

is probably a result of the field not being accurately aligned along the [100] axis and the relatively low purity of their samples. They also report anisotropy of the resistance in fields of 2–4 kOe and attribute it to either anisotropy of the impurity or defect distribution in the sample, or anisotropy of the superconducting energy gap. Measurements by Reed *et al.*⁹ on the

⁹ W. A. Reed, E. Fawcett, P. P. M. Meincke, P. C. Hohenberg, N. R. Werthamer, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966*, edited by M. P. Malkov (Proizvodstvenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967), Vol. IIA, p. 368.

anisotropy of H_2 in niobium and NbTa alloys show that this anisotropy is not due to the superconducting energy-gap anisotropy and is probably due to either the defect distribution or some nonuniformity of the surface.

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Steady-State, ac-Temperature Calorimetry*

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A steady-state technique for measuring heat capacity using ac heating is described. Heat is applied sinusoidally in time to a sample coupled thermally to a reservoir; the resultant equilibrium temperature of the sample contains a term that is both inversely proportional to the heat capacity and measurable with high precision. The effects of various corrections that must be applied to the data are considered in detail. Measurements of the absolute magnitude of the heat capacity of indium and the field dependence of the heat capacity of beryllium have been made and are used to illustrate the power of the method. The observed quantum oscillations in the heat capacity of beryllium are in agreement with predictions based on other measurements.

INTRODUCTION

LOW-TEMPERATURE calorimetry often suffers from the transient nature of the traditional measurements—a characteristic that makes difficult the use of any of the now highly developed signal-averaging techniques to extract the wanted signal from noise. This limitation is of little importance in the measurement of the absolute value of heat capacity where other considerations, mainly thermometer calibration, already limit the accuracy of the measurements. In the determination of small changes in the heat capacity, however, the signal-to-noise ratio can become the limiting factor.

Additional disadvantages of traditional techniques stem from the necessity of thermal isolation of the sample from its surroundings. A sample must be quite large to minimize the effects of stray heat leaks. Helium exchange gas or a complicated heat switch may be required to obtain sufficient isolation during a heat-capacity measurement and yet cool down the sample in a reasonable length of time. A sample suspension system trades off mechanical stability to accomplish thermal isolation, possibly making the apparatus sensitive to vibrations.

To alleviate the problems discussed above, a steady-state calorimetry technique employing ac heating has been developed.^{1–3} This method makes possible a much more precise measurement of heat-capacity changes as a function of an external parameter, although the absolute accuracy of the heat capacity data is no better than that obtainable with the traditional methods. The sample can be quite small. Neither exchange gas nor a heat switch is required. The suspension system can be quite rigid if the sample is of a reasonable size. The sample is connected thermally to a heat reservoir and so rapidly returns to thermal equilibrium after experiencing any extraneous heat input. Finally, a continuous read-out of the heat capacity is possible.

In the following sections the general theory of the method is presented and measurements are reported on indium and beryllium illustrating the power of the technique.

THEORY

A. Sample of Infinite Thermal Conductivity

Consider a system, as in Fig. 1, consisting of a heater, thermometer, and sample, each assumed to have infinite thermal conductivity and heat capacities C_h ,

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¹ P. Sullivan and G. Seidel, *Ann. Acad. Sci. Fennicae* **A210**, 58 (1966).

² P. Sullivan and G. Seidel, *Phys. Letters* **25A**, 229 (1967).

³ P. Sullivan, thesis, Brown University (unpublished).

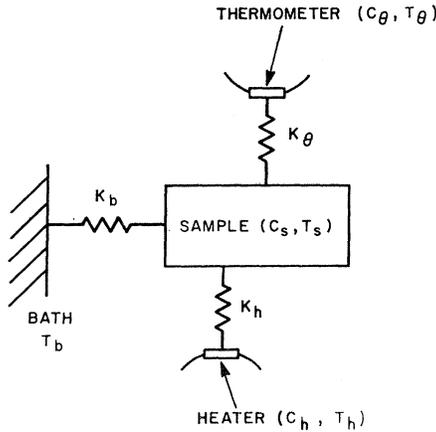


FIG. 1. Diagram of sample coupled to a bath, thermometer, and heater by the thermal conductances K_b , K_θ , and K_h , respectively.

C_θ , and C_s , respectively. These components are interconnected by thermal conductances K_h , K_θ , and K_b as indicated in the figure. If heat is generated in the heater at the rate $\dot{Q} = \dot{Q}_0(\cos\frac{1}{2}\omega t)^2$, then the thermal equations for the system are

$$\begin{aligned} C_h \dot{T}_h &= \dot{Q}_h = \dot{Q}_0(\cos\frac{1}{2}\omega t)^2 - K_h(T_h - T_s), \\ C_s \dot{T}_s &= \dot{Q}_s = K_h(T_h - T_s) - K_b(T_s - T_b) \\ &\quad - K_\theta(T_s - T_\theta), \quad (1) \\ C_\theta \dot{T}_\theta &= \dot{Q}_\theta = K_\theta(T_s - T_\theta). \end{aligned}$$

If the temperature variations are sufficiently small, the various heat capacities and thermal conductivities may be considered constant. The steady-state solution for T_θ of these simultaneous equations consists of two terms, one a constant that depends upon K_b , and the other an oscillatory term inversely proportional to the heat capacity of the sample. The expression for T_θ is

$$T_\theta = T_b + \frac{1}{2} \dot{Q}_0 \left\{ \frac{1}{K_b} + \frac{1-\delta}{\omega C} \cos(\omega t - \alpha) \right\}, \quad (2)$$

where

$$\begin{aligned} C &= C_s + C_\theta + C_h, \\ 1-\delta &= \left[1 + \frac{\tau_\theta^2(1+2K_\theta/K_b) + \tau_h^2(1+2K_h/K_b)}{\tau_s^2} + \frac{1}{\omega^2 \tau_s^2} \right. \\ &\quad \left. + \omega^2 \left\{ \left(\frac{C_s + C_h}{C} \right)^2 \tau_\theta^2 + \left(\frac{C_s + C_\theta}{C} \right)^2 \tau_h^2 \right. \right. \\ &\quad \left. \left. + \frac{\tau_\theta^2 \tau_h^2}{\tau_s^2} \left(1 + 2 \frac{K_b(K_\theta + K_h) + K_\theta K_h}{K_b^2} \right) \right\} \right. \\ &\quad \left. + \omega^4 \tau_\theta^2 \tau_h^2 \left(\frac{C_s}{C} \right)^2 \right]^{-1/2}, \quad (3) \end{aligned}$$

and α is a phase angle of little interest, approximately equal to $\frac{1}{2}\pi$ under the conditions discussed below. The

relaxation times in Eq. (3) are defined as

$$\begin{aligned} \tau_s &= C/K_b, \\ \tau_\theta &= C_\theta/K_\theta, \end{aligned} \quad (4)$$

and

$$\tau_h = C_h/K_h.$$

If (a) the heat capacities of the heater and thermometer are much less than that of the sample, (b) the sample, heater, and thermometer come to equilibrium with a time constant much less than the inverse of the frequency ω , more specifically, $\omega^2(\tau_\theta^2 + \tau_h^2) \ll 1$, and (c) the frequency is much larger than the inverse of the sample-to-bath relaxation time, i.e., $\omega \tau_s \gg 1$, then to first order in $\omega^2(\tau_\theta^2 + \tau_h^2)$ and $(\omega \tau_s)^{-2}$,

$$1-\delta = [1 + 1/\omega^2 \tau_s^2 + \omega^2(\tau_\theta^2 + \tau_h^2)]^{-1/2} \quad (5)$$

and

$$\alpha \approx \arcsin [1 + \{1/\omega \tau_s - \omega(\tau_\theta + \tau_h)\}^2]^{-1/2}. \quad (6)$$

B. Sample of Finite Thermal Conductivity

The discussion of the preceding subsection cannot be applied to a real system without considering the influence of the finite thermal conductivity of the sample. To determine the effect of finite conductivity consider the case illustrated in Fig. 2. A sample in the form of a slab of thickness L and cross-sectional area A is heated uniformly on one side ($x=0$) by a sinusoidal heat flux $\dot{q}(0,t) = (\dot{Q}_0/2A)e^{i\omega t}$. The other side of the slab ($x=L$) is coupled uniformly to a bath at constant temperature T_b through a thermal conductance K_b . Let the thermal conductivity of the sample be κ , its specific heat c , and its density ρ . The thermal diffusivity n is defined by the relation $n = \kappa/\rho c$. The characteristic length $l_0 = (2n/\omega)^{1/2}$ and its reciprocal $k = 1/l_0$ are also introduced.

For the purpose of this discussion of the influence of the finite conductivity of the sample, the heater at $x=0$ and the thermometer at $x=L$ are assumed to be coupled to the sample with very short relaxation time, i.e., $\omega^2(\tau_h^2 + \tau_\theta^2) \ll 1$, as considered in the preceding subsection.

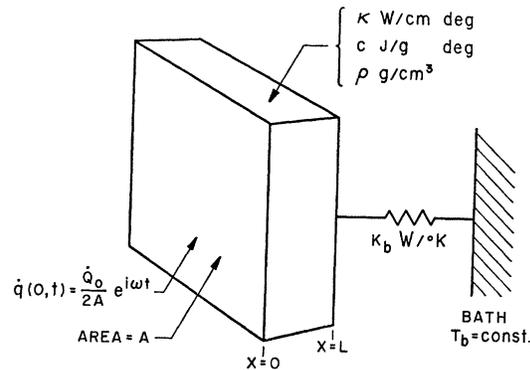


FIG. 2. Slab-shaped sample of thickness L thermally connected through the conductance K_b to a bath at $x=L$ and having a sinusoidal heat input per unit area $\dot{q}(0,t)$ at $x=0$.

By the application of the matrix method of expressing the temperature and heat flux at one point in terms of these quantities at another point,⁴ the oscillatory temperature dependence of the sample at the position $x=L$ is found to be

$$T_{ac}(L,t) = \dot{q}(0,t) \frac{A/K_b}{\cosh\theta + (\kappa K_b \theta / AL) \sinh\theta}, \quad (7)$$

where $\theta = kL(1+i)$.

Under the conditions that $\omega\tau_s = 2\kappa k^2 LA / K_b \gg 1$ and that the sample dimension L is small with respect to the characteristic thermal length $l_0(kL \ll 1)$, the temperature variation can be expressed as

$$\frac{T_{ac}(L,t)}{\dot{q}(0,t)} \approx \frac{L}{\kappa\theta^2} \left[\frac{AL}{\kappa K_b \theta^2} \left(1 + \frac{\theta^2}{2!} \right) + \frac{1}{\theta} \left(\frac{\theta^3}{3!} + \frac{\theta^5}{5!} \right) \right]^{-1}. \quad (8)$$

The expansion of $\cosh\theta$ does not need to be carried to as high an order as that of $\sinh\theta$ since $AL/\kappa K_b \theta^2 \ll 1$. Then

$$\begin{aligned} T_{ac}(L,t) &\approx \frac{L\dot{q}(0,t)}{\kappa\theta^2} \left[1 + \left(\frac{K_b}{2\kappa k^2 LA} \right)^2 + \frac{2k^4 L^4}{45} + \frac{2LK_b}{3A\kappa} \right]^{-1/2} \\ &= \frac{-i\dot{Q}_0 e^{i\omega t}}{2A\omega\rho cL} \left[1 + \left(\frac{K_b}{\omega\rho cLA} \right)^2 + \omega^2 \left(\frac{L^2}{(90)^{1/2}n} \right)^2 \right. \\ &\quad \left. + \frac{2LK_b}{3A\kappa} \right]^{-1/2}. \quad (9) \end{aligned}$$

Note that $\tau_s = c\rho LA / K_b$ and $C_s = \rho cLA$. If in the third term of Eq. (9) we make the substitution

$$\tau_{int} = L^2 / (90)^{1/2} n,$$

where τ_{int} can be associated with the time in which the sample attains thermal equilibrium, the magnitude of T_{ac} becomes

$$|T_{ac}(L,t)| \approx \frac{\dot{Q}_0}{2\omega C_s} \left[1 + \frac{1}{\omega^2 \tau_s^2} + \omega^2 \tau_{int}^2 + \frac{2LK_b}{3A\kappa} \right]^{-1/2}. \quad (10)$$

A comparison of this last expression with Eq. (5) shows that the finite thermal conductivity of the sample results in one correction term of the same form as that arising from the finite thermal conductances between the sample and the thermometer and heater. (This similarity extends to the phase correction of the temperature oscillation as well.) For the case of the sample with finite conductivity, however, there exists a frequency-independent correction term $2LK_b/3A\kappa = 2K_b/3K_s$ (K_s is the thermal conductance of the sample), which does not occur in the treatment of the sample with infinite conductivity. This correction is a geometric term in the sense that its magnitude depends upon the position in the system at which the tempera-

ture is calculated. The position along the sample chosen in this calculation is that at which correction is a maximum.

The ratio of the frequency-independent to frequency-dependent correction term in Eq. (10) is

$$(2LK_b/3A\kappa) / \omega^2 \tau_{int}^2 = 60n / \omega^2 L^2 \tau_s.$$

At low temperature where typical values for a sample could be $L=1$ cm, $\tau_s=1$ sec, and $n=10^4$ cm²/sec, this ratio is greater than unity for frequencies less than 100 Hz. Using these same values the frequency-independent correction

$$2LK_b/3A\kappa = 2K_b/3K_s = 2L^2/3n\tau_s$$

is less than 10^{-4} and can safely be neglected in the measurements discussed here. In the experiments at higher temperatures, such as those reported by Handler *et al.*,⁵ the thermal diffusivity of the sample may be poorer by many orders of magnitude, e.g., 10^{-1} cm²/sec, and consequently for the same value of τ_s the sample thickness must be decreased by several orders of magnitude to keep the correction small.

Since the ac temperature technique may be of use in studying the behavior of the heat capacity of a substance in the neighborhood of a phase transition, the dependence of the correction terms on specific heat is of interest, the thermal conductivity assumed to remain constant. The correction $2LK_b/3A\kappa$ does not change in the vicinity of a transition, whereas the frequency-dependent term $\omega^2 \tau_{int}^2 \propto cL^4$ varies as the specific heat for a given sample thickness. However, the increase of the correction with increasing specific heat can be more than offset by a decrease in the thickness.

MEASUREMENTS

A. Apparatus

A comparison of Eqs. (2), (5), and (10) shows that the amplitude of the ac temperature variation of a slab-shaped sample of finite thermal diffusivity coupled to a bath, heater, and thermometer with finite conductivities can be expressed in the form

$$T_{ac} = \frac{\dot{Q}_0}{2\omega C} \left[1 + \frac{1}{\omega^2 \tau_1^2} + \omega^2 \tau_2^2 + \frac{2K_b}{3K_s} \right]^{-1/2}, \quad (11)$$

where various time constants have been lumped into τ_2 , $\tau_2^2 = \tau_\theta^2 + \tau_k^2 + \tau_{int}^2$ and τ_1 is the sample to bath relaxation time τ_s of the previous section.

The results reported below were obtained by passing current at frequency $\frac{1}{2}\omega$ through a wire resistance and detecting synchronously the voltage variation at the frequency ω developed across a resistance thermometer through which a dc current was maintained. The thermometer consisted of a piece of Allen-Bradley carbon

⁴ H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, London, 1959), 2nd ed., pp. 110ff.

⁵ P. Handler, D. E. Mapother, and M. Rayl, *Phys. Rev. Letters* **19**, 356 (1967).

resistor ground down to a thickness of approximately 0.003 in. and glued to a thin slab of sapphire for backing. The sapphire was in turn glued to the sample as was the heater wire. The thermal link of the sample to the bath was affected by an appropriate length of copper wire or sapphire rod to obtain a sample-bath relaxation time of approximately one second. Since the calculated frequency-independent correction was extremely small, no careful consideration was paid to sample geometry as required by the discussion of the preceding section. The sample-bath relaxation time was experimentally determined by measuring the rate at which the dc temperature of the sample returned to equilibrium upon a change in the rate of heat input. With τ_1 known the value of τ_2 was deduced from measurements of the frequency dependence of T_{ac} . Experimentally measured values of τ_2 ranged from 0.5×10^{-3} to 5×10^{-3} sec, the variations arising primarily from the quality of the thermometer-to-sample bond. At the lowest values of τ_2 , τ_{int} made a significant contribution to the relaxation time.

A block diagram of the electronics³ used to make absolute heat-capacity measurements is given in Fig. 3. An oscillator at frequency $\frac{1}{2}\omega$ supplies current to the heater. Two other oscillators, one at frequency $\frac{1}{2}\omega$ and another at ω , synchronous with the heater source, supply stable voltages for an ac potentiometric voltmeter, which can be calibrated by an ac/dc thermal transfer standard to 2 parts in 10^4 . The lock-in amplifier is used as a null detector for absolute measurements and to provide a dc readout for recording changes in

heat capacity. The over-all electrical noise of the system is approximately 10^{-7} V per Hz bandwidth. This system can detect ac temperature variations of less than 10^{-7}°K at 1°K with the thermometers used.

B. Indium

To demonstrate the usefulness and accuracy of the ac temperature technique, a measurement was made of the heat capacity of indium. A 9-g sample of indium in the form of a 0.5-in. cylinder having a stated purity of 99.9999% and a measured resistivity ratio of 11 000 was studied in the liquid-helium-temperature region. A trace of the heat capacity of this sample as a function of magnetic field at 1.86°K appears in Fig. 4. The change in heat capacity in the vicinity of 175 G is due to the transition from the superconducting to the normal state. The increase in heat capacity with magnetic field is to be expected in the superconducting state below the critical field. The transition is smeared by poor sample geometry.

Absolute measurements of the heat capacity were made using an ac temperature modulation at 10 Hz of 4 mdeg peak-to-peak. The results of these measurements appear in Table I along with the results of previous measurements performed by traditional techniques. Relaxation time corrections [$\tau_1 = 2.5 \pm 0.1$ sec, $\tau_2 = (0.7 \pm 0.3)10^{-3}$ sec] were small and could be safely neglected in the calculations. The main source of error, aside from the thermometer calibration, resulted in the electronics; first, from the fact that the supply for the thermometer

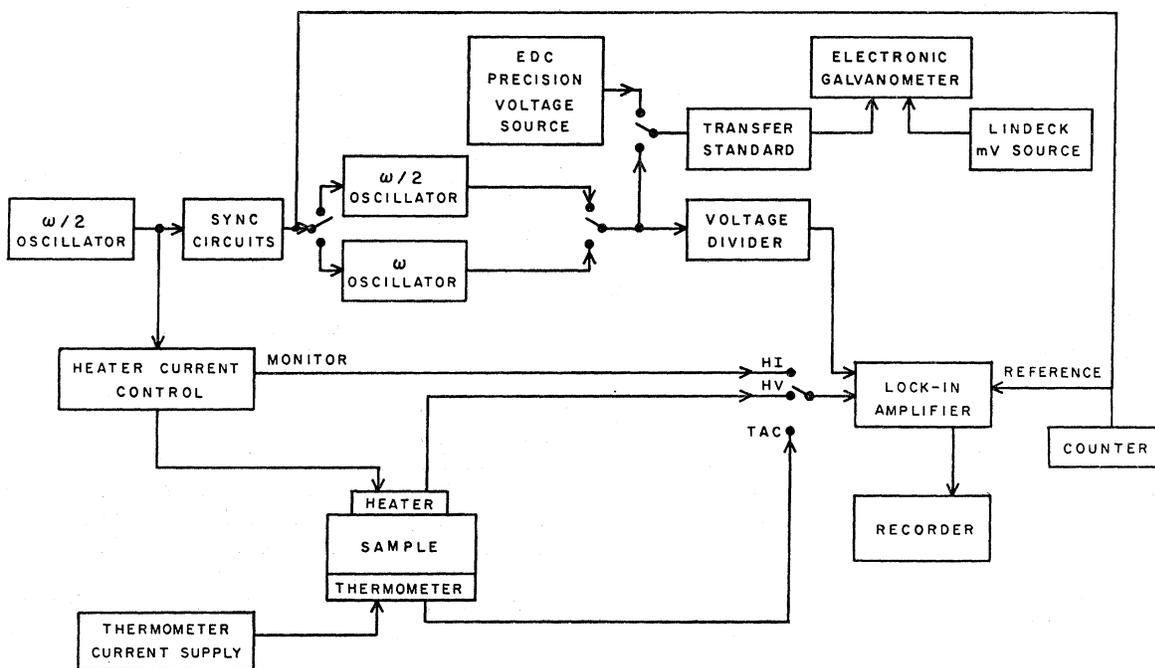


FIG. 3. Block diagram of the electronics used to measure absolute magnitude of the heat capacity.

was not a strictly constant current source, and secondly, from loading of the ac potentiometer by a guard circuit. The estimated limits of error at 1%, and as can be seen from the table, these measurements are in satisfactory agreement with previous work.

C. Beryllium

The heat capacity of a pure single-crystal metal will, at low temperature, exhibit quantum oscillations with magnetic field in a manner similar to the de Haas-van Alphen oscillations in the susceptibility. Both phenomena owe their origin to the variation of the free energy of the metal with the passage of the Landau levels through extrema of the Fermi surface. The calculated magnitude of the heat-capacity oscillations is quite small, well below the sensitivity of traditional techniques. To demonstrate the precision of the ac temperature method and its sensitivity to small changes in heat capacity, the heat capacity of beryllium has been studied as a function of magnetic field.

Measurements were performed on a single crystal beryllium sample in the form of a cylinder 0.07 in. in diameter, and 0.75 in. long. It weighed 82×10^{-3} g and had a resistivity ratio of 80. The axis of the cylinder was within $\pm 1^\circ$ of the crystallographic c axis, and it was in this direction that the magnetic field was applied.

The total heat capacity of the beryllium sample was less than 20×10^{-7} J/°K at 1.0°K. An absolute measurement of the heat capacity at 1.4°K yielded a result which agreed to within 8% with the data of Ahlers,⁶ who worked with a sample 10^8 times larger. The large error in these measurements could certainly be decreased considerably, for it arises entirely from uncertainties in the correction for the heat capacity of the addenda, which amounted to almost 40% of the total. These data indicate that, were it to prove necessary, absolute heat capacity measurements could be made with considerable accuracy on very small samples using the ac temperature technique.

The ability of the ac temperature technique to measure small changes in heat capacity is illustrated in

TABLE I. Specific heat^a of indium at 1.860°K.

	Normal state	Superconducting state	Error
ac temperature technique	12.86	12.59	± 0.15
Clement and Quinnett ^b	13.07	13.15	± 0.13
Bryant and Keesom ^c	13.48	12.82	± 0.26
O'Neal and Phillips ^d	12.96	12.78	± 0.13

^a In units of mJ/mole °K.

^b J. R. Clement and E. H. Quinnett, Phys. Rev. 92, 258 (1953).

^c C. A. Bryant and P. H. Keesom, Phys. Rev. 123, 491 (1961).

^d H. R. O'Neal and N. E. Phillips, Phys. Rev. 137, A748 (1965).

⁶ G. Ahlers, Phys. Rev. 145, 419 (1966).

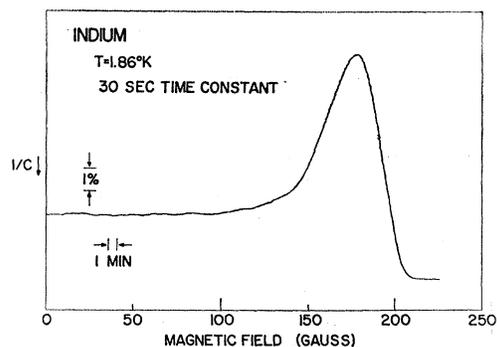


FIG. 4. The heat capacity of indium as a function of magnetic field.

Figs. 5 and 6, where the heat capacity of beryllium is recorded as a function of magnetic field. Quantum oscillations are clearly discernable. The noise level of the system and the precision of the measurement is illustrated by the retrace of the single oscillation in Fig. 6(b). The maximum deviation between the two traces is 0.04% and can be attributed entirely to the 3×10^{-4} °K instability in the bath temperature during the measurements. A reduction in the drift in the bath temperature would increase the precision accordingly since the noise associated with the electronics is at worst 0.01% referred to the signal.

The qualitative behavior of the field dependence of the heat capacity of beryllium can be understood in terms of the nature of the Fermi surface. The long period oscillation, one complete period of which is not shown in Fig. 5, results from the beat of the oscillations arising from the "hips" and "waists" of the electron cigars, which have almost equal de Haas-van Alphen

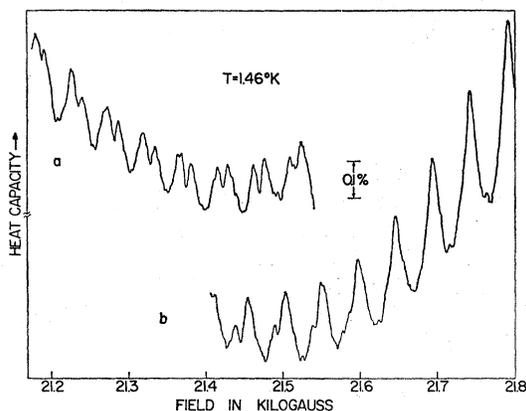


FIG. 5. The heat capacity of beryllium as a function of magnetic field. The field is parallel to the hexagonal axis. The 20-G shift of the two curves is a result of excessive time constant on the lock-in and slight hysteresis in the magnetic field for which no correction has been made. Trace (a) was taken with decreasing field, and trace (b) with increasing field. The lock-in time constant equals 10 sec and $dH/dt = 0.2$ G/sec. Part of the apparent slow field variation of the heat capacity is due to temperature drift. The large harmonic content of the high-frequency oscillations in the nodal region is similar to that observed in the magnetothermal effect.

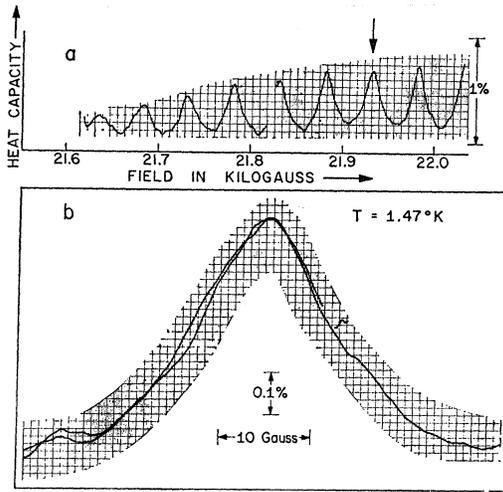


FIG. 6. The heat capacity of beryllium as a function of magnetic field. The difference in relative amplitudes of the slow and fast oscillations in Figs. 5 and 6 is due in part to time constant effects and to the slight change in temperature. The magnitude of the quantum oscillations is extremely temperature-dependent in this temperature region. Trace (b) is of the one quantum oscillation indicated by the arrow in trace (a). For (b) the lock-in time constant equals 30 sec and $dH/dt=0.04$ G/sec.

frequencies. The high-frequency oscillation having a period of approximately 50 G at 21 kG is the average of these two frequencies, while the resolved structure occurs because of the large harmonic content of the two oscillations. When the oscillations are out of phase at approximately 21.5 kG, they do not completely cancel, and appreciable harmonic content, particularly the second harmonic, is observable.

The dependence of the heat capacity of a metal upon the magnetic field can be calculated from the Lifshitz-Kosevich expression for the grand canonical potential. The calculation proceeds from the relation

$$C_{p,\mu,H} = -T \left(\frac{\partial^2 \Omega}{\partial T^2} \right)_{p,\mu,H}$$

The difference in heat capacity at constant pressure or volume and constant chemical potential or particle number is of no significance to these considerations. In the notation of McCombe and Seidel⁷ the field-dependent heat capacity arising from a single extremal cross-sectional area of the Fermi surface [area $\mathcal{Q}(E_f)$] may be written as

$$\Delta C = -H^{3/2} \sum_{r=1} r^{-3/2} P_r \exp(-rX/T_H) \times \cos \left(\frac{2\pi r f}{H} - 2\pi r \gamma \mp \frac{1}{4} \pi \right) \left\{ \frac{2rT \cosh rT/T_H}{T_H \sinh^2 rT/T_H} - \left(\frac{rT}{T_H} \right)^2 \frac{1 + \cosh^2 rT/T_H}{\sinh^3 rT/T_H} \right\}. \quad (12)$$

⁷ B. McCombe and G. Seidel, Phys. Rev. **155**, 633 (1967).

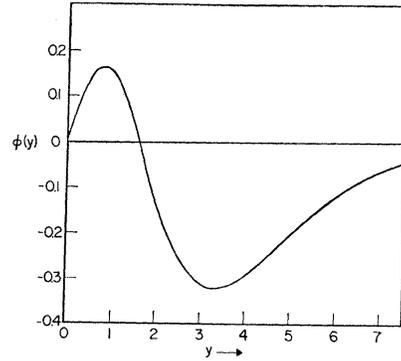


FIG. 7. A plot of the function $\phi(y) = 2y(\cosh y/\sinh^2 y) - y^2[(1 + \cosh^2 y)/\sinh^3 y]$.

In this expression

$$P_r = -2V k_B (e/hc)^{3/2} \left| \frac{\partial^2 \mathcal{Q}(E_f)}{\partial k_z^2} \right|_m^{-1/2} \cos(r\pi g m_c^*/2m_0);$$

$T_H = \beta^* H / 2\pi^2 k_B$, X is the scattering or "Dingle" temperature, $f = \hbar c \mathcal{Q}_m(E_f) / 2\pi e$ is the de Haas-van Alphen frequency, $\beta^* = e\hbar / m_c^* c$ is twice the effective Bohr magneton, where m_c^* is the cyclotron effective mass, g is the effective g value, m_0 is the free-electron mass, γ is a phase constant which may have any value between 0 and $\frac{1}{2}$ depending on the dispersion relation $E(k)$, and the other symbols have their usual meaning.

The temperature dependence of the r th harmonic of the heat capacity at constant field is contained in the function

$$\phi(y) = 2y \frac{\cosh y}{\sinh^2 y} - y^2 \frac{1 + \cosh^2 y}{\sinh^3 y}, \quad (13)$$

where $y = rT/T_H$. This function is plotted in Fig. 7. The oscillatory field-dependent heat capacity vanishes at $T=0^\circ\text{K}$ as it must be the Nernst theorem, and it also vanishes at high temperatures where the thermal energy is much larger than the separation between the Landau levels. The intermediate zero arises from an averaging of the oscillatory density of states over the Fermi distribution of occupied and unoccupied levels.

The magnitude of the quantum oscillations in the heat capacity of a typical metal calculated from Eq. (12) is about one part in 10^4 of the ordinary Sommerfeld electronic heat capacity at low temperatures. For beryllium the curvature of the electron cigar Fermi surface is very small and the normal heat capacity is relatively low. Consequently, with the magnetic field parallel to the hexagonal axis at 22 kG and 1.5°K the calculated value for the relative variation of the heat capacity due to the hip and waist extremals is several percent of the total heat capacity. This estimate from Eq. (12) is of little value, however, because of the added complication of the magnetic interaction problem in

beryllium,⁸ and another method is necessary to predict the magnitude of the quantum oscillations in the heat capacity of this metal.

Adiabatic temperature oscillations—the change in temperature of a metal as the magnetic field is varied adiabatically—can be used to estimate the amplitude of the oscillations of the heat capacity ΔC by the relation

$$\frac{(\Delta C)_T}{C} \approx -\frac{\partial}{\partial T}(\Delta T)_S.$$

From the magnetothermal measurements of Halloran⁸ the estimated peak-to-peak amplitude of the high-frequency heat-capacity oscillations ranges from 0.25 to 0.4% while the estimate for the slow oscillation is less than 1%. Considering the very large uncertainties in these estimates from the published data, the agreement with these measurements is considered satisfactory.

⁸ See J. H. Condon, *Phys. Rev.* **145**, 526 (1966).

CONCLUSIONS

An ac temperature technique for measuring heat capacities has been developed which possesses several advantages: (1) The sample may be coupled thermally to a bath; (2) the method is a steady-state measurement; (3) changes in heat capacity with some experimentally variable parameter may be recorded directly; (4) extremely small heat capacities may be measured with accuracy; and (5) the method possesses a precision an order of magnitude better than existing techniques. Heat-capacity measurements are reported that have an absolute accuracy of 1%, and no serious problem appears to exist in improving on this figure to the limit imposed by the accuracy of the thermometer calibration. The sensitivity of the present measurements to changes in heat capacity is 0.04% with a lock-in time constant of 30 sec. This precision was limited entirely by thermal noise which can easily be reduced by an order of magnitude with improved dc temperature regulation.

Energy Bands and Fermi Surface of Scandium*

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The energy bands for hexagonal close-packed scandium have been calculated using the augmented-plane-wave method. From these calculations, the Fermi surface, density of states at the Fermi energy, and electronic specific-heat coefficient were determined. An important feature of the Fermi surface is the existence of large relatively parallel portions perpendicular to the *c* axis. This feature has also been reported for Y, Lu, Er, and Dy and in the present case can be related to the wave vector of the periodic moment arrangement occurring in alloys of Sc and Tb. Comparisons with the limited number of experimental data are made. There is no indication that the electronic specific-heat coefficient enhancement (due to electron-phonon and electron-electron interactions) is significantly greater for Sc than for Y and the heavy rare earths.

I. INTRODUCTION

CALCULATIONS have been made of the electronic energy bands and Fermi surface of Sc using the augmented-plane-wave (APW) method proposed by Slater¹ and reviewed by Loucks.² The atomic structure of Sc is $3d4s^2$, and the hexagonal close-packed crystal structure is considered here.³ In the next section some

of the details involved in the APW calculation are described. This is followed by a section in which the results are presented and compared with available experimental data¹ and with the results of Altmann and Bradley⁴ who used the cellular method. The similarities between the present results and those presented by Loucks⁵ for Y and by Keeton and Loucks⁶ for Lu, Er, and Dy are also pointed out.

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³ For previous applications of the APW method to the iron transition metals and hcp structures see, for example, L. F. Mattheiss, *Phys. Rev.* **134**, A970 (1964); A. J. Freeman, J. O. Dimmock, and R. E. Watson, *Quantum Theory of Atoms, Molecules and the Solid State* (Academic Press Inc., New York, 1966),

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⁶ S. C. Keeton and T. L. Loucks, *Phys. Rev.* (to be published).