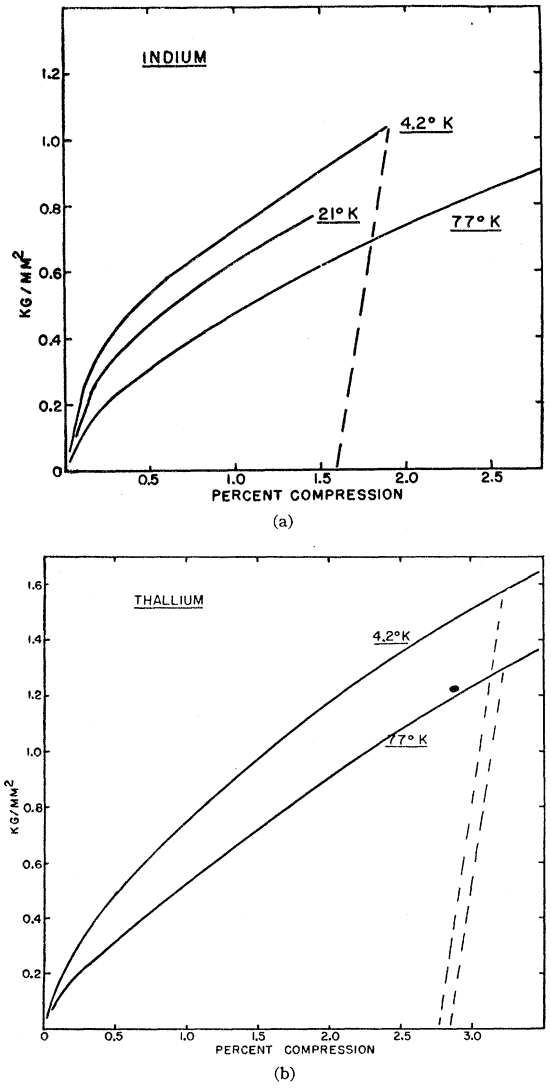

FIG. 3. The stress-strain curves for (a) indium and (b) thallium cylinders (0.4 in. long by 0.353 in. diam) under a compressive load with the sides of the cylinder unsupported. The dashed lines represent the elastic deformation of the cylinder and hydraulic press. The pressures given are not true stress, but are total loads expressed in terms of the initial areas of the samples.

and notes the change in dimensions of the sample ($\Delta V/3V_0$ in length and diameter). Effectively, the sample shrinks in from the walls of the holder during this stage. Next, a pure one-side compression is applied to the sample until it has deformed plastically enough so that is just fills the cylinder. The change in length required to do this, $2\Delta V/3V_0$, is a measure of the total plastic deformation which a sample undergoes upon the increase of pressure from zero to 10 000 atmos. An exactly equivalent argument holds when the pressure is released, and as the sample flows upwards. Thus the plastic deformation per cycle can be estimated at about 3.2%, or, considering the change in area, at about 5% total. This should be roughly independent of temperature, but should only be serious at low temperature where tremendous increases in strength by work-hardening are possible. If this full effect were to apply, an increase in shear yield strength of about 250 atmos would be expected on each cycle.

This effect would show up as an increase in friction during an experiment, since the sample would behave elastically with its behavior governed by both the shear modulus and the compressibility,[19] until the shear yield strength was exceeded, while after this point its change in length would be governed solely by the compressibility and the average pressure. The same would apply in reverse as the pressure was decreased. This would result in a widening of the hysteresis loop from cycle to cycle, or a seeming irreproducibility of the data, something which was never observed. The friction was usually of the order of 250 atmos for both indium and thallium, and about 50 atmos of this was inherent in the hydraulic press, while some was undoubtedly surface friction at the walls. It showed no variation from cycle to cycle on a given sample. This was demonstrated by a special run at 4.2°K, in which the hysteresis loop taken for an indium sample after one seasoning cycle was compared with the loop taken after fifteen subsequent cycles. The two loops coincided exactly. This is very strange, and certainly not what one would expect from the reasoning given in the previous paragraph. The indications are that the mechanism which causes work-hardening ceases to become operative at low temperature when moderate (a few hundred atmos) hydrostatic pressures are present. Bridgman has found many unusual changes in mechanical properties at room temperature and very high pressures and in general finds an increase in ductility with pressure.[20] However, the general trend seems (as is usual) that high-pressure phenomena correspond to low temperature, and in contrast the lack of work-hardening found here would resemble, basically, a high-temperature effect.

Naturally, more work is necessary to verify this effect, since the present conclusions are arrived at rather indirectly. But, this hypothesis does offer an explanation for two previously contradictory phenomena found, respectively, by Fiske[21] at the General Electric Laboratories and Hatton at Harvard.[22] Both of these workers have used solid hydrogen as a "bath" with which to apply hydrostatic pressures to metals for electrical measurements. Fiske finds that the solid hydrogen, supposedly of low shear strength, can deform tin single crystals, while Hatton finds that the strength of solid hydrogen is so low that very fragile arsenic single

[19] See the modulus, χ, defined by F. H. Newman and V. H. L. Searle, *The General Properties of Matter* (Edward Arnold and Company, London, 1948), fourth edition, pp. 94, 116.

[20] P. W. Bridgman, *Studies in Large Plastic Flow and Fracture* (McGraw-Hill Book Company, Inc., New York, 1952).

[21] M. D. Fiske, invited paper read before the American Physical Society Chicago Meeting, 1954 [Phys. Rev. **98**, 244(A) (1955)].

[22] J. Hatton, Phys. Rev. **100**, 681 (1955)

crystals are not injured by repeated pressure applications. The two observations can be reconciled if one postulates that most substances become more plastic under hydrostatic pressures.

A series of rather strange stress-strain curves found for indium in some initial work indicated a shear-sensitive transition at very low temperatures. W. B. Pearson at the National Research Council, Canada, kindly investigated this possibility by taking a Laue x-ray diffraction pattern of an indium wire before and after deformation in liquid helium, with no sign of a change from the room temperature structure.[23] Similar experiments performed by I. Simon at Arthur D. Little, Inc. in conjunction with the author, also gave negative results. The earlier mechanical deformation experiments were quite consistent at the time, and cannot be explained on the basis of any known quirks of the setup. Unfortunately, they could not be reproduced, and are mentioned here solely because of a reference which was made to them by Pearson in his report.

ELECTRICAL RESISTANCE OF INDIUM

This was measured initially to look for the above-mentioned shear sensitive transition, but the work was continued because of an apparent discontinuity in the slope of the resistance-temperature curve at about 210°K. This was found originally in the same indium as was used for the compressibility and mechanical properties work, using wire (0.015 in. diam) which had been extruded in our laboratory. The low-temperature behavior was normal, with a residual resistance of about 0.1% of the ice-point value, and a temperature variation of the resistance after the residual resistance had been subtracted of about T^3 below 20°K. The resistance was linear with temperature above 210°K, and also linear from 160° to 210°K, but with a change in slope of about 10%. In order to verify that this was a true effect, a second lot of indium wire (0.020 in. in diam) was ordered from A. D. Mackay, and a second experiment in a different sample holder, with a different thermocouple attached, was run, with the object being to obtain more precision. Requisite stability was obtained by using the cryostat again for these measurements.

The results of the two sets of experiments were indistinguishable, and the actual experimental points obtained in the second, more accurate, experiment (above 77°K) are listed in Table II, along with smoothed values for the resistance below 77°K. The effect is real, although small, and is unexplained. It is in the opposite direction from what would be expected from the normal change in density with temperature.

Another set of experiments, also inspired by the elusive shear sensitive transition, measured the change in resistance of an indium wire, 0.015 in. in diameter and six inches long, as it was extended in liquid helium. These results were about what would be expected, with no change in resistance noted until the elastic region was passed, and after this, a change of about 2.5% (or 2×10^{-10} ohm-cm) in resistance for every one percent change in length. In giving this result, the geometrical effect due to the change in diameter of the wire on extension has been subtracted. The agreement between two runs on wire from the same source was within 10%, in spite of a great deal of scatter on the first run. The total deformation in each case was of the order of 6 to 8%.

TABLE II. The electrical resistances of indium as a function of temperature. The data above and including 77.7° are actual experimental points, while below 77.7° the values given are smoothed.

T(°K)	$R/R_{273.2}$	
272.2	0.9942	
257.3	0.9286	
242.0	0.8603	$\frac{1}{R_{273}}\frac{dR}{dT}=0.00443$
227.0	0.7929	
210.8	0.7224	
194.7	0.6576	
180.7	0.6023	$\frac{1}{R_{273}}\frac{dR}{dT}=0.00400$
160.5	0.5214	
143.0	0.4549	
117.6	0.3607	
77.7	0.2189	
60	0.152	
40	0.082	Below 20°K,
20	0.020	$\frac{R}{R_{273}}-\frac{R_{4.2}}{273}\propto T^3$
4.2°	0.0010	

CONCLUSIONS

The results of the compression and thermal expansion experiments, given in Table I in terms of molar volumes at constant pressure, show that neither indium nor thallium exhibit any signs of a phase transformation under pressure in the low temperature region. This means that the anomalous behavior with pressure of the superconducting transition in thallium must be a characteristic of the metal as it normally exists at very low temperatures. No consistent effects on the total compression were observed for various rates of cooling, although it would be interesting to verify that this has no effect on the pressure coefficient of the transition temperature. No unusual effects were found in either the low-temperature stress-strain curves, or their temperature dependence, when the variation of compressive yield strength with temperature was measured.

The only anomalous effect which was found was in the electrical resistance of indium, and this showed up as a kink in the resistance *vs* temperature curve at 210°K. This effect is unexplained, and resembles a similar result which has been found for rubidium,[24] although the corresponding effect found in the thermal expansion

[23] W. B. Pearson, Can. J. Phys. **33**, 473 (1955).

[24] D. K. C. MacDonald, Phil. Mag., Ser. 7, **43**, 479 (1952).

by Pearson is lacking.[25] The specific heat, in contrast with the specific heat of rubidium, is also normal in this region.

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[25] F. M. Kelley and W. B. Pearson, Can. J. Phys. **33**, 17 (1955).

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Fast-Neutron Bombardment of GaSb

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Fast-neutron irradiation decreases the carrier concentration of polycrystalline samples of *n*- and *p*-type GaSb, indicating the production of low-lying traps. Vacuum heat treatment evidently removes such traps but also introduces additional acceptors, indicating a different rate of annealing for bombardment produced interstitial and vacancy atoms. Irradiation and heat treatment of *n*-type GaSb therefore results in the production of material of lower carrier concentration and reirradiation results in the conversion to *p*-type material. Repeated irradiations followed by heat treatments, however, do not reduce the net effective concentration of electrons in *n*-type material below $\sim 5\times 10^{17}$ cm^{-3}. The mobility of all samples is decreased by bombardment. Heat treatment subsequent to irradiation increases the mobility of *n*-type material but decreases the mobility of *p*-type samples still further below the decrease produced by bombardment. Low-temperature (−125°C) irradiation and subsequent warm-up and cool-down curves indicate the presence of defects of low thermal stability. No evidence was obtained for regions of low resistivity resulting from superlattice disordering as a result of quenching as might be expected from the thermal spike picture. The type and position of fast-neutron-introduced lattice defects is discussed with relation to previous models for Ge and InSb.

INTRODUCTION

THE effect of fast-neutron bombardment on the electrical properties of InSb has recently been reported.[1] This paper reports the results of similar studies carried out on polycrystalline GaSb.[2] This material, like InSb, is one of a series of semiconducting intermetallic compounds composed of elements of the third and fifth columns of the periodic table. Its electrical and optical properties have been studied by a number of workers.[3–7] It is characterized by a zinc-blende structure, a forbidden energy gap of ~0.7 ev at room temperature, and electron and hole mobilities of ~2000 and ~800 cm^2 volt^{-1} sec^{-1}, respectively.

Prior to this work Moyer[8] exposed several *p*-type GaSb specimens in the Brookhaven reactor and observed a decrease in hole concentration. Behavior other than expected was observed on annealing, consistent with the observations to be reported here.

[1] J. W. Cleland and J. H. Crawford, Jr., Phys. Rev. **93**, 894 (1954); **95**, 1177 (1954).
[2] We are indebted to Dr. Raymond L. Smith of the Franklin Institute for the *p*-type samples and to Dr. H. P. R. Frederikse of the National Bureau of Standards for the *n*-type samples used in these experiments.
[3] H. Welker, Z. Naturforsch. **7a**, 744 (1952); **8a**, 248 (1953).
[4] D. P. Detwiler, Phys. Rev. **94**, 1431 (1954).
[5] H. N. Liefer and W. C. Dunlap, Jr., Phys. Rev. **95**, 51 (1954).
[6] Blunt, Hosler, and Frederikse, Phys. Rev. **96**, 576 (1954).
[7] Briggs, Cummings, Hrostowski, and Tanenbaum, Phys. Rev. **93**, 912 (1954).
[8] J. W. Moyer (private communication).

EXPERIMENTAL PROCEDURES

All room-temperature fast-neutron exposures were carried out in the Oak Ridge graphite reactor in a fission chamber with a fast-neutron flux comparable to or greater than the thermal-neutron flux, and two specimens were irradiated at −125°C in a low-temperature facility of comparable flux distribution. Specimens were cut in the form of rectangular plates and were characterized by measurements of Hall coefficient R and resistivity ρ as a function of temperature (77 to 300°K) before and after bombardment. The conductivity was recorded during exposure. In order to reduce effects of nuclear doping (both Ga and Sb transmute to donor impurities giving Ge and Te, respectively), several of the specimens were shielded against thermal and resonance neutrons by wrapping with layers of Cd and In foil. After exposure and measurement, the specimens were subjected to various annealing treatments and recharacterized. Some of the specimens were reirradiated after extensive annealing periods.

RESULTS

The effect of reactor irradiation on the conductivity of representative samples of shielded and unshielded *n*- and *p*-type GaSb is indicated in Fig. 1 and the initial carrier concentration, temperature of exposure, and the initial rate of removal of current carriers calculated under the assumption that the mobility is initially