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Variation of the Elastic Moduli at the Superconducting Transition

Abstract: Using an ultrasonic technique capable of measuring changes in the elastic moduli as small as one part in 10^7, the small modulus changes associated with the normal-to-superconducting transition have been measured as a function of both temperature and magnetic field. Single-crystal specimens of the cubic metals Pb, V, Nb and Ta were used and all their elastic moduli measured so that changes in the bulk modulus and Debye θ could be computed. The results showed that changes in the zero-point energy of the lattice can be far from negligible. Furthermore, the shear moduli are the most changed by the appearance of superconductivity.

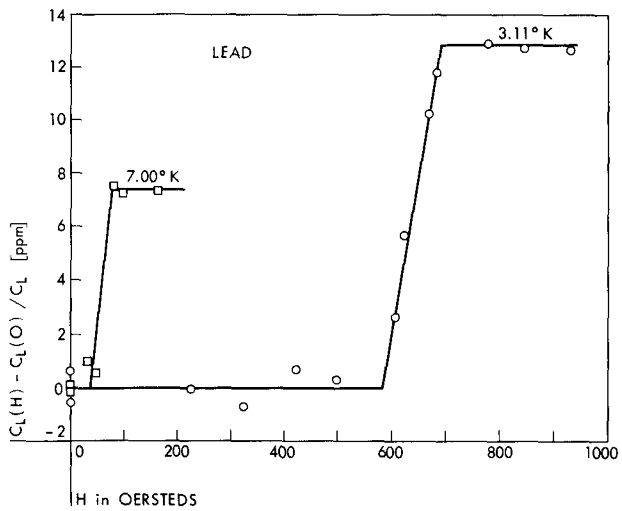
There have been many measurements[1-5] of the changes in a particular elastic modulus at the superconducting transition, but in no case have the changes in all the moduli of one metal been determined. Such data are needed in order to calculate the changes in quantities of particular interest such as the bulk modulus, the Debye θ_0 and the zero-point energy. This paper presents measurements of the change in all three elastic moduli of the cubic superconductors Pb, V and Nb. Tantalum was also studied but the results are not discussed here because they showed impurity-sensitive anomalous behavior in both the normal and superconducting states. Emphasis was put on measuring many different superconducting elements in order to show up common, general features rather than making a complete study of an individual case.

The measurements were made using ten-megacycle sound pulses in a modified "sing-around" apparatus designed and built by R. L. Forgacs[6] to have a sensitivity of one part in 10^7. Changes in the three elastic moduli $C_L = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$, $C = C_{44}$ and $C' = \frac{1}{2}(C_{11} - C_{12})$ were directly determined. The Ta and Nb single crystals were purchased from the Linde Company and were nominally 99.9% pure. The V sample was prepared in this laboratory to a purity of 99.98%. The Pb crystal was grown from high-purity Pb to which 0.02% Bi was added in order to keep the electron mean free path at helium temperatures much less than the wavelength of the sound waves used. With these purities, no difficulty with attenuation changes at the superconducting transition was encountered. Corrections for dimensional changes at the transition are too small to be considered in all cases.[7]

No correction for a deviation from adiabatic sound wave propagation conditions within the samples was necessary for V and Nb, but for Pb a correction of at most two parts per million near 4°K might be necessary for the longitudinal mode and the bulk modulus.

The experimental apparatus was sufficiently stable and sensitive to allow the modulus difference to be measured in two different ways. The simplest method was the isothermal application of a magnetic field. Examples of the data obtained in this way are shown in Fig. 1 for Pb (a soft superconductor) and in Fig. 2

Figure 1 **Variation of the modulus C_L of the soft superconductor lead as a function of magnetic field at two temperatures.**



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for V (a hard superconductor). For the soft superconductor, the specimen remained completely superconducting up to magnetic fields very near the critical field, while for the hard superconductor the intermediate state (characterized by intermediate values of the modulus) appears very near to zero field. Furthermore, there is a hysteresis effect in the hard superconductors in that returning the applied magnetic field to zero does not return the modulus to its original value. The magnetic field value above which the modulus is field-independent is equal to the true critical field for Pb but is much larger than the critical field for V. This is shown in the inset to Fig. 2, where the solid line defines the generally accepted critical field[8] of V and the line with the open circles defines the observed field necessary to make the modulus behave normally.

Measuring the variation of the modulus with temperature in the superconducting state (zero applied field) and again in the normal state (large applied field) yielded a second method of obtaining the differences in the modulus between the two states. Figure 3 gives an example of this method for the C_{44} modulus of V. Note the suppression of the superconductivity by a small magnetic field. Also of interest is the lack of a discontinuity in the shear modulus at the critical temperature, as is expected from symmetry arguments.[9] A discontinuity is expected for compressional sound waves (C_L modulus) and in the bulk modulus.[10] Figure 4 shows this discontinuity as observed in the Pb crystal. The open data points were obtained from the present measurements while the filled points at T_c have been calculated from measurements of the pressure dependence of the critical field using the relation[10]

$$\frac{\Delta B}{B} = \frac{B}{4\pi}\left[\frac{dH_c}{dP}\right]^2 \quad \text{at } T = T_c\,. \tag{1}$$

Column 8 of Table I gives the discontinuous change in the bulk modulus observed in the metals studied at the superconducting transition in zero magnetic field. Column 9 gives the right side of Eq. (1) as computed from the dH/dP data of several authors.[11,12] The agreement is excellent for the soft superconductor Pb but very poor for V and Nb. The failure in the case of the hard superconductors is probably associated with impurity effects and demands further study.

This second method of measurement also yielded the temperature dependence of the elastic moduli in both the normal and superconducting states. In the normal state the moduli varied according to the relationship

$$M = M_0(1 - \alpha T^2) \tag{2}$$

as T approached zero. The values of α are given in column 3 of Table 1. Since the elastic moduli are second derivatives with respect to a strain of the total energy of the solid, it seems reasonable that this T^2 dependence can be attributed to the conduction electrons which have an internal energy proportional to T^2.

Debye temperature θ

Temperature-dependent elastic moduli may be expected to make the Debye θ temperature-dependent. Daunt and Olsen[12] have shown that a temperature-dependent θ can produce a large contribution to the

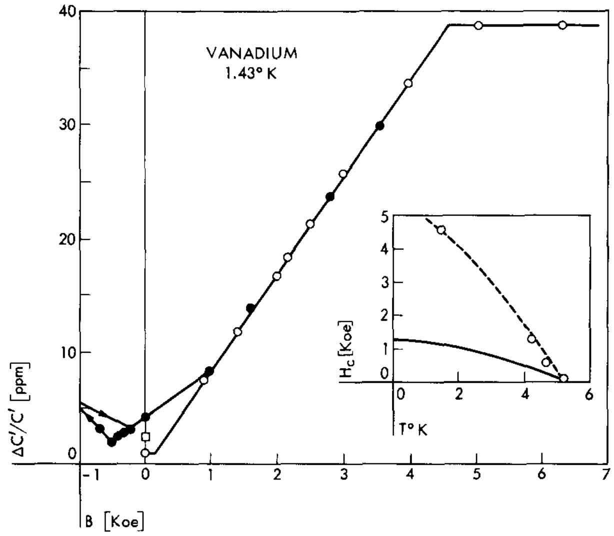
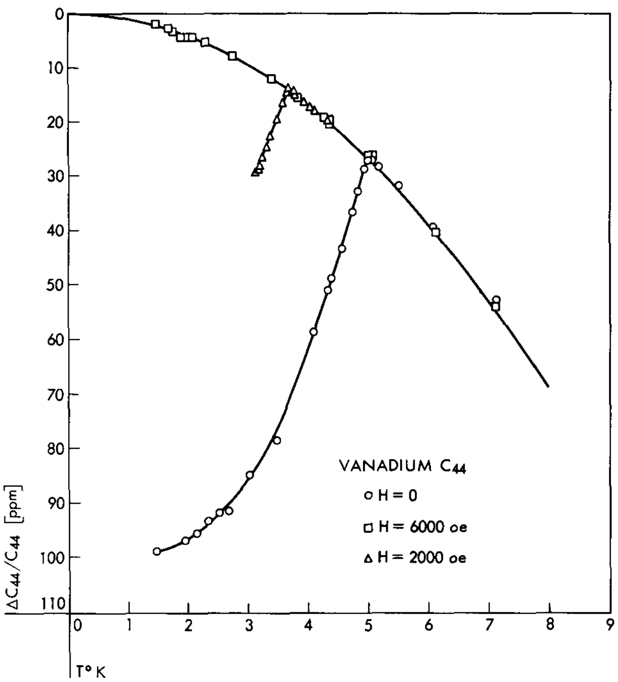


Figure 2 **Variation of the modulus C′ of the hard superconductor vanadium as a function of magnetic field.**

Figure 3 **Variation of the modulus C_{44} of vanadium as a function of temperature in both the normal and superconducting states.**



specific heat from the zero-point lattice vibrations. They have used this contribution to explain the anomalously low specific heat observed in some superconductors.[13] Unfortunately, their argument neglects other energy terms which necessarily compensate for the zero-point energy variations. It is easily shown[14] that a temperature-dependent θ simply introduces a correction factor of the form $(1 - 2d\ln\theta/d\ln T)$ to the usual T^3 lattice specific heat. Using the present measurements to estimate this correction factor, it follows that the contribution to the specific heat from a temperature-dependent θ is too small and of the wrong sign to explain the observed specific heat of superconductors.[13]

The actual measurements of the difference in the elastic moduli between the normal and superconducting states are shown in Figs. 5, 6 and 7. It is to be noted that the moduli in the superconducting state are always less than in the normal state. The dip in the C modulus difference for Nb near 2°K is probably associated with impurities or imperfections since vacuum annealing decreases its depth. The sag in $\Delta C_L/C_L$ for Pb around 4°K can be eliminated by a reasonable correction for the deviation from adiabatic conditions for the sound wave. But the drop in $\Delta C_L/C_L$ below 2°K would remain.

It is interesting to note that the modulus most affected by the transition to superconductivity is the smallest shear modulus (C for Nb and V and C' for Pb and Ta). Since the change in modulus is related thermodynamically to the change in the critical field with stress,[15] the present results would indicate that a shear stress would be most effective in changing the critical field. Pippard[9] has shown that the critical field in

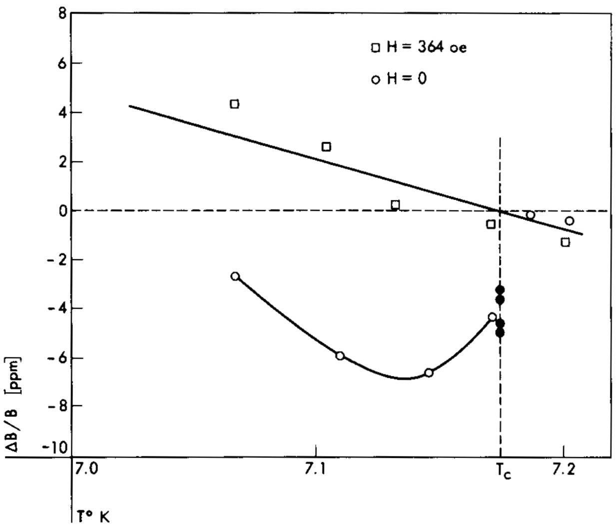
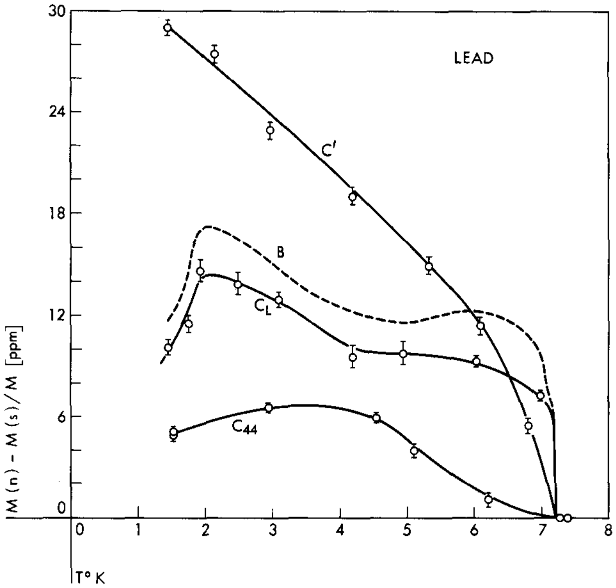
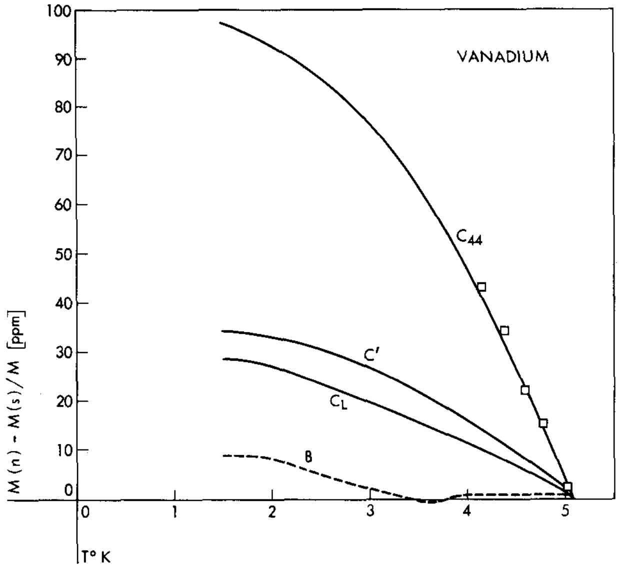


Figure 4 **Variation of the bulk modulus *B* of lead near the zero field superconducting transition temperature.**

Table 1 **The adiabatic elastic moduli at 4.2°K and the Debye temperature θ_0 computed from them for the superconductors Pb, V and Nb. The other columns are quantities derived from the present measurements, as is described in the text.**

Element	*Modulus* [10^{11}dyne cm^{-2}]	α [10^{-7} deg K^{-2}]	θ_0 [°K]	$\theta_{(n)}-\theta_{(s)}$ [°K]	(9/8) $K\Delta\theta$ [10^{-7} ev/atom]	$\frac{H_0^2}{8\pi}$ [10^{-7} ev/atom]	$\frac{\Delta B}{B}$ [ppm]	$\frac{B}{4\pi}\left(\frac{\partial H_c}{\partial p}\right)^2$ [ppm]
Pb	C_L = 6.99	34	105	4.6×10^{-4}	0.45	4.7	4.0	3.2 3.6 4.6 4.7
	C = 1.94	57.5						
	C' = 0.506	69.2						
V	C_L = 22.18	3.3	400	1.5×10^{-2}	15	6.2	<1/2	2.1
	C = 4.60	10.3						
	C' = 5.65	4.6						
Nb	C_L = 22.50	2.7	277	1.6×10^{-2}	15	17	0.7	2.7
	C = 3.09	12.8						
	C' = 6.01	2.3						





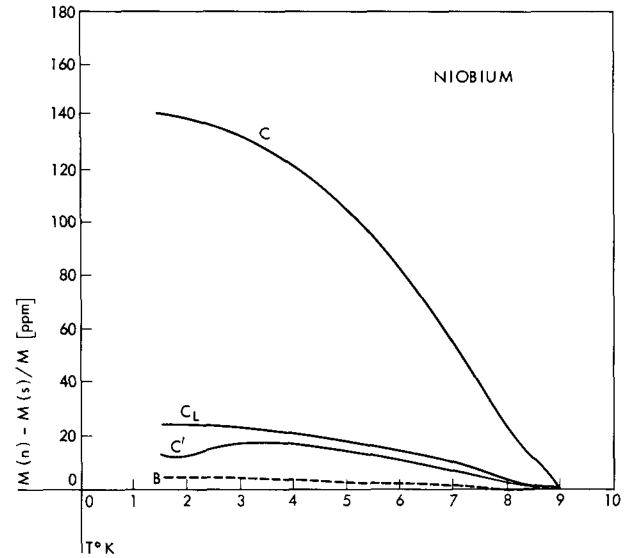


Figure 5 **The difference in the elastic moduli of lead between the normal and the superconducting states as a function of temperature.**

Figure 6 **The difference in the elastic moduli of vanadium between the normal and superconducting states as a function of temperature.**

Figure 7 **The difference in the elastic moduli of niobium between the normal and superconducting states as a function of temperature.**

cubic superconductors must depend upon a higher power of the shear stress than the first. Thus measurements of the variation of the critical field with shear stress should not only be large but also nonlinear. This effect has been observed recently by Seraphim and Marcus.[16]

Zero-point energy

Even though the zero-point energy does not appreciably affect the specific heat, it is an important part of the total lattice kinetic energy. Chester[17] has shown that the difference in the lattice kinetic energy between the normal and superconducting states should be comparable to the total free energy difference between the two states. If one assumes that the relative changes in sound velocity observed at ten megacycles are the same at all frequencies, then the change in zero-point energy between the normal and superconducting states can be calculated. Column 6 of Table 1 gives this calculated change in zero-point energy, while column 7 shows the total free energy change at 0°K as determined from the critical magnetic field. The two energy changes are indeed quite comparable. Thus *if all the frequencies are changed by a fractional amount equal to the changes observed at ten megacycles*, then the zero-point energy contribution to the lattice kinetic energy must not be neglected.

Acknowledgments

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