Zeitschrift: Helvetica Physica Acta
Band: 30 (1957)
Heft: I

Artikel: The volume change at the superconducting transition
Autor: Olsen, J.L. / Rohrer, H.
DOI: https://doi.org/10.5169/seals-112803

The Volume Change at the Superconducting Transition

by **J. L. Olsen** and **H. Rohrer**
Institut für Kalorische Apparate und Kältetechnik,
Eidg. Techn. Hochschule, Zürich.

(15. X. 1956.)

Abstract. The changes in length of polycrystalline rods of Tin, Lead, Indium, Thallium and Tantalum on destruction of superconductivity by a magnetic field have been measured. The change in critical magnetic field H_c with pressure p derived from these observations may be described within the limits of experimental error by $\partial H_c/\partial p = a + b\,(T/T_c)^2$ with the following values for a and b in units of 10^{-9} Oersted $dyn^{-1}cm^2$.

$$\text{Pb: } a = -6{\cdot}3,\ b = -4{\cdot}8;\ \text{In: } a = -3{\cdot}4,\ b = -2{\cdot}4;$$
$$\text{Ta: } a = +7,\ b = -11.$$

In the case of Thallium $a \sim 0$, and b is highly anisotropic with a value for polycrystalline material consistent with Hattons value of $+1{\cdot}6$.

For Tin we find $a/(a+b) = 0{\cdot}58$.

1. Introduction.

Early attempts to measure a volume change on destruction of superconductivity were unsuccessful[1]), but such a change amounting to only 1 part in 10^7 was observed experimentally in 1949 by LASAREW and SUDOVSTOV[2]) in tin. Since then no further measurements on the volume change in superconductors have been reported.

Such measurements are, however, useful because a simple thermodynamic relationship[3]) allows $\partial H_c/\partial p$ (where H_c is the critical magnetic field, and p is the pressure) to be calculated from ΔV, the volume change. Reliable information on the temperature dependence of $\partial H_c/\partial p$ is of considerable interest since one may calculate from it the pressure dependence both of γ, the normal electronic specific heat, and of H_0 the critical magnetic field at the absolute zero which is closely connected with the "condensation energy" of the superconducting phase. Owing to the width of the transition in many superconductors direct measurements of $\partial H_c/\partial p$ are often unreliable and in some cases impossible to make. Data obtained from

the volume change can then help to fill in gaps and to confirm doubtful values.

Observations of the order of magnitude of the effect of pressure on the transition were first made by SIZOO and ONNES[4]) and by SIZOO, DE HAAS and ONNES[5]) in 1925, but no reliable quantitative data existed until the experiments of LASAREW and coworkers in 1944. By using an ice bomb technique[6]) pressures of about 1750 atmospheres could be applied to the metals under observation. The temperature dependence of $\partial H_c/\partial p$ was determined for indium and tin[7]), and the change in T_c was observed for thallium[8]), while data of a qualitative nature was collected for lead, mercury and tantalum[9]), and for a number of bismuth alloys. More recently work at high pressures has been carried out by CHESTER and JONES[10]), BOWEN and JONES[11]), MUENCH[12]), and HATTON[13]) on thallium, tin and aluminium, while FISKE[14])[15]) has also made measurements at moderate hydrostatic pressures up to 100 atmospheres on tin, indium and thallium. GRENIER, SPÖNDLIN and SQUIRE[16]), and GRENIER[17])[18])[19]) have investigated the effect of pure tension on single crystals of tin and mercury and found a considerable anisotropy. GRENIER[20])* has also given a detailed account of the thermodynamic relationships involved in these measurements.

In spite of all this work unresolved discrepancies in the results of different investigators remain even for the most extensively investigated of these metals. We have therefore thought it of value to supplement existing direct measurements of $\partial H_c/\partial p$ with observations on changes in length at the superconducting transition. We have already reported briefly on measurements on lead[21]), indium and thallium[22]). In the present paper more accurate work on these metals and on tantalum is described. We have also made measurements on tin which are more accurate than those obtained in the pioneer work of LASAREW and SUDOVSTOV[2]).

2. Theoretical.

The critical magnetic field, H_c, of a superconductor at a temperature, T, below the transition temperature, T_c, may be expressed by

$$H_c = H_0 f(t) \tag{1}$$

where H_0 is the critical field at $T = 0$, and $t = T/T_c$. We define $f(t)$ so that $f(0) = 1$, and obviously then $f(1) = 0$. It is well known that

*) We are very grateful to Dr. GRENIER for sending us a copy of his thesis prior to its publication.

to an accuracy of approximately 2 per cent $f(t)$ is identical for all superconductors, and may be expressed by $f(t) = 1 - t^2$. T_c and H_0 are related to the normal state electronic specific heat per mole, γT, by the relation[23]).

$$\frac{\gamma}{V} = \frac{H_0^2}{4\pi T_c^2} \{f(t) f''(t)\}_{t=0} \tag{2}$$

where V is the molar volume and $f''(t)$ is the second derivative of $f(t)$ with respect to t. H_c can thus be considered either a function of H_0, T and T_c, or of H_0, T and γ/V. For convenience in what follows we shall denote γ/V by γ^*.

We now consider the effect on H_c of changing some parameter x. This may for example be the pressure, volume or isotopic weight, and the change will affect H_0, T_c and γ^*. Differentiating (1) we find

$$\left(\frac{\partial H_c}{\partial x}\right)_T = \frac{\partial H_0}{\partial x} \{f(t) - t f'(t)\} + \frac{1}{2} H_0 t f'(t) \left\{\frac{1}{\gamma^*} \frac{\partial \gamma^*}{\partial x} + \frac{1}{f''(0)} \frac{\partial}{\partial x} f''(0)\right\}. \tag{3}$$

As remarked above $f(t)$ may be described with considerable accuracy by $f(t) = 1 - t^2$. This would yield $f''(0) = -2$, and in fact all observed values of $f''(0)$ lie between -1.6 and -2.3. On the other hand observed values of γ^* in superconductors vary by a factor 10, and observed values for H_0 by a factor 100. For this reason we believe it to be justifiable to neglect changes in $f''(0)$, i. e. to neglect the term $1/f''(0)\ \partial/\partial x\ f''(0)$ in equation (3), and we shall do so in the following. It is, however, well to remember that our conclusions about $\partial\gamma^*/\partial x$ may need modification if this assumption is wrong.

Thermal conductivity work below $1^0\,K$ [24]), and specific heat data[25])[26])[27]) has shown the need for an exponential form of $f(t)$ for small t, and the thermodynamic functions for this case have been discussed by various authors[28])[29]). It does not, however, seem that this in any way invalidates our approximate calculations in the present section where we shall continue to use $f(t) = 1 - t^2$ for its much greater simplicity.

In the case of the isotope effect it has been established with fair accuracy[30]) that γ^* is independent of atomic weight. This combined with the constancy of $f''(0)$ leads to

$$\left(\frac{\partial H_c}{\partial x}\right)_T = \frac{\partial H_0}{\partial x} \{f(t) - t f'(t)\} \tag{4}$$

the so-called "similarity principle" which gives similar critical field curves for all specimens. In the early discussion of work on the dependence of the critical field on pressure, p, it was generally assumed that the similarity principle should also hold for critical

field curves displaced by the effect of pressure, and results were therefore discussed in terms of deviations from the similarity principle. In fact there seems no special reason why (4) should hold, but it does appear that all data so far on the temperature dependence of $(\partial H_c/\partial p)_T$ can be described within experimental error by (3) with a suitable choice of $\partial H_0/\partial p$ and $1/\gamma^* \, \partial\gamma^*/\partial p$. Values thus determined are shown in Table III.

From a knowledge of $(\partial H_c/\partial p)_T$ the change in volume on applying a magnetic field may be deduced. Let V_s be the volume of the specimen in the superconducting state in the absence of a field, and let $V_{s,H}$ be that in a field H less than H_c then [3])

$$V_s - V_{s,H} = \frac{H^2}{8\pi}\left(\frac{\partial V_s}{\partial p}\right)_T. \tag{5}$$

In a field great enough to destroy superconductivity the normal volume, V_n, is given by

$$V_n - V_s = V_s \frac{H_c}{4\pi}\left(\frac{\partial H_c}{\partial p}\right)_T + \frac{H_c^2}{8\pi}\left(\frac{\partial V_s}{\partial p}\right)_T. \tag{6}$$

As remarked in the introduction this volume change was first observed by LASAREW and SUDOVSTOV[2]) who obtained good agreement between their directly observed change in volume ΔV, and the results on $\partial H_c/\partial p$ by KAN, LASAREW and SUDOVSTOV[7]).

The temperature dependence to be expected is most easily seen if we use $f(t) = 1-t^2$. Then we have

$$\left(\frac{\partial H_c}{\partial p}\right)_T = \frac{\partial H_0}{\partial p}(1-t^2) - \frac{H_0}{\gamma^*}\frac{\partial\gamma^*}{\partial p}t^2. \tag{7}$$

This may of course be expressed in the form

$$\left(\frac{\partial H_c}{\partial p}\right)_T = a + b\,t^2, \tag{8}$$

and we shall make use of this notation when discussing our results. For the volume change one obtains

$$4\pi\frac{V_n - V_s}{V_s} = H_0\frac{\partial H_0}{\partial p}(1-t^4) - \frac{H_0}{\gamma^*}\frac{\partial\gamma^*}{\partial p}t^2(1-t^2) + \frac{H_0^2}{2V}\left(\frac{\partial p}{\partial V}\right)_T(1-t^2)^2. \tag{9}$$

We shall occasionally require (6) in a form applicable to the anisotropic case. It has been pointed out by GRENIER[20])[31]) that if $l_{\Theta,s}$ and $l_{\Theta,n}$ are the superconducting and normal lengths in direction Θ, then

$$l_{\Theta,n} - l_{\Theta,s} = l_{\Theta,s}\frac{H_c}{4\pi}\left(\frac{\partial H_c}{\partial p_\Theta}\right)_T + \frac{H_c^2}{8\pi}\left(\frac{\partial l_{\Theta,s}}{\partial p_\Theta}\right)_T \tag{10}$$

where p_Θ is a pure uniaxial pressure in the direction Θ.

3. Experimental Method.

To measure these small volume changes use was made of a previously described optical lever device[32]) which is capable of detecting rotations of 10^{-8} radian. A system of spring hinges as described by R. V. JONES[33]) converted changes in length of the ca. 10 cm long rod shaped specimens into rotations of a mirror at room temperature. Motion of the mirror was detected by a beam of light and a split barrier-layer photocell. The output was amplified and the final galvanometer deflection recorded photographically. The sensitivity of the apparatus allowed changes in length of 10^{-8} cm i. e. one part in 10^9 to be observed. As in the case of our previously described work on the modulus of rigidity of superconductors[32])[34])[35]) the accuracy was limited by the disturbing effects due to the boiling helium and liquid air in the cryostat. Certain problems connected with the absolute calibration may introduce systematic errors of up to 10% in our absolute values of the changes in length. The effective lever arm of the spring hinge system may also change slightly on mounting a new specimen causing possible errors of 5% in the relative effects for different specimens.

Table I.

Specimen	Diameter	σ_{273}	σ_{273} for isotropic polycrystal
		10^4 ohm^{-1} cm^{-1}	
Tin			
V—Sn—3	3·33 mm	10·1	9·9
Indium			
V—In—1	3 × 3 mm square	11·6	12·2
V—In—3	3 × 3 mm square	11·3	12·2
Lead			
V—Pb—2	7 mm		
V—Pb—4	3 mm		
Thallium			
V—Tl—1	3 mm	5·56	6·2—6·7
V—Tl—2	3·5 mm	6·47	6·2—6·7
V—Tl—3	3·5 mm	6·12	6·2—6·7
V—Tl—4	3·5 mm	6·86	6·2—6·7
Tantalum			
V—Ta—1	4 mm		

Observations were made on switching on or off a magnetic field homogeneous to better than 1% over the length of the specimen.

Each point plotted in figures 2—8 represents the mean of 10—15 applications and removals of the field.

The specimens investigated in our work are tabulated in table I. They are all of effective length 9.8 cm.

4. Field dependence.

In figure 1 we show the variation with magnetic field H of the length of the lead rod V-Pb-4 at 3.93° K. We have plotted the difference between the length, l_0, in zero field and that, l_H, in a field H against H^2. It will be seen that there is first an increase in length

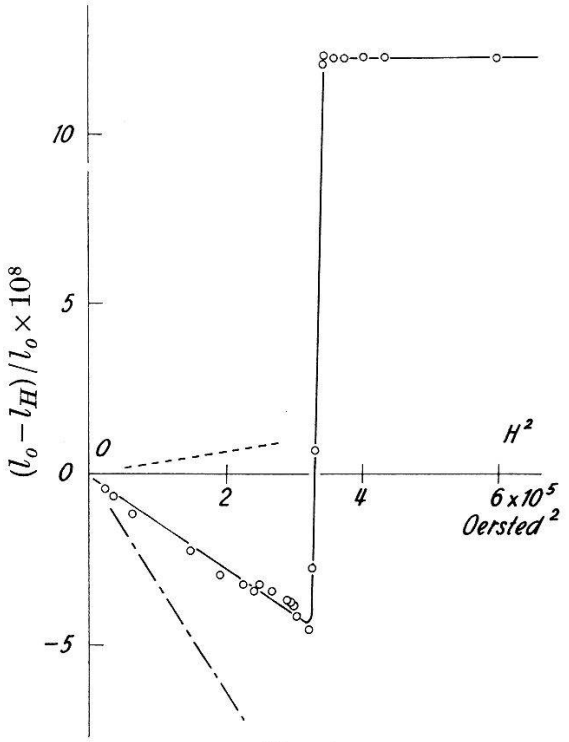

Fig. 1.
Change in length of lead rod V—Pb—4 at 3·93° K.
$(l_0-l_H)/l_0$ plotted against H^2.
Theoretical magnetostriction for infinite cylinder: ----
and for sphere: — · — · —

proportional to H^2, and then an abrupt transition to the normal state value of the length. A further increase in field does not affect the length of the rod.

The change in length in subcritical fields has not so far received a satisfactory explanation. Equation (5) indicates that a certain change in volume proportional to H^2 should occur in subcritical fields, but this is of the opposite sign to that observed by us. Owing to the form effect in magnetostriction the change in length of the rod $\Delta l/l$ may, however, deviate considerably from the value indic-

ated in equation (5). By making use of BECKERS[36]) calculation we find for a superconducting ellipsoid of demagnetising factor $N = 4\pi n$

$$\frac{l_H - l_0}{l_0} = \frac{H^2}{8\pi(1-n)^2}\left\{\frac{1}{3K}(2n-1) + \frac{na}{2G}\right\} \tag{11}$$

where K is the bulk modulus, G the rigidity modulus, and $a = l\partial N/\partial l$. For a long ellipsoid $n = 0$, and $\Delta l/l$ has the value of $1/3 \cdot \Delta V/V$ with a $\Delta V/V$ corresponding to equation (5). At an axial ratio depending on the material the effect changes sign (this ratio is ca. 4 for lead), and for a body where $n = \frac{1}{2}$ the change in diameter in the direction of the field is given by:

$$\frac{l_H - l_0}{l_0} = \frac{H^2}{8\pi}\frac{a}{G}. \tag{12}$$

In figure 1 the calculated effects for long cylinder and sphere are also shown. Since the axial ratio of our specimes is at least 15 it seems unlikely that our results can be explained as a magnetostrictive effect.

A more likely explanation appears to be that the slight inhomogeneity of the field produces forces on the specimen, and thus distorts the suspension. This explanation must, however, remain somewhat unsatisfactory since no clear-cut effect of the position of solenoid on this pseudo-magnetostriction could be observed. Intermediate state regions at the ends of the specimen may possibly have some such effect.

5. Temperature dependence.

In figures 2—10 we show the results of our measurements of $(l_s - l_n)$ in polycrystalline rods of tin, indium, lead, thallium and tantalum. While the scatter in the results for individual specimens is quite small in most cases, we must repeat the warning that our absolute calibration of the apparatus is subject to an error of as much as 10%, and that this error varies a little from specimen to specimen. The absolute values should not, therefore, be relied upon to better than 10% although the temperature dependence may be accepted as trustworthy to within the limits of scatter. Our results are summarised and compared with those of other workers in Table II.

5.1. Tin.

Measurements on tin have been reported by LASAREW and SUDOVSTOV[2]), but we have considered it worth while to remeasure this substance, both in view of the spread of their data, and in order

to check the capabilities of our method. In figure 2 we show measurements of $\Delta l/l$ plotted against temperature for our two specimens. The room temperature conductivity is somewhat greater than that of randomly oriented polycrystalline material, and we may assume

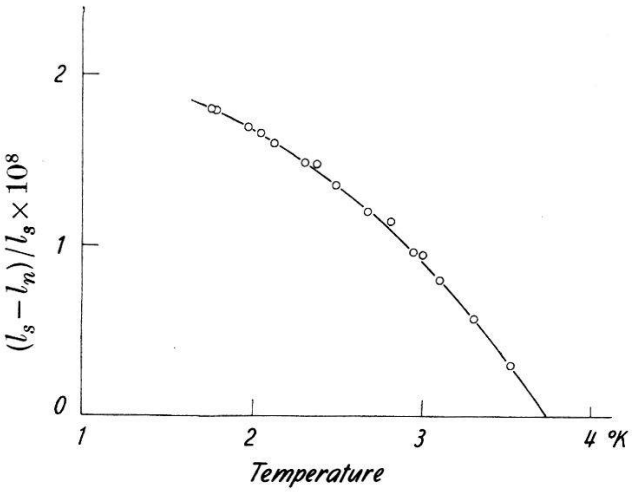

Fig. 2.
$(l_s - l_n)/l_s$ in Tin V—Sn—3.

that for this specimen 3 $\Delta l/l$ is smaller than $\Delta V/V$. In figure 3 $\partial H_c/\partial p_\Theta$ (i.e. the effect on H_c of uniaxial pressure p_Θ paralell to the specimen) derived from our measurements is plotted against t^2. In doing this the magnetostrictive second term in (6) has been taken

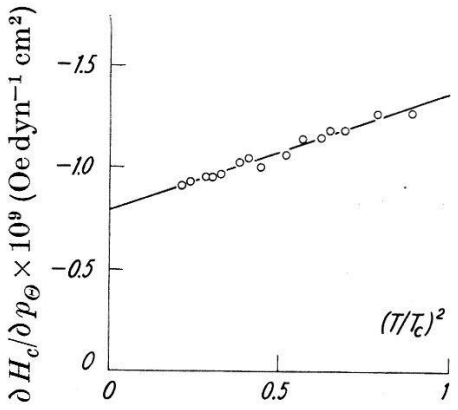

Fig. 3.
Calculated $(\partial H_c/\partial p_\Theta)$ for V—Sn—3.

into account. It will be seen that the dependence on t^2 is linear, as predicted by (7) and (8).

Since our conductivity differs from that of randomly oriented material we cannot calculate $\partial H_c/\partial p$ for hydrostatic pressure from our results. We can, however, quote a value for the ratio $a/(a+b) = (\partial H_c/\partial p_\Theta)_{0^\circ}/(\partial H_c/\partial p)_{T_c} = 0.58$. This is in fair agreement with the recent results of MUENCH[12]) and GRENIER[19]).

5.2. *Indium.*

Our measurements on indium have already been reported briefly by one of us[22]), and they are only reproduced in figure 4 for completeness. (The graph in reference[22]) contains the same experimental data plotted on a larger scale). A few comments are, however, necessary. It will be seen from table I that both specimens have very nearly the conductivity of polycrystalline material. The change in length is the same for both specimens. It is therefore justifiable to assume that $\Delta V/V = 3\,\Delta l/l$ and to calculate $\partial H_c/\partial p$ from these

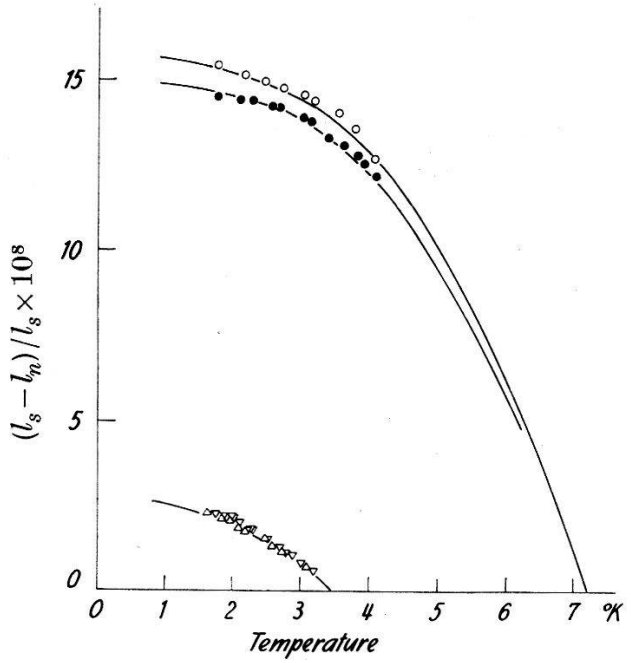

Fig. 4.
$(l_s - l_n)/l_s$ in Lead and Indium
○ V—Pb—2 • V—Pb—4 △ V—In—1 ▽ V—In—2.

measurements. The values of $\partial H_c/\partial p$ at $T = 0$ and $T = T_c$ are -3.4×10^{-9} and -5.8×10^{-9} Oersted dyn^{-1} cm^2 respectively. The uncertainty in the absolute value does not, of course, affect the ratio of these two quantities. This is 0.59 and thus closer to the value of KAN, LASAREW and SUDOVSTOV[7]) than to MUENCH's[12]) value. In attempting to decide the most reliable value for $a/(a+b)$ we consider it reasonable to weight our results somewhat more than that of the two earlier workers, and consider 0.65 a fair value.

5.3. *Lead.*

Lead is probably the ideal case of a metal where a measurement of $\Delta l/l$ provides more reliable information on $\partial H_c/\partial p$ than a direct measurement. The change in length is the greatest so far observed,

and the metal has a cubic crystal structure so that $3\,\Delta l/l = \Delta V/V$. In addition the ordinary transition in a magnetic field is so smeared out as to make direct measurements on $\partial H_c/\partial p$ exceedingly difficult, as shown by the inability of KAN, LASAREW and SUDOVSTOV[7]) to give more than a lower limit for $\partial H_c/\partial p$ at T_c.

We have already published preliminary results[21]) for this metal, but the present more careful measurements are of considerably greater accuracy. The results are shown in figure 4. The difference between the two specimens can be attributed to the difficulties in absolute calibration mentioned at the beginning of this paragraph.

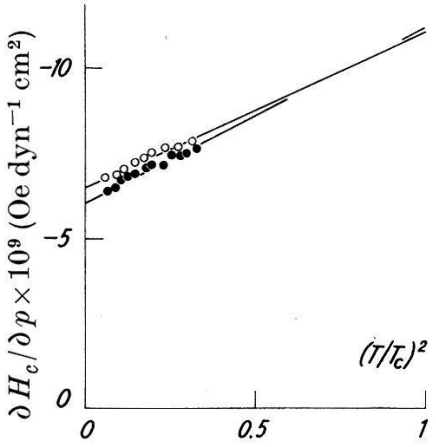

Fig. 5.
Calculated $(\partial H_c/\partial p)$ for Lead
○ V—Pb—2 • V—Pb—4.

Figure 5 shows the values of $\partial H_c/\partial p$ deduced. For this metal it is essential to take the magnetostriction term in (6) into account. Its value at 0° K is 0.9×10^{-9} Oe. dyn^{-1} cm^2. These new measurements modify the values of $(\partial H_c/\partial p)$ at 0° and at T_c given in our original publication slightly. We now obtain -6.3×10^{-9} and -11.1×10^{-9} Oersted dyn^{-1} cm^2. The ratio of these two quantities: 0.57 is thus of the order observed in tin and indium.

5.4. *Thallium.*

The effect of pressure on the transition temperature of thallium has caused considerable interest because of its anomalous sign at low pressures and because of the disagreement between different authors[11])[14])[15]). The pressure dependence at T_c now appears to have been finally cleared up by the detailed investigations of HATTON[13]) at hydrostatic pressures up to 12000 atm. No information on the temperature dependence of $(\partial H_c/\partial p)_T$ has, however, been reported so far. We therefore thought it interesting to measure $\Delta l/l$ and we have recently reported on such measurements for a

single specimen[22]). The value thus obtained corresponded to a $\partial T_c/\partial p$ roughly four times that obtained in Hattons measurements.

Thallium at low temperatures has a hexagonal structure and it therefore seemed possible that the discrepancy between the hydrostatic measurements and ours might arise from an anisotropy of the specimen. This is confirmed by the results for three different speci-

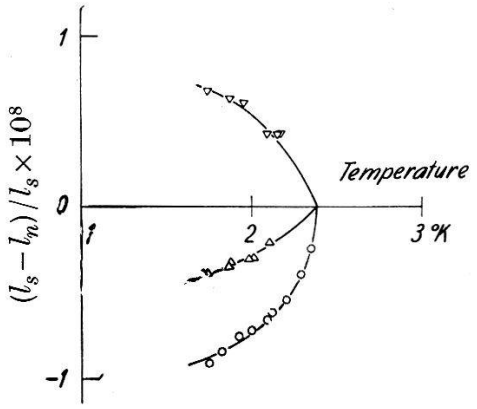

Fig. 6.
$(l_s-l_n)/l_s$ in Thallium
○ V—Tl—1 △ V—Tl—3 ▽ V—Tl—4 No effect observed in V—Tl—2.

mens shown in figure 6. A fourth specimen Tl 2 was also investigated, but no effect was observable. The values of $\partial H_c/\partial p$ derived are shown in figure 7 where we also show the value at T_c derived from direct measurement. These measurements provide the first example

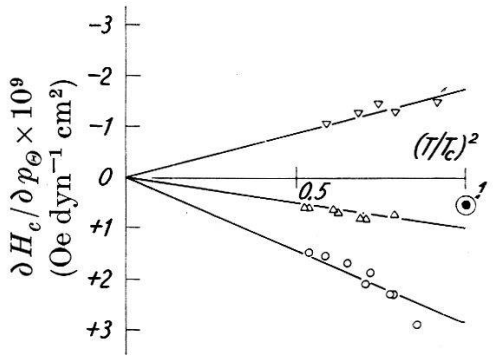

Fig. 7.
Calculated $(\partial H_c/\partial p_\Theta)$ for Thallium specimens
○ V—Tl—1 △ V—Tl—3 ▽ V—Tl—4
⊙ Hattons value at low pressures.

of a substance where $\partial H_c/\partial p_\Theta$ has a different sign for different crystal directions.

The actual change in length is small, and the calculated value of $(\partial H_c/\partial p_\Theta)_T$ which has an error proportional to $(1-t^2)^{-1}$ is consequently rather inaccurate near T_c. The extrapolation to $T=0$ is

clearly also somewhat a matter of guesswork. Some assistance may be obtained by making use of the fact that $(\partial H_c/\partial p_\Theta)$ for an arbitrary direction Θ must be a linear combination of $(\partial H_c/\partial p_{//})$ parallel to, and $(\partial H_c/\partial p_\perp)$ perpendicular to the hexagonal axis. All $(\partial H_c/\partial p_\Theta)$ lines must therefore go through a single point in the diagram. We have made use of this in drawing the lines in figure 7, but the degree of reliability of our choice of the origin as point of intersection is probably still open to question.

In figure 8 we show $(\partial H_c/\partial p)_{T=T_c}$ plotted against σ_{273} the conductivity at 273° K. It will be seen that as in the case of Grenier's

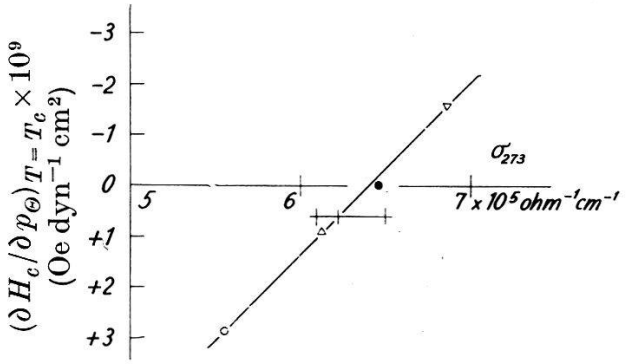

Fig. 8.

$(\partial H_c/\partial p_\Theta)$ at $T = T_c$ as a function of conductivity σ_{273} at ice point for Thallium specimens. + + + indicates Hattons value plotted for different published values of conductivity.

work on tin there is an approximately linear correlation between conductivity and $(\partial H_c/\partial p_\Theta)_{T_c}$. Unfortunately no single crystal resistivity data exist for thallium*) and even the published values for the resistivity of polycrystalline metal vary widely. It is therefore impossible to determine what the extreme values of $\partial H_c/\partial p_\Theta$ are, or to determine exactly how good the agreement is between our data and that of other workers on $\partial T_c/\partial p$. We have plotted the low pressure value for $\partial T_c/\partial p$ using the three different values of σ_{273} found in the literature. It will be seen that the points so plotted straddle the line through our data.

Our measurements yield $(\partial H_c/\partial p_\Theta)_{T=0} = 0$ for all Θ, and we may thus take it that $(\partial H_c/\partial p)_{T=0} = 0$. For $T = T_c$ it is best to use the published low pressure hydrostatic value which is

$$(\partial H_c/\partial p)_{T=T_c} = 1{\cdot}9 \times 10^{-9} \text{ Oersted dyn}^{-1} \text{ cm}^2.$$

*) Recently[37]) it has been shown that thallium single crystals may be grown in spite of the hcp — bcc transformation which takes place at 260° C.

5.5. *Tantalum.*

Tantalum is a hard superconductor with the well known tendency to trap flux which this implies. This creates experimental problems since the specimen does not return to the pure superconducting state on removing the magnetic field once superconductivity

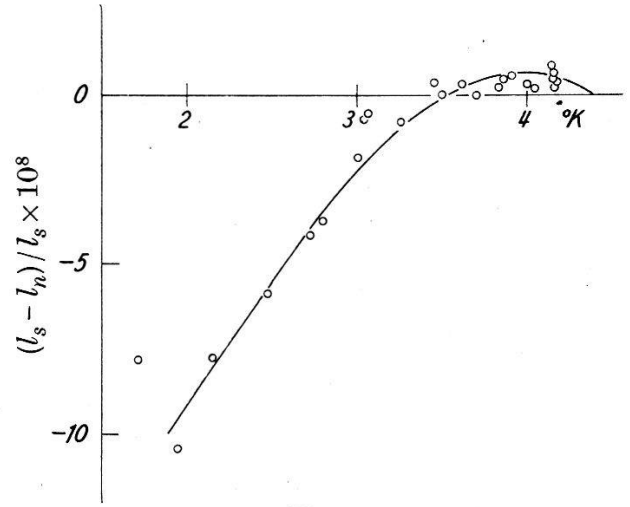

Fig. 9.
$(l_s - l_n)/l_s$ in Tantalum.

has been destroyed. Our specimen was a rod of spectroscopically pure material as supplied by Johnson, Matthey & Co., and no attempt was made to anneal it. We may probably assume that the material is polycrystalline with a random orientation of crystallites.

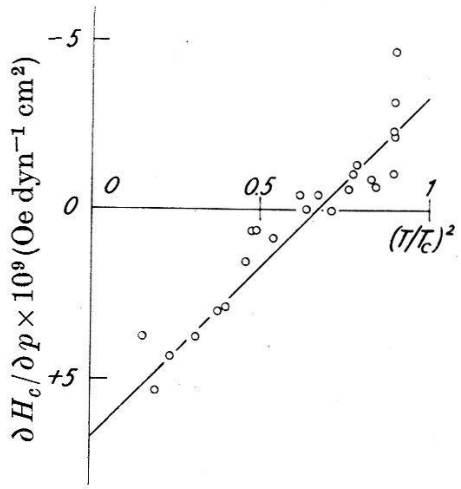

Fig. 10.
Calculated $(\partial H_c/\partial p)$ for Tantalum.

It was found that the change in length on removing the field was less than that occuring at the first application of the field. Deflections on subsequent applications and removals of a magnetic field tended gradually to zero. We therefore heated the specimen to

4·34° K between each observation, and only made use of the results obtained on switching on the field. The results on tantalum shown in figure 9 are therefore much less accurate than those for the other metals where each point is calculated from an average of 10 or so deflections. Even with this low accuracy the anomalous shape of the curve shows up quite clearly. $(l_s - l_n)$ is of the usual sign close to T_c, but changes sign and becomes negative below about 3·5° K. This change of sign is perhaps seen more clearly and naturally in the plot of $(\partial H_c/\partial p)$ against t^2 in figure 10. The curve in figure 9 corresponds to the straight line in figure 10.

6. Discussion.

It seems useful to compare the most recent data on $\partial H_c/\partial p$, and we have done this in Table II. All results published to date can be

Table II.

	Author	a Oersted dyn^{-1} cm^2 $\times 10^{-9}$	$(a+b)$ Oersted dyn^{-1} cm^2 $\times 10^{-9}$	$a/(a+b)$
Lead	KLS		< -6	
	OR	$-6{\cdot}3$	$-11{\cdot}1$	0·57
Mercury . . .	KSL		< 0	
	Hatton (1)		$-7{\cdot}5$	
	Grenier	$-4{\cdot}6$	$-6{\cdot}0$	0·77
Tin	KLS	$-4{\cdot}5$	$-8{\cdot}7$	0·52
	Fiske	$-4{\cdot}5$	$-6{\cdot}56$	0·68
	Muench	$-4{\cdot}2$	$-6{\cdot}9$	0·61
	Grenier	$-4{\cdot}1$	$-7{\cdot}1$	0·58
	OR			0·58
Indium . . .	KLS	$-4{\cdot}9$	$-7{\cdot}6$	0·64
	Muench	$-4{\cdot}8$	$-6{\cdot}2$	0·77
	OR	$-3{\cdot}4$	$-5{\cdot}8$	0·59
Thallium . .	Fiske		$+3{\cdot}0$	
	Hatton (2)		$+1{\cdot}8$	
	OR	0	$+1 \pm 2$	0
Tantalum . .	KSL		< 0	
	OR	$+7$	-4	$-1{\cdot}75$
Aluminium . .	Muench		$-3{\cdot}3$	
	Grenier		$-3{\cdot}7$	

References

Fiske[15]); Grenier[20]); Hatton (1)[48]); Hatton (2)[13]); KLS: Kan, Lasarew, Sudovstov[7]); KSL: Kan, Sudovstov and Lasarew[8]); Muench[12]); OR: Present work.

described with sufficient accuracy by $\partial H_c/\partial p = a + b\ (T/T_c)^2$. We give a and $a+b$ where available, where only $(\partial H_c/\partial p)_{T=T_c}$ has been measured, we give $a+b$. The measurements of GRENIER[17])[18]) on tin and mercury show a very considerable anisotropy in the effect due to tension, but to avoid undue complication we have shown the values for pure hydrostatic pressure calculated by GRENIER from his anisotropic results. It is not easy to choose the most reliable results, but in Table III we have made some attempt to do this for each of the metals. The physical meaning of the values so obtained is most easily seen if we calculate the dimensionless quantities

$$h = \frac{V}{H_0}\frac{\partial H_0}{\partial V} \tag{13}$$

and

$$g = \frac{V}{\gamma}\frac{\partial \gamma}{\partial V} \tag{14}$$

for each substance. Clearly then

$$H_0 \propto V^h \tag{15}$$

and

$$\gamma \propto V^g \quad \text{or} \quad \gamma^* \propto V^{g-1}. \tag{16}$$

We may note that from (3) neglecting changes in $f''(0)$

$$h = \frac{-a}{k \cdot H_0} \qquad g = \frac{-2}{k \cdot H_0}\left\{a + \frac{a+b}{f'(1)}\right\} + 1 \tag{17}$$

where k is the compressibility. For a reasonably accurate calculation account must be taken of the deviations from parabolic form of the critical field curves, and this has been done in our evaluation of the data using critical field data from SHOENBERG's book[3]).

Table III.

	a Oersted dyn^{-1}cm^2 $\times 10^{-9}$	$(a+b)$ Oersted dyn^{-1}cm^2 $\times 10^{-9}$	h	g
Lead	−6·3	−11·1	3·4	1·7
Mercury . . .	−4·6	− 6·0	3·1	3·2
Tin.	−3·8	− 6·56	6·7	1·5
Indium	−3·8	− 6·0	5·3	2·7
Thallium . . .	0	+ 1·8	0	4·3
Tantalum . . .	+7	− 4	−15	−39
Aluminium . .		− 3·5	$2h-g = 24$	

Very little can be said about the values of h to be expected on the basis of existing theories. SCHAFROTH's recent work[38])[39]) which

compares the superconducting transition to a BOSE-EINSTEIN condensation leads in its most primitive form to $h = 1{\cdot}5$. This figure, which is simply that for an ideal BOSE-EINSTEIN condensation, cannot be taken very seriously. The value of g which may be expected is, however, more easily amenable to theoretical discussion. The simple SOMMERFELD theory gives $\gamma = V^{2/3}$ or $g = 2/3$. It will be seen that our values of g imply $\gamma \propto V^{\alpha}$ where $1{\cdot}5 < \alpha < 4{\cdot}3$ for the soft superconductors so that even here the pressure dependence of γ is very much greater than on the free electron model. The exceptionally large value of g found in tantalum is perhaps not very

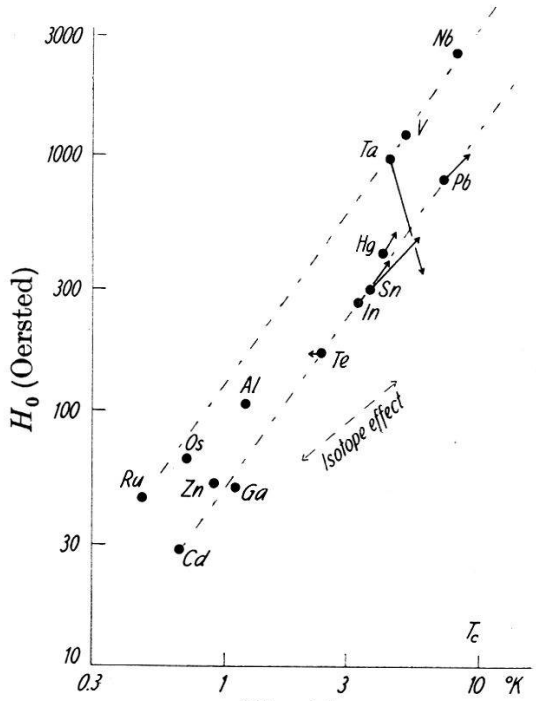

Fig. 11.

Effect of volume on T_c and H_0. The arrows indicate the direction and relative magnitude of motion in diagram resulting from increase in volume.

surprising in view of the known peculiarities of the transition metals[40]). The value of $\partial T_c/\partial p$ for aluminium also indicates that here h or g must be unusually large. This is somewhat more difficult to understand since here the electronic structure should be less abnormal.

Since a compression of the crystal does not affect the degree of filling of a Brillouin zone it seems that this strong pressure dependence in γ must be ascribed to a pressure sensitivity in $(\partial E/\partial k)$ (where E is the energy of an electron with wave vector k) rather than to any special form of E (k).

A recent paper of LEWIS[41]) has again drawn attention to the remarkable correlation[42]) existing between the soft superconductors

where a plot of H_0 against T_c for different soft superconductors yields.

$$H_0 \alpha T_c^{1.37}$$

with considerable accuracy. In view of the realtionship

$$H_0 = \text{Const} \cdot (\gamma/V)^{\frac{1}{2}} T_c$$

that implies that

$$H_0 \alpha (\gamma/V)^{1.85} \quad \text{and} \quad T_c \alpha (\gamma/V)^{1.35}.$$

If now transition from one superconductor to another obeys this relationship so well it might be expected that a slight modification of the superconductor such as that caused by pressure should also obey this rule. We ought then to have

$$h = 1.85\,(g-1).$$

An examination of our Table III shows that this is by no means always the case. To show the effect of this deviation on Lewis's rule we have copied his diagram in figure 11 where it will be seen that the "hard" and the "soft" superconductors lie on two parallel lines. We have indicated by arrows the motion in the diagram caused by increase in volume of 7% for the superconductors of table III. A universal validity of Lewis's criterion would have implied that all motion should take place parallel to the main lines of his diagram. The corresponding effect of change in isotopic constitution which according to LOCK, PIPPARD and SHOENBERG[23]) does not affect γ has been indicated by the dotted lines in the diagram.

In conclusion it may be remarked that the main results of our work so far has been to show the great differences in the rate of variation in γ with volume for different metals. No reliable correlation appears to exist between the volume sensitivity of γ and H_0. Work on single crystals would appear highly desirable.

Acknowledgements.

We are very grateful to Professor Dr. P. GRASSMANN in whose Institute these measurements were carried out, and we wish to thank him for his constant interest and encouragement. We owe Dr. GRENIER our heartiest thanks for his readiness to inform us of his results, both experimental and theoretical, prior to publication. We also acknowledge with thanks the generosity of the Schweizerischen Aluminiumfonds for financial assistance with this project. Part of the present work is contained in a "Habilitationsschrift" deposited in the library of the Eidgenössischen Technischen Hochschule in Zürich.

*

References.

[1]) J. C. McLennan, J. F. Allen and J. O. Wilhelm, Trans. Roy. Soc. Can. **25**, III, 1 (1931).

[2]) B. G. Lasarew and A. I. Sudovstov, Dokl. Akad. Nauk., S.S.S.R. **69**, 345 (1949).

[3]) see e. g. D. Shoenberg, "Superconductivity" (Cambridge 1952), p. 74.

[4]) G. J. Sizoo and H. K. Onnes, Leiden Commun. 180b (1925).

[5]) G. J. Sizoo, W. J. de Haas and H. K. Onnes Leiden Commun. 180c (1925).

[6]) B. G. Lasarew and L. S. Kan, J. Exp. Theor. Phys. USSR. **14**, 439 (1944).

[7]) L. S. Kan, B. G. Lasarew and A. I. Sudovstov, J. Exp. Theor. Phys. USSR. **18**, 825 (1948).

[8]) L. S. Kan, A. I. Sudovstov, and B. G. Lasarew, Dokl. Akad. Nauk. S.S.S.R. **69**, 173 (1949).

[9]) B. G. Lasarew and V. I. Khotkewich, J. Exp. Theor. Phys. USSR. **18**, 807 (1948).

[10]) C. F. Chester and G. O. Jones, Phil. Mag. **44**, 1281 (1953).

[11]) D. H. Bowen and G. O. Jones, Proc. 4th Int. Conf. Low Temp. Phys. Paris (1955), p. 514.

[12]) N. L. Muench, Phys. Rev. **99**, 1814 (1955).

[13]) J. Hatton, Phys. Rev. **100**, 1784 (1955).

[14]) M. D. Fiske, Proc. 3rd Int. Conf. Low Temp. Phys. Houston (1953), p. 20.

[15]) M. D. Fiske, Proc. 4th Int. Conf. Low Temp. Phys. Paris (1955), p. 518.

[16]) C. Grenier, R. Spöndlin, and C. F. Squire, Physica **19**, 833 (1953).

[17]) C. Grenier, Comptes rendus **238**, 2300 (1954).

[18]) C. Grenier, Comptes rendus **240**, 2302 (1955).

[19]) C. Grenier, Comptes rendus **241**, 862 (1955).

[20]) C. Grenier, Thesis, Paris (1956).

[21]) P. Grassmann, J. L. Olsen, and H. Rohrer, Z. Naturforschg. **11** a, 609 (1956).

[22]) H. Rohrer, Helv. Phys. Acta **29**, 215 (1956).

[23]) J. M. Lock, A. B. Pippard, and D. Shoenberg, Proc. Camb. Phil. Soc. **47**, 811 (1951).

[24]) B. B. Goodman, Proc. Phys. Soc. A **66**, 217 (1953).

[25]) A. Brown, M. W., Zemansky, and H. A. Boorse, Phys. Rev. **92**, 52 (1953).

[26]) W. S. Corak, B. B. Goodman, C. B. Satterthwaite, A. Wexler, Phys. Rev. **96**, 1442 (1954).

[27]) B. B. Goodman, Proc. 4th Int. Conf. Low Temp. Phys. Paris (1955), p. 511.

[28]) P. M. Marens and E. Maxwell, Phys. Rev. **91**, 1035 (1953).

[29]) H. W. Lewis, Phys. Rev. **102**, 1508 (1956).

[30]) Vide e. g. B. Serin, p. 143, in Progress Low Temp. Physics (Gorter, Amsterdam 1955).

[31]) C. Grenier, Comptes rendus **241**, 1275 (1955).

[32]) P. Grassmann and J. L. Olsen, Helv. Phys. Acta **28**, 24 (1955).

[33]) R. V. Jones, J. Sci. Inst. **28**, 38 (1951).

[34]) J. L. Olsen, Nature, **175**, 37 (1955).

[35]) J. L. Olsen, Proc. 4th Int. Conf. Low Temp. Phys. Paris **1955**, p. 521.

[36]) R. Becker, Z. Phys. **87**, 547 (1934).

[37]) K. D. Alexopoulos, Acta Cryst **8**, 235 (1955).

[38]) M. R. Shafroth, Phys. Rev. **96**, 1149 (1954).

[39]) M. R. Schafroth, Phys. Rev. **100**, 463 (1955).

[40]) N. F. Mott, Proc. Phys. Soc. **47**, 571 (1935).

[41]) H. W. Lewis, Phys. Rev. **101**, 939 (1956).

[42]) J. G. Daunt, Phys. Rev. **80**, 911 (1950).

[43]) J. Hatton, Bull. Am. Phys. Soc., Jan. 1956.