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Mechanical Effects at the Superconducting Transition

Abstract: Work in Zürich on the difference in size and in expansion coefficient between the normal and the superconducting states is summarized. The volume dependences of the critical temperature and of the electronic density of states at the Fermi surface are discussed.

Introduction

The critical field of a superconductor depends upon pressure. Simple thermodynamic considerations then show that there must be differences between the mechanical properties of the superconductor in the normal and in the superconducting state. Such differences are to be expected in the volume, the elastic constants, and the expansion coefficient. Calculation of these differences shows that they must be very small, and it is not surprising that early measurements failed to detect any of these effects.[1]

Lasarew and Sudovstov[2] first observed the difference in volume between the two states, and changes in elastic constants were first observed by Landauer[3] and by one of the present authors in tin.[4,5] A difference in the thermal expansion of normal and superconducting lead has very recently been reported by Andres and Rohrer.[6]

In the present paper we shall summarize the work done in Zürich on the volume difference and expansion coefficient, and we shall discuss the information which may be derived concerning the pressure dependence of the critical field. We shall not attempt to discuss the work on the change in elastic constants by Mason and Bömmel,[7] Gibbons and Renton,[8] and more recently by Alers and Waldorf.[9]

The pressure dependence of the critical field may be used to deduce the volume dependence of the density of states at the Fermi surface and of the parameters determining the superconducting energy gap.[10] The first of these is of interest for comparison with band-theoretical calculations. The change in the purely superconductive properties appears to show some difference between "phonon" and "electron" superconductors.

Thermodynamics

The thermodynamic relationship involving $(\partial H_c/\partial p)_T$, the pressure derivative of the critical field H_c of a superconductor, has been discussed by Shoenberg,[1] who finds that

$$(V_n - V_s) = V_s \frac{H_c}{4\pi}\frac{\partial H_c}{\partial p} + \frac{H_c^2}{8\pi}\frac{\partial V_s}{\partial p}, \tag{1}$$

where p is the hydrostatic pressure and V_n and V_s are the volumes in the normal and superconductive states, respectively. Differentiation with respect to pressure or temperature yields the difference in compressibility κ or thermal expansion coefficient α.

Equation (1) has been written for the hydrostatic case, but it is obvious that extensions may be made to take care of more complicated stress systems. Thus changes in length in a given direction are obtained by considering the effect of uniaxial stresses.

Certain limitations are placed upon the temperature dependence of $\partial H_c/\partial p$ if it is assumed that the function $f(t)$ in the relation

$$H_c = H_0 f(t) \tag{2}$$

is independent of stress, i.e. $(\partial f(t)/\partial p)_t = 0$. H_0 is the critical field at $T = 0$, and $t = T/T_c$, where T_c is the transition temperature.

We may use the relation

$$4\pi\gamma^* T_c^2 = H_0^2[f''(t)]_{t=0}, \tag{3}$$

where γ^* is the electronic specific heat per unit volume, and $f''(t)$ is the second derivative of $f(t)$ with respect to t. It is then found that

$$\frac{\partial H_c}{\partial p} = \frac{H_0}{T_c}\left(\frac{dT_c}{dp}\right)[f(t) - tf'(t)] + \frac{H_0}{2\gamma^*}\left(\frac{d\gamma^*}{dp}\right)f(t). \tag{4}$$

$\partial H_c/\partial p$ is then completely determined by the values of $H_0/T_c \cdot dT_c/dp$ and $H_0/\gamma^* \cdot d\gamma^*/dp$. Conversely measurement of $\partial H_c/\partial p$ near $T = 0$ and near T_c allows a unique determination of dT_c/dp and $d\gamma^*/dp$ if $f'(t)_{t=1}$ and H_0/T_c are known.

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It is instructive to write down the form which (4) takes if it is assumed that the critical field curve is parabolic so that

$$f(t) = 1 - t^2 \,. \tag{5}$$

We make use of the abbreviations

$$g = \frac{d \ln \gamma}{d \ln v} \quad \text{and} \quad s = \frac{d \ln T_c}{d \ln v}, \tag{6}$$

where γ is the electronic specific heat per mole, and v is the molar volume. ($\gamma^* = \gamma/v$.) Then

$$\frac{dH_c}{dp} = -H_0\kappa\left[s(1+t^2) + \frac{g-1}{2}(1-t^2)\right], \tag{7}$$

where κ is the compressibility.

$$\frac{1}{v}(v_n - v_s) = \frac{H_0{}^2\kappa}{4\pi}\left[s(1-t^4) - \frac{g}{2}(1-t^2)^2\right], \tag{8}$$

$$\frac{1}{v}(\alpha_n - \alpha_s) = \frac{H_0{}^2\kappa}{4\pi T_c}[4st^3 + 2g(1-t^2)t], \tag{9}$$

$$\kappa_n - \kappa_s = \frac{H_0{}^2\kappa^2}{4\pi}\left[2sg(t^4-1) - \frac{g^2}{2}(1-t^2)^2 - 2s^2(1+t^4)\right] + \frac{H_0{}^2\kappa}{4\pi}\left[\frac{ds}{dp}(1-t^4) + \frac{1}{2}\frac{dg}{dp}(1-t^2)^2\right] + \frac{H_0{}^2}{4\pi}\frac{d\kappa}{dp}\left[s(1-t^4) + \frac{g}{2}(1-t^2)^2\right]. \tag{10}$$

Experimental results

- *The volume difference*

The change in length on destruction of superconductivity by a magnetic field has been measured here using an optical method,[10,11] and by Cody[12] using a capacitive method. A sensitivity allowing detection of length changes of only a few angstroms in specimens about 10 cm long is required. The experimental details have been described fairly fully elsewhere.[11]

The results obtained on polycrystalline metals are summarized in Fig. 1. The length changes in single crystals may be highly anisotropic. We have reported previously on thallium[10] where $l_s - l_n$ is of different sign along different axes. More recent work on mercury and indium single crystals is shown in Figs. 2 and 3. Where reliable information on $\partial H_c/\partial p$ is available from other sources we usually find good agreement between our measurements of $v_n - v_s$ and values calculated using Eq. (8). Only in the cases of lead

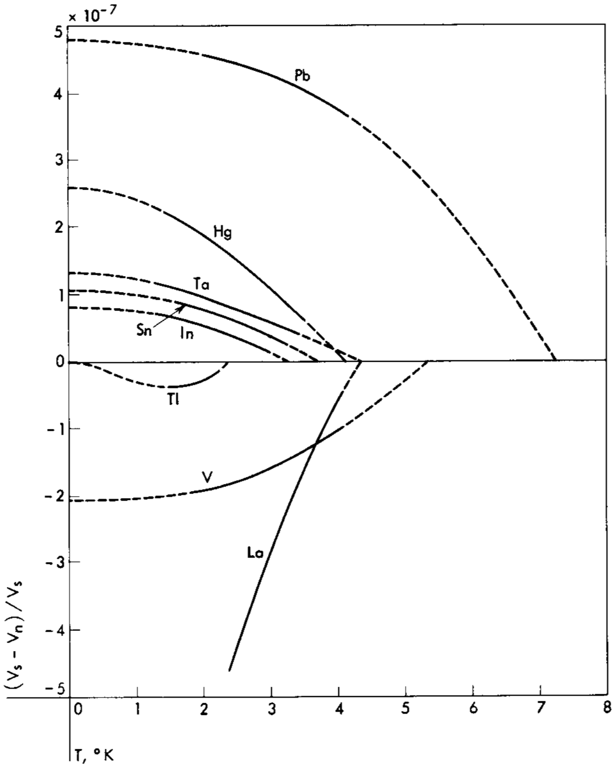
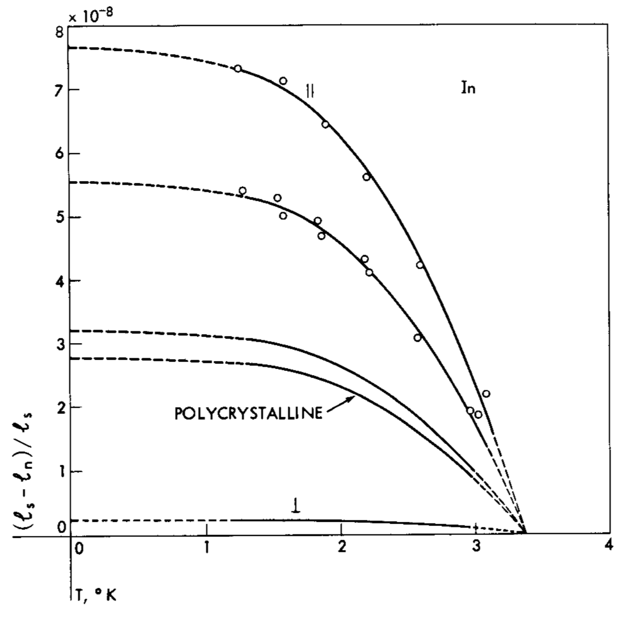


Figure 1 **The temperature dependence of $(v_s - v_n)/v_s$ in polycrystalline materials.** *The dashed portions of the curves are extrapolations using (8). (After Rohrer.[11])*

Figure 2 **The temperature dependence of $(l_s - l_n)/l_s$ in indium single crystals.** (*Rohrer.*[11])



and tantalum does there appear to be a severe disagreement between our work and other careful measurements of $\partial H_c/\partial p$.[13,14]

- *The elastic constants*

While $\partial H_c/\partial p$ can be measured directly, $\partial^2 H_c/\partial p^2$ is too small to be observed at the relatively small stresses which can be applied without permanent deformation of the material investigated. Some of the information required in (10) for a calculation of the difference in compressibility in the two states is therefore lacking. It is fortunate therefore that recent work by Alers[9] supplements the work by Landauer,[3] Mason and Bömmel,[7] and Gibbons and Renton[8] on the sound velocity in the normal and superconducting states.

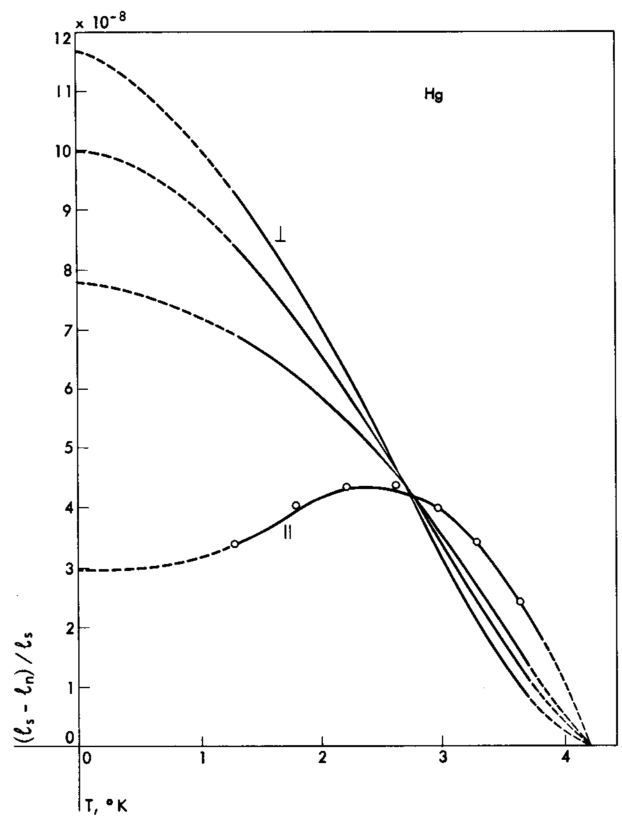
Previous work here[4,5] on the change in modulus of rigidity of polycrystalline tin provided information on the second derivative of H_c with respect to a shear strain only.[15]

- *Expansion coefficients*

Andres and Rohrer[6] have recently investigated the difference in expansion coefficient between the normal and superconducting states in lead. Their results, which are shown in Fig. 4, are in agreement with our observations on $v_n - v_s$.

Measurements of the expansion coefficient in the normal state are further of interest since they provide

Figure 3 **The temperature dependence of $(l_s - l_n)/l_s$ in mercury single crystals.** (*Rohrer.*[11])



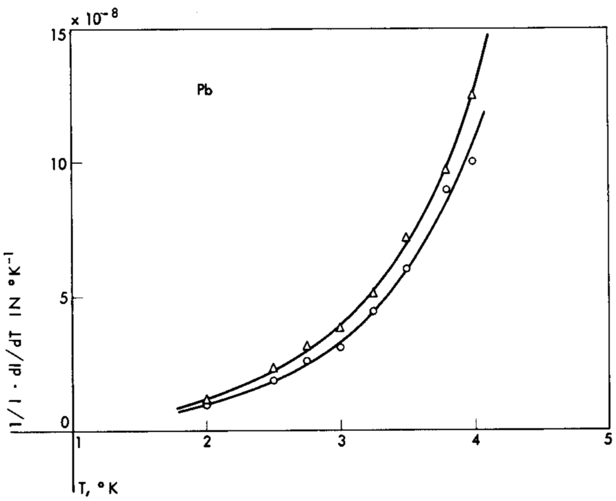


Figure 4 **Preliminary results on the thermal expansion coefficients of normal and superconducting lead.** △ *normal* ○ *superconducting* (*Andres and Rohrer.*[6])

an estimate of $d\gamma^*/dp$ which is independent of the value obtained from measurements of $\partial H_c/\partial p$. Such work has recently been reported by White,[16,17] Andres and Rohrer,[6] and Andres.[28]

Discussion

- *The pressure dependence of γ*

We have recently summarized existing measurements and calculations of $\partial H_c/\partial p$, and have tabulated the values of $s = d \ln T_c/d \ln v$ and $g = d \ln \gamma/dn \ln v$, which may be calculated from them.[18]

Mapother[19] has strongly criticized our estimates of the probable errors in these two quantities. He points out that the uncertainties in our present knowledge of $[f'(t)]_{t=1}$ are so large as to make our estimates of the error in g much too optimistic. In spite of their uncertainty, however, the estimates of g are of interest because they vary between -5 and $+10$ while the value to be expected for a free electron gas is $g \equiv d \ln \gamma/d \ln v = 2/3$. At present the information is too uncertain to make attempts at a comparison of theory and experiment very fruitful, and it is essential that further data on the volume dependence of γ be collected using an alternative method.

The work by White[16,17] in Australia* and by Andres and Rohrer[6] in Zürich should help fill this gap.

Preliminary work by both groups now indicates $g \simeq 1.6$ in aluminium while work on $\partial H_c/\partial p$[20] had indicated $g = 7 \pm 5$. In this metal a very large uncertainty is introduced into calculations of g from $\partial H_c/\partial p$ by the uncertainty in $[f'(t)]_{t=1}$. In lead two estimates of g

* Dr. G. K. White[27] has recently obtained the following values of g from expansion coefficient measurements:

	Al	Cr	Cu	Fe	Pb	Pd
$g \simeq$	1.8	−9	0.7	2.1	1.8	2.1

existed; one[10] based on $v_n - v_s$ gave $g = 1.8$, and another[13] based on direct measurements of $\partial H_c/\partial p$ gave $g = 6$. Andres and Rohrer's measurements of the expansion coefficient now suggest $g = 0.7$.

• *The pressure dependence of* T_c

Bardeen, Cooper and Schrieffer have expressed the critical temperature of a superconductor in terms of the Debye temperature, θ_D, and the product $N(0)A$ of the density of states at the Fermi level, and a constant A determining the strength of the interaction causing superconductivity. Rohrer[11] has recently shown that the relative change of $[N(0)A]$ with volume v, which is given by $d \ln [N(0)A]/d \ln v$, is approximately the same for all soft superconductors except thallium. This combined with

$$\frac{d \ln T_c}{d \ln v} - \frac{d \ln \theta_D}{d \ln v} = \ln \frac{0.85\theta_D}{T_c} + \frac{d \ln N(0)A}{d \ln v} \qquad (11)$$

suggests that a plot of $(d \ln T_c/d \ln v + \gamma_G)$ against $\ln (0.85\theta_D/T_c)$ should be a straight line. (Note that $d \ln \theta_D/d \ln v = -\gamma_G$, the Grüneisen constant.)

Such a plot is shown in Fig. 5. It will be seen that the soft superconductors lie remarkably close to a straight line. The only exception is thallium, which must be regarded as very doubtful because of lack of knowledge about the very strong anisotropy in the compressibility and in the influence of stress on T_c.

The hard superconductors so far investigated obviously do not obey the relation which exists among the soft superconductors.* This may perhaps be understood in the light of the discovery by Geballe, Matthias, Hull and Corenzwit[21] that there is no isotope effect in the transition metal ruthenium. These authors suggest that this is an indication that the mechanism causing superconductivity in the transition metals may not involve the phonons. If the phonons are not involved then there would, of course, be no reason for any correlation between $d \ln T_c/d \ln v$ and θ/T_c, and we should not be surprised by a failure of the Rohrer rule for tantalum, vanadium and lanthanum.

Zero-point energy

It has recently been pointed out by Daunt and Olsen[22] that the difference between the mechanical properties of a metal in the normal and superconducting states must cause a temperature-dependent difference in the Debye θ. The temperature dependence causes changes in the zero-point energy of a magnitude sufficient to explain the anomalous specific heats observed by Bryant and Keesom[23] in indium, and Boorse, Hirschfeld and Leupold[24] in niobium.

The zero-point energy of a Debye solid is $(9/8)\,R\theta$ per mole, and our initial estimate of the contribution ΔC

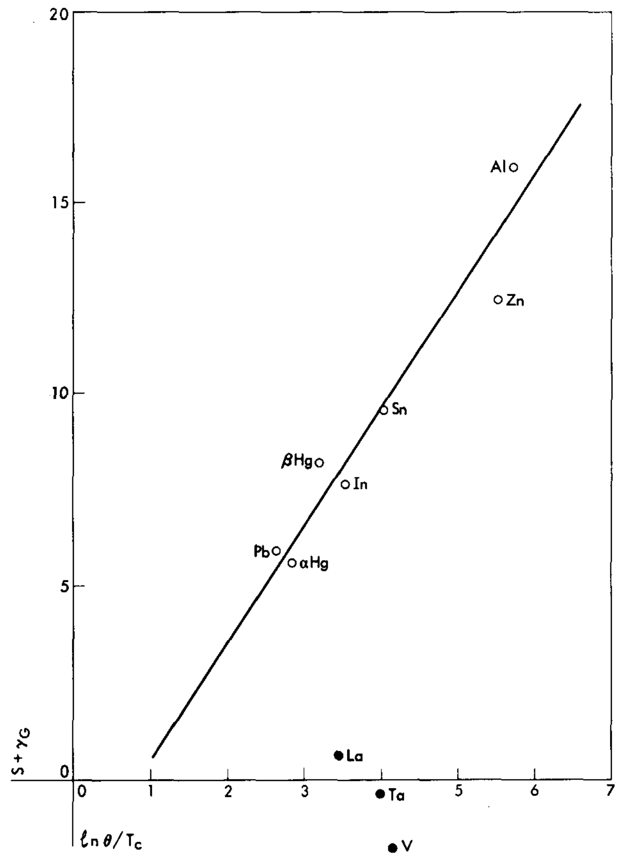


Figure 5 **$(d \ln T_c/d \ln v + \gamma_G)$ as a function of (θ_D/T_c). The soft superconductors are marked with open circles, the hard superconductors with black circles.** *The data used have been collected from work by various authors.*

which changes in θ might make to the specific heat was simply $\Delta C = (9/8)R(\partial\theta/\partial T)$. This very crude estimate gives some idea of the order of magnitude of anomalies which may be expected.

A more rigorous treatment consists in writing down the partition function, Z, and thence calculating the free energy, F, and the specific heat. If this is done for a harmonic oscillator with a temperature-dependent frequency $\nu(T)$, then terms arise in the specific heat $C_{\nu(T)}$ in addition to those usually found in the specific heat $C_{\nu\,\mathrm{const.}}$ for a temperature-independent oscillator. Most of these terms become small at low temperatures, and the main difference $\Delta C = C_{\nu(T)} - C_{\nu\,\mathrm{const.}}$ is given by

$$\Delta C = -\tfrac{1}{2} h T \frac{\partial^2 \nu}{\partial T^2}. \qquad (12)$$

If a similar treatment is carried out for a Debye solid it is found that[25]

$$\Delta C = -\tfrac{9}{8} R T \frac{\partial^2 \theta}{\partial T^2}. \qquad (13)$$

* *Note added in proof:* Recent work here has shown that the value of $(d \ln T_c/d \ln v + \gamma_G)$ used in Fig. 4 is about 30% too high. (This value was taken from work of Alekscevski and Gaidukov.) We have also found[29] that ruthenium lies far below the line for non-transition-metal superconductors in Fig. 4.

This may easily be calculated from the formulae given by Daunt and Olsen, and turns out to be somewhat larger in absolute magnitude than $(9/8)R(\partial\theta/\partial T)$. The change in sign gives agreement in sign between the temperature-dependent elastic constants observed by Alers and Waldorf[9] and the specific heat anomaly observed by Boorse, Hirschfeld and Leupold.[24]

The approach sketched above would appear to meet the objections made to our original procedure by Ferrell,[26] and to support our view that variations in zero-point energy play a noticeable role in determining the specific heat at very low temperatures.

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