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# The Temperature and Pressure Dependence of Critical Field Curves*

**Abstract: A brief discussion is given of the analysis of recent critical field measurements. In particular, a negative volume coefficient of thermal expansion is predicted for tin in the superconducting state.**

## Introduction

One of the major interests in obtaining critical field data for superconductors is to be able to calculate thermodynamic quantities, for both the normal and superconducting states, which are not readily obtainable from other measurements. The shape of the reduced critical field curve also affords a direct comparison between experimental data and basic theory.

A rather complete picture of the electronic contributions to the thermodynamic properties of a superconductor in both the normal and superconducting states can be derived from critical field measurements as a function of both temperature and pressure. There are several approaches to this, some of which are given in these Proceedings. The details of some recent measurements on tantalum[1] and the mercuries, which utilize one method of approach, have been given elsewhere,[2] and the following discussion summarizes the results and the method of analysis which was used in these measurements. Additional data for tin,[3] obtained using the same techniques, will be discussed also.

The method of analysis of critical field data depends to a great extent on the prejudices of the individual worker. The method which is suggested below seems to be, in principle, capable of yielding results with fewer complications than other methods. No details will be given, and basic references and comparisons with other data are given in References 1 and 2.

The free-energy difference between the normal and superconducting states can be written as

$$F_n^{el} - F_s^{el} = -\tfrac{1}{2}\gamma T^2 - F_s^{el} = (H_c^2 - H_0^2)V/8\pi\,, \quad (1)$$

where the free energy, $F(T, P) = U - TS$, has been assumed to approach zero as the temperature approaches zero for both states. Any changes in the lattice or other contributions at the superconducting transition have been assumed to be negligible, although this may not be the case. At low temperatures, the free energy of the superconducting state is believed to approach zero very rapidly, at least as fast as $T^4$ and probably as $e^{-1/t}$. Hence, in this limit,

$$H_c^2 = H_0^2 - (4\pi\gamma/V)T^2\,, \quad (2)$$

and a linear dependence of $H_c^2$ on $T^2$ would be expected to occur with the slope of the resulting curve proportional to $\gamma/V$. An inspection of precision critical field data for tin, indium, tantalum, mercury and lead shows that this is the case even above 1°K for these metals, and the values of $\gamma$ which can be calculated from these data are in excellent agreement with calorimetric data.[2] Indeed, Eq. (2) suggests a plot of $(1 - h^2)/t^2$ vs $t^2$ (where $h = H_c/H_0$ and $t = T/T_c$) as a convenient method of displaying low-temperature critical field data, although this plot is very sensitive to the proper (extrapolated) value of $H_0$.[1,2]

Once $\gamma$ has been obtained, it is a simple matter to use standard thermodynamic formulas to calculate the electronic contribution to the superconducting specific heat. The necessary formulas simplify considerably if the variables are chosen as $H_c^2$ and $T^2$, and, indeed, if the critical field data can be fitted to a power series $[H_c^2(T^2)]$ over a limited temperature region, it is possible to write down an explicit expression for the specific heat over this region in terms of the coefficients of the power series, and $\gamma$.

## Pressure effect

The thermodynamic description of the electronic properties of the superconductor can be complete only

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if the critical field also is measured as a function of pressure. Equation (2) can be used again as a guide, since at low temperatures,

$$(\partial H_c^2/\partial P)_T = dH_0^2/dP - 4\pi(\partial/\partial P)(\gamma/V)T^2 \,. \qquad (3)$$

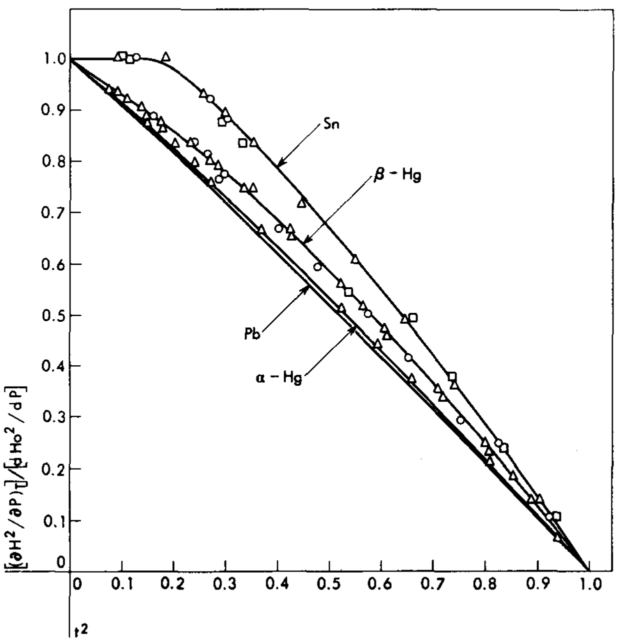
The natural variables appear to be $H_c^2$ vs $T^2$, and a plot of $2H_c(\partial H_c/\partial P)_T$ vs $T^2$ should give a straight line at low temperatures, with the slope being a measure of the pressure dependence of $\gamma$, the electronic specific heat coefficient. Typical data for several superconductors are given in Fig. 1, where the linear dependence is very marked at low temperatures. The data for tin illustrate very well the dangers which are involved in the extrapolation of high-temperature data to low temperatures.

The pressure-effect data (or $d\gamma/dP$) are of interest since by a Maxwell relationship,

$$\beta_n^{el} = -V^{-1}(\partial S_n^{el}/\partial P)_T = -V^{-1}T\, d\gamma/dP$$
$$= k_T(\gamma T/V)(d \ln \gamma/d \ln V) \,. \qquad (4)$$

For an ideal electron gas, $d \ln \gamma/d \ln V = +\frac{2}{3}$. For those superconductors for which reliable data are available, $d \ln \gamma/d \ln V$ is positive and fairly large (up to 8). Again, straightforward thermodynamic arguments can lead to a calculation of the electronic contribution to the thermal expansion in the superconducting state, and a power series representation of $(\partial H_c^2/\partial P)_T$ as a function of $T^2$ over a limited region of temperature is most convenient for the analysis of the data.

*Figure 1* **Typical data for the pressure effect in superconductors.** *The lead data are taken from M. Garfinkel and D. E. Mapother, Phys. Rev.* **122**, *459 (1961), while the tin and mercury data are as given in References 1 and 2.*



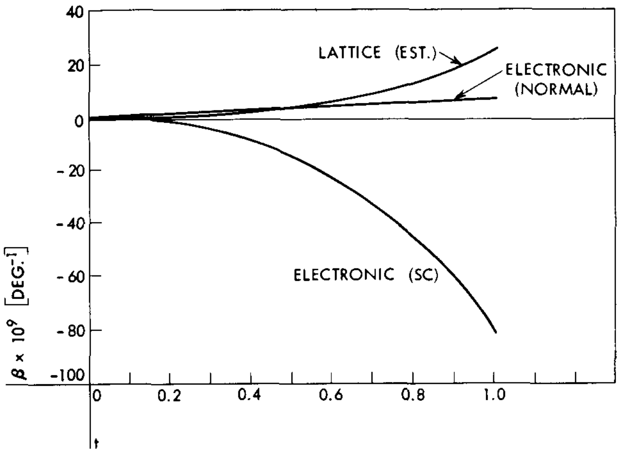




*Figure 2* **Calculated values of the thermal expansion contributions for tin due to the electrons in the normal and superconducting states, as well as an estimated lattice contribution** *(obtained using a Mie-Grueneisen equation of state with $\Gamma = 1.8$).*

## Results for tin

Figure 2 gives the results of such an analysis for tin. Figure 1, combined with Eq. (2), indicates that $d \ln \gamma/d \ln V = 1$ for this metal, and $\beta_n^{el} = k_T\gamma T/V$. The thermal expansion due to the electrons in the superconducting state was obtained from this result and $(\partial H_c^2/\partial P)_T$ as a function of $T^2$, while the lattice thermal expansion was estimated from a Mie-Grueneisen equation of state. The negative thermal expansion contribution due to the superconducting electrons is quite large, and should be directly observable. Unfortunately, tin may be expected to be very anisotropic in its behavior, and this calculated thermal expansion refers only to the net volume effect.

This superconducting electron contribution can be shown to be negative for all superconductors where reliable data exist, except for tantalum. No explanation can be given except that the anomalous behavior ($\beta_s^{el} > 0$) for tantalum may be associated with the fact that it is a transition metal. Reliable pressure-effect data do not exist for any other transition metal.

## References

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2. J. E. Schirber and C. A. Swenson, "The Superconductivity of α and β Mercury," *Phys. Rev.* **123**, 1115 (1961).
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