

with solid He³ it seems likely that the new γ phase is body-centered cubic.

[†]Assisted by the National Science Foundation and the Army Research Office (Durham).

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COMPRESSIBILITY, ZERO-POINT ENERGY, AND SPECIFIC HEAT IN SUPERCONDUCTORS*

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(Received February 9, 1961)

Keesom and Bryant¹ showed that the specific heat of indium in the superconducting state at the lowest temperatures is considerably smaller than the lattice specific heat deduced from measurements in the normal state. The work of Boorse, Hirschfeld, and Leupold² and of Zavaritskii³ indicates a similar effect in niobium and tin. Such a phenomenon would be easily understood if there were correspondingly large differences in the elastic constants and in the Debye characteristic temperatures, θ_D , of the two states. Work by Chandrasekhar and Rayne⁴ has now confirmed the generally accepted view in ruling out the possibility of any differences in θ_D greater than 1 part in 10^4 . We wish to show here that even the very much smaller changes in θ_D which are known to exist can influence the zero-point energy enough to allow an explanation of the observations.

The total energy, E , of a Debye solid at low temperatures may be written

$$E = 1.125 R \theta_D + 58.5 RT^4 / \theta_D^3, \quad (1)$$

where R is the gas constant. The first of these terms is usually known as the zero-point energy of the lattice. If θ_D is constant, we obtain the well-known expression for the T^3 lattice specific heat, C_g , at low temperatures:

$$C_g = \partial E / \partial T = 234 RT^3 / \theta_D^3. \quad (2)$$

An attempt to explain the observed differences in specific heat using this formula requires com-

plicated and unlikely changes in the phonon spectrum.

On the other hand, it is well known that the difference in compressibility between the two states is temperature dependent and given by⁵

$$\frac{1}{V} \left(\frac{\partial V_n}{\partial p} - \frac{\partial V_s}{\partial p} \right) = \frac{1}{4\pi} \left(\frac{\partial H_c}{\partial p} \right)^2 + \frac{H_c}{4\pi} \frac{\partial^2 H_c}{\partial p^2}, \quad (3)$$

where V_n and V_s are the volumes in the normal and superconducting states, H_c is the critical magnetic field, and p is the pressure. The compressibility in one of the states at least must then be temperature dependent, and θ_D must clearly be so, too.

Such a temperature dependence of θ_D affects the zero-point energy and contributes to the specific heat, which now becomes

$$\begin{aligned} C_E &= \partial E / \partial T \\ &= 1.125 R (\partial \theta_D / \partial T) + 234 RT^3 / \theta_D^3 \\ &\quad \times [1 - (3T/4\theta_D)(\partial \theta_D / \partial T)]. \end{aligned} \quad (4)$$

It is obvious that even a very small value of $\partial \theta_D / \partial T$ at the lowest temperatures may produce effects comparable with the value of C_g given by Eq. (2).

The expressions (3) and (4) and the known dependence of θ_D on compressibility can be used to calculate the difference between the lattice specific heats, C_{gn} in the normal and C_{gs} in the superconducting states, from the pressure de-

pendence of the critical field. Straightforward but tedious algebra leads to

$$C_{gs} - C_{gn} = -9R\theta_D T_C^{-1} (32\pi)^{-1} \left\{ \frac{K}{2} \left[\left(\frac{\partial H_0}{\partial p} \right)^2 F(t) + \frac{H_0^2}{\gamma^*} \frac{\partial^2 \gamma^*}{\partial p^2} G(t) + H_0 \frac{\partial^2 H_0}{\partial p^2} H(t) \right] + \frac{2}{3} H_0 \frac{\partial H_0}{\partial p} J(t) \right\}, \quad (5)$$

where K is the bulk modulus, p is the pressure, H_0 is the critical field at $T=0$, $\gamma^* T$ is the electronic specific heat per unit volume, $t = T/T_C$, and T_C is the transition temperature.

$$F(t) = (2\alpha - \alpha^2) [f'(t)f(t) - tf'(t)^2 - tf''(t)f(t)] + (1 - \alpha)^2 [3t^2 f''(t)f'(t) + t^2 f'''(t)f(t)], \quad (6a)$$

$$G(t) = f'(t)f(t) + tf'(t)^2 + tf''(t)f(t), \quad (6b)$$

$$H(t) = f'(t)f(t) - tf'(t)^2 - tf''(t)f(t), \quad (6c)$$

$$J(t) = (1 + \alpha)f(t)f'(t) - (1 - \alpha)[tf'(t)^2 + tf(t)f''(t)], \quad (6d)$$

where

$$\alpha = \frac{1}{2} \left(\frac{1}{\gamma^*} \frac{\partial \gamma^*}{\partial p} \right) / \left(\frac{1}{H_0} \frac{\partial H_0}{\partial p} \right),$$

and $f(t)$ is defined by $H_C = H_0 f(t)$. Primes denote differentiation with respect to t .

These expressions are greatly simplified if it is assumed that $f(t) = 1 - t^2$. Then

$$F(t) = 4t^3(3 - 2\alpha)(1 - 2\alpha), \quad (7a)$$

$$G(t) = 8t^3 - 4t, \quad (7b)$$

$$H(t) = -4t^3, \quad (7c)$$

$$J(t) = -4t^3(1 - 2\alpha) - 4\alpha t, \quad (7d)$$

and Eq. (5) reduces to the form:

$$C_{gs} - C_{gn} = AT + BT^3. \quad (8)$$

The coefficients of $F(t)$ and $J(t)$ can be obtained since $\partial H_0/\partial p$ and K are known. The value of α is somewhat less certain, but information about its value is available.^{6,7} The coefficient of $H(t)$ which involves $\partial^2 H_0/\partial p^2$ can be estimated for tin from work on the differences in the velocity of sound in the normal and superconducting states.^{8,9} No data are available at present allowing more than a guess at $\partial^2 \gamma^*/\partial p^2$ which appears in the coefficient of $G(t)$. Work on the difference in the modulus of rigidity¹⁰ seems to suggest that in tin this is about one-tenth of $\partial^2 H_0/\partial p^2$.

Table I lists available information for various superconductors. B_{calc} gives the coefficient of the term in T^3 in Eq. (8), under the further simplifying assumption that $\partial^2 H_0/\partial p^2 = \partial^2 \gamma^*/\partial p^2 = 0$. B_{obs} is that obtained from the observed specific heats.

The order of magnitude and sign of B_{calc} encourages the belief that the specific heat anomalies are, in fact, created by a temperature dependence of the zero-point energy of the lattice.

Table I. Data for calculation of the term B of Eq. (8) together with observed values of B for various superconductors.

	Nb	Pb	Sn	In	Al
T_C (°K)	8	7.2	3.73	3.37	1.2
θ (°K)	250	90	160	109	419
α	1.5 ± 0.5	0.10	0.05	0 ± 0.03	0.25
$\frac{1}{2}K(\partial H_0/\partial p)^2 \times 10^6$	17	16	5	1.6	3.3
$(\frac{1}{2}KH_0^2/\gamma^*)(\partial^2 \gamma^*/\partial p^2) \times 10^6$	0 ± 3
$\frac{1}{2}KH_0(\partial^2 H_0/\partial p^2) \times 10^6$	+18
$\frac{3}{4}H_0(\partial H_0/\partial p) \times 10^6$	-5	-4	-1.0	-0.6	-0.2
B_{obs} (μjoule/mole deg)	-22	...	-20(?)	-300 ^a	...
B_{calc} (μjoule/mole deg)	-1.3	-4	-50	-12	-2500

^aThe observations on In may perhaps better be described using $A = -30$ and $B = -10$.

For a further advance, more data on α , $\partial H_0/\partial p$, $\partial^2 H_0/\partial p^2$, and $\partial^2 \gamma^*/\partial p^2$ for various directions of stress are required.

Our calculation gives rise to a linear term, A , in $C_{gs} - C_{gn}$. The sign and magnitude of this term depend upon the coefficients of $G(t)$ and $J(t)$ in (5). The experimental data indicate that the coefficient of $J(t)$ in general makes a small positive contribution to A . The coefficient of $G(t)$, which involves $\partial^2 \gamma^*/\partial p^2$, is not known, but it might be negative in some cases. If so, and assuming that the parabolic form of $f(t)$ remains valid, formally one deduces an apparent negative specific heat in the superconducting state at the lowest temperatures. It is not clear what modifications or mechanisms should be invoked in order to avoid this conclusion, since existing data do not extend to low enough temperatures. Bryant and Keesom's results indicate $A < 0$, but in their case a positive nuclear quadrupole term keeps the total specific heat from becoming negative.

We should point out that the role of the zero-point energy in causing the observed specific-heat anomalies was realized independently by Schrieffer who has approached the problem from a microscopical point of view.

We are most grateful to Dr. J. R. Schrieffer and also to Dr. B. S. Chandrasekhar and Dr. J. A.

Rayne for telling us of their results prior to publication. We also wish to thank Dr. H. Rohrer for providing an estimate of $\partial H_0/\partial p$ in niobium from his unpublished measurements.

*This work was supported by the Office of Naval Research.

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OSCILLATIONS IN THE LONGITUDINAL TUNNEL CURRENT OF TUNNEL DIODES

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(Received January 18, 1961)

It has been observed by Chynoweth, Logan, and Wolff¹ that the tunnel current in InSb tunnel diodes displays oscillations at low temperatures and large longitudinal magnetic fields ($H \parallel F$). The field dependence of the periodicity of these oscillations suggests a relation to the de Haas-Schubnikow oscillations in galvanomagnetic properties. These oscillations are due to density of state fluctuations in the highest occupied Landau level. Such oscillations are not to be expected for transverse magnetic fields,^{1,2} and none were observed.¹

If the observed oscillations are of the de Haas-Schubnikow type, their magnitude suggests that a significant portion of the tunneling current is due to electrons with the highest possible magnetic quantum number. This conclusion is sur-

prising, since the tunneling process strongly favors the low quantum numbers. The dependence of the tunneling rate on quantum number is given by²

$$\exp[-\frac{3}{2}(n\hbar\omega/\epsilon)\lambda],$$

where

$$\lambda = \frac{2}{3}(2m\epsilon)^{3/2}/\hbar m F,$$

$F = [\mu_1 + \mu_2 + \epsilon - qV]/a$ = average junction field, a = junction width, n = quantum number, $\omega = eH/mc$, ϵ = energy gap, m = electron-hole reduced mass, V = applied voltage. For the particular InSb diode used in reference 1 we have $\lambda \sim 30$. Hence, the ratio of the contributions of the largest and smallest quantum numbers is $\sim \exp(-45\mu_1/\epsilon)$, where μ_1 is the electron Fermi