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THE HEAT CAPACITY OF BISMUTH AS A FUNCTION OF PRESSURE AND TEMPERATURE

Berardo Jurado
(Ph. D. thesis)

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THE HEAT CAPACITY OF BISMUTH AS A FUNCTION OF PRESSURE AND TEMPERATURE

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THE HEAT CAPACITY OF BISMUTH AS A FUNCTION
OF PRESSURE AND TEMPERATURE

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ABSTRACT

The heat capacity of bismuth is measured as a function of pressure and temperature in the two high pressure polymorphic phases of Bi III and Bi V. An isotherm at room temperature (30 to 90 Kbar) and two isobars at 52 and 95 Kbar (90 to 290°K) are obtained. In Bi III the pressure data show a 13% increase of $C_p$ from 30 to 40 Kbar and a 12% decrease from 40 to 80 Kbar. A 15% increase of $C_p$ in the III-V transition at 88 Kbar is in agreement with published results. The temperature data in both phases show a strong linear behavior up to room temperature. A rough upper limit of 150°K for the Debye temperature $\theta$ of Bi III and of 200°K for Bi V can be established. A discussion of the results is given.
I. INTRODUCTION

The heat capacity of a substance is one of the most fundamental thermodynamic properties. As with any other physical property, much more is known, both theoretically and experimentally about its behavior as a function of temperature than of pressure. However, pressure (or volume) is just as important a thermodynamic variable as temperature in the understanding of physical phenomena and theories. Most physical scientists feel more at ease in knowing or predicting the general trend of many physical properties with temperature than with pressure.

The explanation lies in the simple fact that in general, the measurement of a physical property as a function of pressure is much more difficult to perform than a similar experiment at room pressure due to:

1) The restricted size of the samples required by small volume sample cells needed for the concentration of large forces over a small area;

2) The difficulty of introducing measuring probes into the sample and at the same time maintaining high pressure;

3) In the case of thermodynamic measurements such as heat capacity and enthalpy of transition, the large heat capacities and thermal conductivities of the metal alloys and steels that transmit the load of the hydraulic press render conventional calorimetric measurements impossible since the small heat effect experienced by the sample would be completely swamped by the surrounding medium. All conventional calorimetric techniques need to subtract the heat capacity of the calorimeter.
which in this case would be many orders of magnitude greater than that of the sample.

The interest in heat capacity measurements arises partly from the fact that all thermodynamic functions (\(E, H, S, G, A\)) can be derived from a knowledge of \(C_p\) (or \(C_v\)) and \(V\) in terms of two independent variables such as \(P\) and \(T\). A knowledge of the function \(G\), for example, for each of the reactants of a chemical reaction would make it possible to predict whether a thermodynamically unfavorable reaction (\(\Delta G^0 > 0\)) at room pressure and temperature (\(P = 1\) atm, \(T = 298^\circ K\)) could become favorable (\(\Delta G < 0\)) at a high pressure \(P\) and temperature \(T\). In that case, we would like to find the conditions of \(T\) and \(P\) such that

\[
\int_{298}^{T} \int_{1}^{P} d\Delta G(T,P) > \Delta G^0
\]

Heat capacity measurements are also important because of the relationship between \(C_p\) and the equation of state of a substance \(V = V(P,T)\). This relationship is developed in the theory from a strictly thermodynamic (that is, macroscopic) viewpoint, and consequently does not result in the development of an analytical function. In the case of a solid, a very simplified treatment considering only the quantized vibrational energies of a system of harmonic oscillators can yield a partition function \(Z\) from which the Mie-Gruneisen equation of state can be derived with additional assumptions.\(^1\) The Gruneisen constant \(\gamma = -\frac{\partial \ln \Theta}{\partial \ln V}\), the central parameter in this equation, was obtained by Raimondi\(^2\) for Al and Yee\(^3\) for Fe from high pressure heat capacity work. Since the heat capacity
is the temperature derivative of the energy or enthalpy, one can learn a

great deal about the nature of a solid polymorphic transformation by
measurements over a wide range of temperature and pressure before, during
(if possible), and after a transition. In combination with crystal struc-
ture data and electronic properties one can learn whether the measurements
are consistent with a mere change of crystal structure, or with a profound
change in the electronic structure, or whether there is an order/disorder
phenomenon (spin or lattice type), or perhaps different combinations of
these.

The microsecond pulsing technique used in my work was developed by
Albert Yee after significant improvement of Stark's apparatus. This
technique has been demonstrated to be quite successful by Yee and Chen.
On iron, at room pressure, they have reproduced calorimetric measurements
from 85°K to 1100°K including the \( \lambda \) transformation to within 2%.

A significant improvement in the recording of the pulse going from
a Polaroid picture of the oscilloscope trace to modern digital recorders
has allowed an in-depth analysis of the conductive heat losses.

Within the last year of 1973 high pressure heat capacity work has
been reported in the literature on copper and on bismuth at room tem-
perature up to 100 Kbar using electrical pulsing techniques. In none of
these works is there a satisfactory treatment of the heat leakage problem
as developed here. They still use zero-time limiting expressions of the
type first used by Stark in 1967.

Bismuth has been the subject of my experiments and a source of
continuous fascination. It is a very unique element in its properties
at room pressure and at high pressures. Five solid polymorphic phases
and the liquid phase can be observed from 0 to 100 Kbar at temperatures less than 300°C. By varying $P$ and $T$ within this domain one can make bismuth a semi-metal, a semi-conductor, an insulator, and a metal showing superconductivity.

In this work no equation of state is obtained for bismuth of either an empirical or semi-empirical nature like the Mie-Gruneisen because there are only two isobars, each one in a different phase (Bi III and Bi V) connected by room temperature $C_p$ measurements. Besides, the Mie-Gruneisen equation of state may not be applicable to these two phases because there could be significant electronic contributions to the total energy as will be discussed in the results.
II. THEORY

A. The Equation of State and Heat Capacity

A great deal of interest in \( C_p \) (or \( C_v \)) lies in its relation to the "equation of state" \( V = V(P,T) \) of a substance. This relation, by the way, need not be defined in terms of an analytical equation such as \( PV = nRT \) for an ideal gas where the dependence of \( V \) on \( P \) and \( T \) can be explicitly stated. It can also be expressed in the form of a table where for a given \( P \) and \( T \) one can obtain \( V \).

From the basic thermodynamic identity:

\[
\left( \frac{\partial C_p}{\partial P} \right)_T = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P
\]  

(1)

We can proceed to integrate both sides of the equation twice with respect to temperature:

\[
V_{P,T_2} = V_{P,T_1} + \left( \frac{\partial V}{\partial T} \right)_{P,T_1} \cdot (T_2 - T_1) - \int_{T_1}^{T_2} \left[ \int_{T_1}^{T} \frac{1}{T} \frac{\partial C_p}{\partial P} \left( P,T_1 \right) dT \right] dT
\]  

(2)

Equation (2) tells us that, for a given pressure \( P \), we can obtain \( V \) as a function of \( T \) if we know the volume \( V_{P,T_1} \), the thermal expansion \( (\partial V/\partial T)_{P,T_1} \) at a reference temperature \( T_1 \), and we also need to know the behavior of \( C_p \) with \( P \) and \( T \) so we can find the pressure derivative \( (\partial C_p/\partial P)_{P,T} \) needed to compute the right hand integral.

We can experimentally obtain a whole series of \( V, T \) isobars. Figure 1 gives these isobars for a typical solid. Provided that we know the compressibility along an isotherm \( T_1 \), as well as the thermal expansion
Fig. 1. $V, T$ isobars for a typical solid.
along that isotherm, then a complete mapping of \( V = V(P,T) \) can be obtained within a given area of \( P,T \) space (i.e., a polymorphic phase of a solid) provided that \( C_p(P,T) \) is completely known experimentally.

Things are simpler, at least in theory, in the case of a crystalline solid since the Third Law of Thermodynamics requires that \( S = 0 \) at \( 0^\circ K \) independently of the pressure. Thus,

\[
\left( \frac{\partial V}{\partial T} \right)_P = -\left( \frac{\partial S}{\partial P} \right)_T = 0 \quad \text{at} \quad T = 0^\circ K
\] (3)

For the polymorphic phase of a crystalline solid that extends to \( 0^\circ K \) then we only need the compressibility curve at absolute zero and the \( C_p = C_p(P,T) \) data to get the equation of state within the \( P,T \) domain of the phase.

B. Effect of Pressure on \( C_p \)

As can be seen from Eq. (1), the effect of pressure on \( C_p \) is determined by the curvature of the \( V-T \) curve. As depicted in Fig. 1 the volume of a typical solid will increase approximately linearly at high temperatures. We also know that \( \left( \frac{\partial C_p}{\partial P} \right)_0 = 0 \) at \( 0^\circ K \) since \( C_p \) is zero regardless of the pressure. Thus, the second derivative \( \frac{d^2V}{dT^2} \) will be positive and will approach zero at low and high temperatures going through a maximum somewhere in between. For most solids, then, the effect of pressure will be to decrease \( C_p \), the effect being the greatest at low temperatures. The greater the pressure becomes, the smaller the effect on \( C_p \) since the curvature becomes smaller at higher pressures.

It is possible for \( C_p \) to increase with pressure whenever the curvature of \( V \) is concave as it is in water near \( 4^\circ C \).
Another way of looking at the effect of pressure on the heat capacity of solids is to break it down into its basic components:

\[ C_v = C_v^L + C_v^e + C_v^m \]  \(\text{(4)}\)

Here, \( C_v^L, C_v^e, \) and \( C_v^m \) are the lattice, electronic and magnetic contributions, respectively. The lattice terms would include the vibrational heat capacity and terms resulting from geometrical imperfections of the crystal.

The temperature behavior of the lattice heat capacity \( C_v^L \) is quite adequately described by the Debye theory. This treatment can be found in any standard solid state physics textbook such as Kittel. An excellent review article on the lattice theories of heat capacity by De Launay describes the more rigorous treatment of Born and von Karman. In the Debye theory an expression for the vibrational energy is obtained in terms of the sum of the energies of all the normal modes of the crystal:

\[ E = \int_0^{\omega_D} \frac{\hbar \omega \mathcal{S}(\omega)}{\hbar \omega/kT} e^{-\frac{\hbar \omega}{kT}} \]  \(\text{(5)}\)

where \( \frac{\hbar \omega}{kT} e^{-\frac{\hbar \omega}{kT}} - 1 \) is the average energy in each normal mode

\( \mathcal{S}(\omega) \) is the phonon density of states

\( \omega_D \) is the maximum "Debye" frequency given by

\[ \int_0^{\omega_D} \mathcal{S}(\omega) = 3N - 6 \]  \(\text{(6)}\)

where \( 3N - 6 \) is the total number of vibrational degrees of freedom of
the crystal.

Several simplifying assumptions are made by the Debye theory to obtain the density of states \( \Omega(\omega) \) such as the substitution of a sphere (in k-space) for the true Brillouin zone, and regarding the velocity of sound \( v_s \) as independent of \( \omega \). A final expression is obtained where \( \Omega(\omega) \propto \omega^2 \). The expression for \( E \) becomes

\[
E = 9NkT \left( \frac{T^3}{\theta^3} \right) \int_0^{\chi_D} \frac{x^3}{e^x - 1} \quad \text{where} \quad \chi = \frac{\hbar \omega}{kT}
\]

In order to obtain \( C_v \), Eq. (7) is differentiated with respect to temperature

\[
C_v = \frac{dE}{dT} = 9Nk \left( \frac{T^3}{\theta^3} \right) \int_0^{\chi_D} \frac{x^4 e^x}{(e^x - 1)^2}
\]

Equation (8) is a one parameter equation, where \( C_v(T) \) is completely defined by \( \theta = \hbar \omega_0 / k \). A plot of \( C_v \) vs. \( (T/\theta) \) is given in Fig. 2.

Equation (7) predicts the correct \( T^3 \) dependence of \( C_v \) at low temperatures and the classical limit of \( 3R \) at high temperatures.

We can also use the Debye model to predict the effect of pressure on \( C_v \). The argument is as follows: With pressure all the frequencies in the lattice increase due to the stiffening caused by the repulsive potential of the atomic cores. The maximum frequency will also increase, as well as \( \theta \). When \( \theta \) increases for a given temperature \( T \), the ratio \( T/\theta \) will decrease and we move to the left on Fig. 2 to a lower value of
Fig. 2. Debye model of the lattice heat capacity.
Thus, P causes $C_v$ to decrease. The same applies to $C_p$ since the difference $C_p - C_v = VT\alpha^2/\beta$, where $\alpha$ is the thermal expansion, and $\beta$ the compressibility, is generally small for solids at low temperatures.

We can also observe that the effect of pressure on $C_v$ is much greater for $T < \theta$. At a temperature of $T > \theta$, $C_v$ is within less than 5% of the classical limit so we expect a very small effect. Raimondi in our lab measured the change in $\theta$ of Al with pressure from resistance measurements by fitting the data to the Bloch-Gruneisen resistance equation. He found a change in $\theta$ from 395°K at room pressure to 485°K at 100 Kbar. This corresponds to a 4.3% decrease in the heat capacity of Al at room temperature, and a 24% decrease at $T = 100^\circ$K.

The electrons also contribute to the total heat capacity, but not to any appreciable extent at room temperature since, in general, the heat capacity of the metallic elements is only slightly greater than that of non-metallic elements.

It can be shown that the low $T$ limit of the electronic heat capacity $C_v^e$ is given by

$$C_v^e = \frac{\pi^2}{3} \mathcal{D}(\epsilon_F) k^2 T \quad \text{or} \quad C_v^e = \gamma T$$

(9)

where $\mathcal{D}(\epsilon_F)$ is the density of electronic states at the Fermi surface. From the free electron theory $\mathcal{D}(\epsilon_F)$ can be calculated and $C_v^e$ becomes

$$C_v^e = \frac{\pi^2}{2} N_k \frac{T}{T_F}$$

(10)

where $T_F$ is the Fermi temperature of the metal. A typical $T_F$ is on
the order of $3 \times 10^4 \text{°K}$, so we find $C_v^e \approx 2\%$ of $3R$ at room temperature.

The difference between the heat capacity of electrons and of phonons lies in the fact that electrons are "fermions", subject to the Pauli exclusion principle and Fermi-Dirac statistics whereas phonons are "bosons" following Bose-Einstein statistics. Thus, only the electrons at the tail of the Fermi distribution $F(\varepsilon)$ contribute to the heat capacity at low temperatures. A graph of $F(\varepsilon)$ vs. $\varepsilon$ where

$$F(\varepsilon) = \frac{1}{(e - \mu)/kT + 1} \tag{11}$$

and $\mu$ is the chemical potential is given in Fig. 3 for $kT = \frac{1}{2}\mu$ and $kT = 0$. (Ref. 8)

At very high temperatures $C_v^e$ for a free electron gas is given by

$$C_v^e = \frac{3}{2} n_0 R \left[ 1 - \frac{1}{6(2\pi)^{3/2}} \left( 1 - \frac{1}{6(2\pi)^{3/2}} \left( \frac{T}{T_F} \right)^{3/2} \right) \right] \tag{12}$$

where $n_0$ is the number of free electrons per atom.

We can see that as $T \to \infty$, $C_v^e \to \frac{3}{2} n_0 R$ giving the classical value of $3/2R$ per mole of electrons. This is what we expect since at these high temperatures each electron occupies one electronic state which can accommodate two electrons of spin $1/2$ and $-1/2$. Thus all electrons are available for thermal excitation and can contribute to the heat capacity in the same way as a boson. Of course, the metal will melt at a temperature $T < T_F$ so this classical limit is never reached for electrons. A plot of $C_v^e$ vs. $T/T_F$ is given in Fig. 4.10
Fig. 3. Fermi-Dirac distribution function.
Fig. 4. Heat capacity per electron of an electron gas.
We can predict the effect with pressure on $C^e_v$ by making an analogy between the electrons in a metal and a particle in a three-dimensional box. As the dimensions of the box are reduced by pressure we expect the spacing between the quantized energy levels to increase and so $C^e_v$ will decrease. By the same token, a compression of the three-dimensional lattice in real space corresponds to an expansion of the reciprocal lattice in $k$-space and a consequent reduction in the density of electronic states. This leads, according to Eq. (9), to a decrease in $C^e_v$.

The term $C^m_v$ is important for ferromagnets and antiferromagnets in the vicinity of the Curie or Neel temperature where it shows as a $\lambda$-point in the heat capacity. $C^m_v$ can be obtained by subtracting the lattice and electronic contributions. $C^m_v$ is shown for iron in Fig. 5. The large contributions are due to the temperature effects on the disalignment of the spins which interact by the "internal or molecular field." At the Curie point $T_c$ this spontaneous magnetization or long range spin order is lost and the substance becomes an ordinary paramagnet.

Ferromagnetism is only observed in elements or alloys of the transition metals with incomplete $d$ or $f$ bands. The effect of pressure on $C^m_v$ is not clearly understood, but it can be reduced to the effect of $P$ on the Curie temperature. For a temperature $T < T_c$ if $dT_c/dP < 0$ then $C^m_v$ will increase but if $dT_c/dP > 0$ it will decrease. For $T > T_c$ the opposite will be true. For iron Leger et al. found $dT_c/dP$ to be zero up to 17 Kbar and for gadolinium Phillips measured $dT_c/dP = -1.5^oK/Kbar.$
Fig. 5. Magnetic heat capacity of iron.
III. HEAT CAPACITY ANALYSIS

The treatment necessary to obtain the heat capacity and the heat leakage constant from the experimental data are developed in this section.

The heat capacity of a substance is defined as the limiting ratio of the heat absorbed to its temperature rise. For a system which can do only pressure-volume work the amount of heat absorbed is a function of the state of that system only under the conditions of either constant volume \( (Q = \Delta E) \) or constant pressure \( (Q = \Delta H) \). Thus, there are two types of heat capacity, \( C_v \) and \( C_p \). For high pressure work on solids it is much easier to keep the pressure rather than the volume constant, and so \( C_p \) is the property measured.

\[
C_p = \left( \frac{\partial H}{\partial T} \right)_p 
\]

(13)

Now, the amount of heat that goes into the metal is equal to the total heat input minus the amount leaked out to the surroundings.

\[
dH = dH_{\text{in}} - dH_{\text{L}} 
\]

(14)

where \( dH_{\text{in}} = \) total heat input

\( dH_{\text{L}} = \) amount of heat leaked

For an electrical pulse of constant current:

\[
dH_{\text{in}} = I^2Rdt 
\]

(15)

The total heat input is equal to the power times the time differential. A functional dependence of \( dH_{\text{L}} \) on temperature can be obtained if it is
assumed that conduction is the main mode of heat loss. This assumption is valid for the wire under pressure in intimate contact with the pressure medium. Then we can use Newton's law of cooling which says that the time rate of heat loss of a hot body is proportional to the temperature difference between the body and its surroundings:

\[ \frac{dH}{dt} = K(T - T_a)dt \]  

where \( K \) is the heat leakage constant and \( T_a \) is the ambient temperature. Thus,

\[ dH = I^2Rdt - K(T - T_a)dt \]  

and

\[ C_p = \frac{I^2R}{(\frac{\partial T}{\partial t})_p} - \frac{K(T - T_a)}{(\frac{\partial T}{\partial t})_p} \]  

We can express temperature \( T \) in terms of the resistance of the wire \( R \) which can be easily measured by monitoring the voltage drop \( E = IR \):

\[ \left( \frac{\partial T}{\partial t} \right)_p = \left( \frac{\partial T}{\partial R} \right)_p \left( \frac{\partial R}{\partial E} \right)_p \left( \frac{\partial E}{\partial t} \right)_p = \frac{1}{IR'} \left( \frac{\partial E}{\partial t} \right)_p \]  

where \( R' \) is the thermal coefficient of the resistance.

Upon substitution on Eq. (18) we get

\[ C_p = \frac{I^3R'R}{(\frac{\partial E}{\partial t})_p} - \frac{IR'K(T - T_a)}{(\frac{\partial E}{\partial t})_p} \]  

(20)
If we assume that the resistance $R$ is a linear function of temperature, which is reasonable since a typical increase of the temperature due to the pulse is only $3^\circ C$, then

$$R = R_0 + R'(T - T_a) \tag{21}$$

where $R_0$ is the initial resistance of the wire at a temperature $T = T_a$ before the application of the pulse. Using Ohm's Law

$$E = E_0 + IR'(T - T_a) \tag{22}$$

Further substitution gives us

$$C_p = \frac{I^2RR'}{dE/dt} - \frac{K(E - E_0)}{dE/dt} \tag{23}$$

Here, in the last expression we do not explicitly write the constancy of the pressure although it must be kept in mind.

In the limiting case, when $t \to 0$ and $E \to E_0$, then

$$C_p = \frac{I^2R_0R'}{(dE/dt)_0} \tag{24}$$

Equation (24) can be used to obtain $C_p$ only if there is a region well beyond rise time effects (in practice $> 200 \mu s$) where $E$ remains linear with $t$. Since we have assumed linearity of the resistance with temperature this is the region over which $T$ would also increase linearly with time.
However, the only metal studied in our lab which shows a linear behavior with time is iron. Iron shows a relatively linear region of $E$ vs. $t$ for about one millisecond. In the case of bismuth, the subject of my studies, and of aluminum which was done by Dr. Chen we have found significant departures from linearity which make it impossible to find $C_p$ by measurement of the limiting slope and use of Eq. (24). This departure from linearity is due to a significant fraction of heat leakage from the wire which is at a temperature higher than its surroundings. In order to understand the factors that influence the curvature of the pulse I have constructed a model from some simple assumptions that enable me to get an analytic expression for temperature $T$ as a function of time $t$. After discussion of the curvature problem I shall then proceed to discuss how we can use Eq. (23) which takes into consideration heat losses in order to obtain $C_p$ and $K$.

Rewriting Eq. (18) we obtain

$$C_p = \frac{\int [I^2 R - K(T - T_a)] \, dt}{dT}$$

(25)

Separating variables enables us to express this equation in integral form:

$$\int_{T_a}^{T} \frac{dT}{I^2 R - K(T - T_a)} = \int_{0}^{t} \frac{dt}{C_p}$$

(26)

In order to integrate this expression I will assume

$$\begin{cases} R = R_0 + R'(T - T_a) & \text{linearity of } R \\ C_p, K, R', \text{ and } T_a & \text{are independent of temperature} \end{cases}$$
For the purposes of the model, $R\,'$ can be either positive (normal metal) or negative (semiconductor).

Substituting for $R$ we get

\[
\int_{T_a}^{T} \frac{dT}{I^2(R_0 + R\,'(T - T_a)) - K(T - T_a)} = \frac{t}{C_p}
\]

\[
\frac{1}{I^2R\,' - K} \ln \left[ I^2R_0 + (I^2R\,' - K)(T - T_a) \right]_{T_a}^T = \frac{t}{C_p}
\]

\[
\ln \frac{I^2R_0 + (I^2R\,' - K)(T - T_a)}{I^2R_0} = (I^2R\,' - K) \frac{t}{C_p}
\]

\[
1 + \left( \frac{I^2R\,' - K}{I^2R_0} \right)(T - T_a) = e^{(I^2R\,' - K)t/C_p}
\]

\[
T - T_a = \left[ e^{(I^2R\,' - K)t/C_p} - 1 \right] \frac{I^2R_0}{(I^2R\,' - K)}
\]

A plot of $T - T_a$ as a function of time is given in Fig. 6a for two distinct cases:

1. $(I^2R\,' - K) < 0$

2. $(I^2R\,' - K) > 0$

Since $K$ is defined as a positive constant, case 1. corresponds to the case where either $R\,'$ is negative (such as a semiconductor) or for a normal metal when the heat leakage constant $K$ is greater than $I^2R\,'$. Case 2. would apply, for example, to a normal metal (that is $R\,' > 0$) in a vacuum so that heat leakage due to conduction would be very small and
(a) Plot of $T - T_a$ vs $t$ for case (1) $(I^2R' - K) < 0$, and case (2) $(I^2R' - K) > 0$.

(b) $dT/dt$ vs $t$

Fig. 6
K = 0. I am excluding from my model the possibility of energy losses due to radiation.

Case 1. is by far the most common case, always being observed in systems at high pressure, or even when the medium is air at room pressure because of the conductive heat losses. Case 2. has never been observed and it is only mentioned here because it is a mathematical alternative although not in general physically existing.

It is interesting to explore Eq. (27), case 1. in the limits when t → 0 and t → ∞. As t → 0 the exponential can be expanded in a power series neglecting terms of a higher order than one. Thus T approaches T_a linearly as t → 0. As t → ∞ since the coefficient of the exponent is negative we find that the exponential drops to zero. Thus, a maximum temperature of value

\[ T_{\text{max}} = \frac{I^2 R_0}{(I^2 R' - K)} \]  

is approached asymptotically. This temperature corresponds to a steady state condition when all the heat input leaks to the surroundings.

We can also find an expression for the slope of the temperature expression which is the following

\[ \frac{dT}{dt} = \left( I^2 R' - K \right) t / C_p \]

\[ \frac{dT}{dt} \text{ at } t = 0 \]

A plot of Eq. (29) is shown in Fig. 6b.

The time \( \tau_{1/2} \) at which the value of the slope is half of the
limiting value is from Eq. (29):

\[ \tau_{1/2} = \frac{C_p}{\ln 2} \ln 2 \]  

(30)

This expression can be further simplified since experimentally \( I^2R' \) is much smaller than \( K \), on the order of 1%. Thus,

\[ \tau_{1/2} = \frac{C_p}{k} \ln 2 \]  

(31)

This time constant \( \tau_{1/2} \) can also be shown to be the time at which 50% of the heat leaks out. The greater \( \tau_{1/2} \) is, the longer the time region over which the pulse will be linear. What are the properties that determine \( \tau_{1/2} \) for a metal wire? They will be those that determine its heat capacity per unit volume \( C_p/V \) and the heat leakage constant per unit volume \( K/V \). At room temperature \( C_p/V \) for an element is determined mainly by its position in the periodic table and its density, provided, of course, that the atomic heat capacity is at its classical value of 3R. The following is a table that compares the volume heat capacities for various elements as well as their resistivities.

<table>
<thead>
<tr>
<th></th>
<th>( C_p ) (cal/cc)</th>
<th>( \rho ) (( \mu \text{Ohm-cm} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.58</td>
<td>2.6</td>
</tr>
<tr>
<td>Fe</td>
<td>0.86</td>
<td>10</td>
</tr>
<tr>
<td>Bi</td>
<td>0.29</td>
<td>110</td>
</tr>
<tr>
<td>Pt</td>
<td>0.67</td>
<td>10</td>
</tr>
</tbody>
</table>

It can be seen that iron has a high and bismuth a low volume heat capacity.
K/V will be determined mainly by two factors: the surface to volume ratio of the wire which is inversely proportional to its diameter, and by the heat conductivity of the pressure medium, in this case AgCl. Since metals are so much better heat conductors than dielectrics their thermal conductivities will not influence the value of K to any considerable extent. Thus the best combination involves a high \( C_p/V \) such as in iron and as large a wire diameter as possible in accordance with the dimensions of the pressure cell. Wires of up to 0.008 in. diameter can be used in our small sample cells.

Another important factor concerns the resistivity of the wire. If it is very small the magnitude of the pulse signals will be small with a consequent large noise/signal ratio. Thus, even though aluminum has a favorable \( C_p/V \), its resistivity is so low that one needs to use a very thin wire (0.001 in. diameter instead of the more common 0.005 in.) to increase the resistance. Of course these thin wires have a very large surface to volume ratio, and thus a short time constant \( \tau \) and great curvature in addition to the noise problem. If, on the other hand, the resistivity is too high, as in Bi, other problems stem resulting from the limits on the voltage drop through the sample (\( IR_s \leq 1 \) volt) imposed by the different electronic amplifiers necessary at the present state of the art. Since it is necessary to keep the sample load to \( \leq 1 \) volt, this implies that the voltage leads have to be placed very close to one another (3 mm apart) so as to limit the length of the section of the wire in order to keep the resistance down. This may introduce extra complications arising from end effects such as heat loss through the metallic probing leads, and also they may render inaccurate the simplified form of Ohm's
law \((E = IR)\) as we generally know it and use it for the calculations.

In short, the model proposed here brings some understanding into the factors that influence the curvature of the \(T\) vs. \(t\) curve or the \(E\) vs. \(t\) curve as is experimentally determined. The derivation of the time constant (which is another measure of curvature) of the system in terms of familiar atomic parameters and the dimensions of the wire provides the experimentalist with the physical properties to be considered when selecting a new metal for experimentation.

Now let us return to Eq. (23) in order to develop a workable equation other than (24) with which to analyze the data for the more common case when the pulse is curved.

Equation (23) can be rewritten as

\[
\frac{dE}{dt} = \frac{(I^2R' - K)}{C_p} E + \frac{k}{C_p} E_0
\]

If all the constants \((C_p, K, R', T_a)\) remain "constant" during the pulse then a plot of \(\frac{dE}{dt}\) vs. \(E\) would yield a straight line whose slope and intercept could be used to solve for the two unknowns \(C_p\) and \(K\). A graph of \(\frac{dE}{dt}\) vs. \(E\) is shown in Fig. 7 for a bismuth sample at 50 Kbar. The differentiation is performed numerically.

Even though \(C_p\) and \(K\) are not obtained directly from the equation on this form, such plots, however, help to test the validity of the assumptions involved and to find the time interval over which they hold. In general there is a time interval roughly from about 200 to 700 \(\mu\text{sec}\) for bismuth where \(\frac{dE}{dt}\) is linear with \(E\). For times less than 200 \(\mu\text{sec}\), rise time effects introduce considerable distortions and for times greater
Fig. 7. $\frac{dE}{dt}$ vs $E$ for bismuth at 50 Kbar (phase III).
than 700 μsec dE/dt tails up, suggesting that the ambient temperature Ta might be increasing due to the heat dissipated from the wire.

After checking Eq. (32) against the data it is changed from a differential to an integral form:

\[ C_p \int_1^2 \frac{dE}{2} + K \int_1^2 (E - E_0) dt = I^2 R \int_1^2 E \ dt \] (33)

The integrations required can be performed numerically by the use of the Trapezoidal Rule. \( E_0 \) cannot be measured directly because of the rise time distortions, however, it can be found by fitting the experimental points after the initial part of the pulse to a polynomial equation of quadratic or cubic order and then by back extrapolating to zero time.

The integration method suggested by Eq. (33) is preferred to that using Eq. (32) because of the inherent difficulties in computing a derivative numerically. Also, once \( E_0 \) is determined as explained, there is no need to find any parameters by extrapolation using Eq. (33).

A computer program was written for the CDC 7600 in order to perform all the numerical integrations and other computations. In principle, in order to solve for \( C_p \) and \( K \) only two equations are needed. However, a whole series of integrations were performed taking one reference point as the lower limit of integration and creating a system of overdetermined linear equations. A general least squares subroutine (GLSQ) was then called to obtain the best solutions of \( C_p \) and \( K \).
IV. EXPERIMENTAL

A. High Pressure System

The production of nearly hydrostatic pressure in the range of 0 to 200 Kbars* for the study of the properties of metals in our laboratory is effected by the application of the load of a hydraulic press to a pair of opposed Bridgman anvils. A Bridgman anvil is a cylinder of cemented tungsten carbide hot-pressed into a steel jacket of high tensile strength. See Fig. 8a.

Tungsten carbide cemented with cobalt as a binder is the strongest alloy known to man. The mechanical properties of the carbide depend on the percentage of Co (usually 3-20%), the trend being the higher the Co content the less strong but also less brittle it becomes. For example, the compressive strength of WC decreases from 42.4 Kbar to 37.6 Kbar in going from 3 to 16% Co, whereas the ductility, as measured by percent elongation increases from 0.60% to 2.70%. The accompanying very drastic reduction of the elastic limit from 34.5 Kbar to 6.55 Kbar is further indication of the increase in the plastic properties of the cemented carbide.

For room temperature work Kennametal K-11 (2.5% Co) is used. For liquid N₂ temperatures or below a higher Co content alloy and a softer steel jacket are used to avoid cracking.

The following is a table that compares the mechanical properties between 3% Tungsten Carbide and those typical of most steels.

---

*1 bar = 10⁶ dyne/cm² = 0.987 atm = 1.020 Kg/cm²
Bridgman anvils

Sample cell

High pressure set-up

Fig. 8
<table>
<thead>
<tr>
<th></th>
<th>3% Co, WC</th>
<th>Average Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's modulus</td>
<td>7.24×10³</td>
<td>2.03×10³</td>
</tr>
<tr>
<td>Elastic limit</td>
<td>34.5</td>
<td>--</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>--</td>
<td>7.0</td>
</tr>
<tr>
<td>Ductility (% elongation)</td>
<td>0.60</td>
<td>27.0</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>61.3</td>
<td>--</td>
</tr>
<tr>
<td>Rockwell hardness, C scale</td>
<td>91</td>
<td>50</td>
</tr>
</tbody>
</table>

All data — expressed in Kbar, except where indicated — were compiled from Refs. 15, 16, and 17.

Pressures much greater than 200 Kbar and several times greater than the compressive strength of the carbide are achieved due to the massive support given by the surrounding steel jacket. This principle of "massive support" was first introduced by P. W. Bridgman,¹⁸ considered the father of modern high pressure research, and has been extensively used in the design of belt¹⁹ and girdle²⁰ apparatus and of multi-anvil devices such as the tetrahedral¹⁹ and cubic presses.²¹

The use of a steel block with a carbide insert to "back up" the anvil is necessary, otherwise the carbide will penetrate into the steel with a consequent reduction of the load.

The sample cell (see Fig. 8b) consists of the bismuth wire specimen (99.99% pure) in the shape of a loop sandwiched between two discs of the pressure medium, usually AgCl. The circular geometry is chosen in order to avoid radical pressure gradients in the AgCl as measured by Montgomery et al.²² Two retaining pyrophyllite rings serve as walls to prevent sideways extrusion of the AgCl. Probing leads (0.005 in. Pt) are introduced between the pyrophyllite rings and the AgCl discs and placed
directly on the sample wire. Good contact generally occurs after the application of a few kilobars of pressure. It is desirable to flatten out the tips of the leads in contact with the specimen so as to avoid contact failure due to their cutting through the specimen. This is particularly important when the metal under study is very soft, such as Pb or In, but it is a good general practice.

A solid is needed to transmit very high pressures since most liquids will solidify below 30 or 40 Kbar. AgCl is generally chosen since it is the best compromise between low shear strength and low thermal and electrical conductivities. The last two properties are of critical importance for an electrical pulsing technique. Figure 9 shows the shear strength of a few substances as a function of pressure as measured by Bridgman in his high-pressure shear strength apparatus. As can be seen, there are substances of comparable or even lower shear strength than AgCl at low pressures. The shear strength of some of them rises much faster than that of AgCl with pressure; the increase of Na, for example, being quite dramatic. Those metallic substances such as Pb and In, whose shear strengths remain below AgCl throughout this pressure range are not suitable because they are good electrical and thermal conductors. The electrical resistivity of AgCl is in the Megaohm-cm range and its thermal conductivity of $1.2 \times 10^{-2}$ watts/cmK is lower than that of most dielectrics with the exception of Thallium bromide iodide (KRS-5) ($\lambda = 1.2 \times 10^{-3}$ watt/cmK) which can also be used as a pressure transmitting medium.

The retaining rings are made of pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{12}\text{H}_2$, found in volcanic lava) because of its high shear strength, availability, and the ease with which it is machined and ground to the specified dimensions.
Fig. 9. Shear strength of some solids vs pressure.
After Bridgman.\textsuperscript{14}
They are coated with rouge (Fe₂O₃ powder) to increase the friction between the rings and the anvils in order to avoid ring blow-out with pressure. It was found by Stromberg and Jura that the "pinching off" effect of the leads at low pressures could be eliminated by using wider rings (3/32 in.) and mechanically strong wires such as tungsten, molybdenum, and platinum to avoid shear. Thermocouple wires such as alumel and chromel are also resistant and are introduced for temperature measurements.

For isobaric temperature studies a metal can insulated with poly-styrene foam is introduced in the pressure column surrounding the anvil area (see Fig. 8c). For experiments around room temperature (20 to 30°C) a mineral oil bath is used. The oil is cooled with dry ice and then heated with two 250-watt Leviton knife heaters. The oil is stirred for thermal equilibrium. The experiments are also performed isobarically from liquid N₂ to room temperature. The can is filled with copper rods tightly stacked around the pressure column, which improve the thermal equilibrium and reduce the large temperature gradients that would otherwise develop as the liquid N₂ boils off and the system begins to warm up slowly to room temperature. All measurements are taken with increasing temperature. The warm-up rate is kept at 4 min/°C by varying the voltage from a Variac to heating tapes which are strapped around the copper rods.

The pressure was monitored by a load cell -- which consists of wire coils -- whose resistance varies linearly with pressure, and also by a Heise gauge which measures the oil pressure in the base of the ram. This measurement of the oil pressure gives only a rough estimate of the mean load on the anvil face. The resistance of the load cell is measured by a Baldwin-Lima-Hamilton bridge. The load was calibrated according to the
pressure scale established by Montgomery et al., specifically for the geometry used here, in which two polymorphic transitions of bismuth (25.4 and 88 Kbar at room temperature), detected by abrupt changes in the resistance-load curve, are used as the two reference points for interpolation. Since bismuth is the subject of heat capacity measurements it also provides a nice internal calibration of the pressure.

The pressure scale is only accurate to ± 4% to 100 Kbar, however, the load can be measured with a precision of 0.01 Kbar. During the isobaric low temperature runs it is important to keep the load absolutely constant, so the load must be adjusted every degree shortly before making a resistance or heat capacity measurement in order to compensate for the change in pressure caused by the thermal expansion of the pressure column. This is particularly critical in the low temperature semi-conducting region of the first phase of bismuth (≈ 100°K, 15 to 30 Kbar) where the resistance is much more sensitive to pressure than to temperature. The load cell is kept outside the tank inside a plastic bag with a dessicant (Drierite, anhydrous CaSO₄) to prevent water condensation. It is also important to cover the top of the tank with a polyurethane lid since the cold air can "freeze" the load cell.

B. Electrical Pulsing Technique

1. General Introduction

The electrical pulsing technique for measuring the heat capacity of metals takes advantage of the rise in temperature of a metal wire caused by the internal "joule heating" which is generated by the passage of an electrical current. The pulses must be of sufficiently short duration,
(on the order of milliseconds or less) so that only a fraction of the heat, the smaller the better, leaks out by conduction to the surrounding solid medium. The first successful effort was made by Stark who used his constant-current pulse generator to measure the heat capacity of iron and gadolinium under pressure.

A significant improvement in the pulse generator was achieved by A. Yee both in the constancy of the current (constant to .05%) and in the rise time (25 μsec). His constant current power supply, which is used in my experiments, is capable of producing a square pulse from 1 to 10 amps for a length of time variable between 200 μsec and 20 msec. Rise time effects (ringing, overshoot) introduce significant distortions only during the first 200 μsec of the pulse. The maximum external load that the power supply can handle is 15 volts.

In principle the msec constant-current pulse can be passed through the sample and the voltage drop measured directly. For metals the resistance increases with temperature, so the pulse looks like in Fig. 10a. The increase in resistance is usually on the order of 1%. Since the significant information for the heat capacity lies at the top of the pulse where the resistance is changing it is necessary to have a very sensitive recorder to measure the msec pulse. If one wants to measure the 1% rise in resistance with an accuracy of 1 part per thousand, then it is necessary to measure the 1 volt signal to one part in 10^5 with a fast 18-bit recorder capable of digitizing the msec pulse with a desirable resolution of 10 μsec/point or less. The most recent pulse analyzers such as the Nicolet 1092 Digital Storage oscilloscope have an amplitude resolution of 12 bits with the fastest plug-in units at one μsec/point. Thus, a direct
measurement of the voltage drop without amplification is not possible, although the rapid developments in the field of digital electronics will probably make it possible in a few years.

The problem was solved by Stark who introduced an adjustable "bucking voltage" of dimensions $V_b = IR_0$, where $R_0$ is the initial resistance of the sample and $I$ the current used. The bucking voltage is produced by passing the same current through another resistor of very large heat capacity, so that its resistance remains essentially constant. This bucking voltage cancels the bulk part of the voltage drop through the sample as is shown in Fig. 10b. The net result, which contains only the changing voltage, can then be amplified and recorded by a less sensitive detector. An amplification of 100, for example, cuts down by almost 7 bits the sensitivity required from the recording instrumentation.

2. Measurement of the Parameters Needed to Calculate the Heat Capacity

In order to calculate the heat capacity $C_p$ and the heat constant $K$, the following data are needed, as developed in the analysis:

a) A permanent record of $E$ vs. $t$, the voltage drop across the sample as a function of time.

b) The measurement of $I$, the pulsing current.

c) $R_0$, the initial resistance of the sample.

d) $R'$, the thermal coefficient of the resistance.

The easiest, but not the most accurate, way of obtaining a permanent record of the pulse is by taking a Polaroid picture of the oscilloscope trace. This is found to be satisfactory for those metals like iron where the pulse is quite linear beyond the first 100 μsec of rise-time effects,
(a) Direct measurement of sample resistance.

\[ E = IR_S - E = IR_0 \]

- Amplification

\[ R_S = \text{Sample Resistance} \]
\[ R_B = \text{Bucking Resistance} \]
\[ \text{CCPS} = \text{Constant current power supply} \]

(b) Two-stage amplification with a bucking voltage.

**Fig. 10**
indicating that the heat leakage fraction is small. In these cases a measurement of the limiting slope \( (dE/dt)_0 \) is possible and is sufficient, together with \( I, R_0, \) and \( R' \) to calculate \( C_p \) using Eq. (24). In the case of bismuth the pulse is curved, the reasons previously explained in the analysis section, and thus the more complicated treatment which takes into consideration the heat losses is required. In order to analyze the pulse one must know the coordinates of the points that define the trace. These coordinates can be measured directly from the picture by placing it on a plate whose \( x-y \) motion is coupled to a pair of dial indicators; the center of the trace is visually aligned with the cross-hairs of a microscope placed perpendicularly above the picture. This process of reading each of the points from the trace one at a time is tiring, time-consuming, and possibly inaccurate due to the broadness of the trace and to the fact that the oscilloscope introduces its own optical distortions. Also, more time is required to key-punch the data into IBM cards for subsequent computer analysis.

Two superior ways of recording the pulse were used in my experiments. One involved feeding the signal into a Fabritek 1070 digital signal averager with a 9-bit AD (analog-to-digital) signal conversion and 20 \( \mu \)sec/point maximum time resolution. The digital output of the Fabritek was coupled through an interface to a Kennedy Incremental 1040 Magnetic Tape Recorder. The Fabritek was borrowed from Prof Browne of the Chemistry Department.

Another way consisted of sending both signals (pulse and trigger) through 300 ft of shielded twisted-pair cables into Prof Rollie Myers' PDP8 minicomputer equipped with the LAB-8 basic averager with 9-bit AD
vertical resolution and 30 µsec/point. A series of eight pulses were averaged, increasing the amplitude resolution of the signal in either the Fabritek or the PDP8 averager to one part in 724 \( (2^8 \times \sqrt{2}) \). One of the nine bits contain information on the sign of the voltage. It is very important to ground the shielding of the twisted-pair cables to avoid high-frequency Mega-Hertz pick-up. The cables act as very good antennas. Due to its limited core capacity the data from the PDP8 must be retrieved after each series of averaged pulses through a teletype where a paper tape punch and/or a printout can be obtained.

The pulse current \( I \) is obtained by measuring the voltage drop across the bucking resistor whose resistance has been determined \( (R_b = 0.1000 \text{ ohm}) \).

The initial resistance of the sample \( R_0 \) is measured by the passage of a low constant DC current of 0.1 amps or less through the sample. This current is different from the pulse current which is a msec pulse from 1 to 10 amps. Any amount of joule heating is quickly dissipated into the AgCl pressure medium and does not affect the resistance reading. However, if too great a current is used (greater than 1 amp) the resistance measured will be higher for a metal than that obtained with a lower current because the wire will be in a steady state (heat input = heat output) at a temperature higher than its surroundings. This "static" voltage drop (to be distinguished from the "dynamic" msec voltage) is stepped down through a voltage divider by a factor of 10 and measured by a Newport digital microvoltmeter with a sensitivity of ± 1 µvolt.

The temperature of the wire before the pulse is applied is measured by Alumel-Chromel thermocouple wires in direct contact with the sample.
(see Fig. 8b). An ice bath is used as the reference cold junction. The emf. of the thermocouple is also measured by the Newport microvoltmeter. There is no attempt to directly measure the temperature of the sample with the thermocouple during the pulse due to the small temperature increase of the sample (in the order of 3°C) and the thermoelectric power of the Alumel-Chromel couple which is 40 \( \mu \text{volt/°C} \) at room temperature. The temperature rise of the wire during the pulse must be measured by obtaining the thermal coefficient of the resistance. In the case of an isobaric run, when the temperature and the resistance are changing with time, \( R' \) as well as \( C_p \) can be obtained during the course of the same experiment. For an isothermal run when only the pressure is varied, it is necessary to determine \( R' \) in a separate experiment as a function of pressure by varying the temperature a few degrees below and above the temperature in question. The measurement of \( R' \) amounts to the calibration of our resistance thermometer.
In this section I will present the results of my experiments on bismuth and will make an attempt to correlate them with theory and other experiments reported in the literature.

The physical properties concerned are the resistance $R$, the thermal coefficient of the resistance $R'$, the ratio $C_p/R'$, the heat capacity of bismuth $C_p$, and the heat leakage constant $K$ of AgCl, the pressure transmitting medium. The results are presented as a function of pressure and temperature with the exception of $C_p/R'$ which is only given vs. $P$ at room temperature.

In order to understand the physical properties of bismuth it is necessary to take a look at its phase diagram in Fig. 11 which was constructed from data by Kennedy et al. and Bundy. There are five well known solid polymorphic phases within easy experimental access of pressure and temperature: 0-100 Kbar, 0-200°C. The phase diagram of bismuth is typical of those substances such as water and antimony that have a volume contraction upon melting and consequently a negative-slope melting curve. Such substances invariably undergo high pressure transitions to phases of positive melting curves. A negative melting curve that would continue all the way to absolute zero would imply a pressure at 0°K above which the substance would be a liquid. Even liquid helium, the only substance known to remain liquid down to 0°K becomes solid with the application of 25 atm. Thermodynamics does not preclude the existence of a substance with such a phase diagram, however, it cannot guarantee its existence. The fact that it has never been observed is an experimental one.
Fig. 11. Phase diagram of bismuth.
A. Resistance Measurements

At room temperature three of these transitions are usually detected by discontinuities in the electrical resistance as in Fig. 12. The Bi I–II transition at 25.4 Kbar and the III–V transition at 88 Kbar are used as calibration points for high pressure apparatuses. As can be observed, the overall trend of the resistance is to decrease with pressure. At room P and T the resistivity of Bi is 110 μ-ohm-cm which is reduced to about 15 μ-ohm-cm at 100 Kbar. Bismuth I is exceptional in that the resistance increases with pressure. This is in contrast with the behavior of most metals which are more like Bi III and Bi V, where the resistance decreases with pressure.

For metals, whenever the number of carriers is not changed by pressure, the resistance is proportional to the mean square amplitude of the atomic vibrations $\bar{x}^2$. As the interatomic distances decrease with pressure so will $\bar{x}^2$ and therefore we expect a decrease in the resistance. Furthermore, since the compressibility decreases with pressure we expect the decrease in the resistance to be smaller at higher pressure, and this is what is typically observed.

For Bi I the increase of the resistance with pressure is due to a decrease in the number of carriers, and in order to understand how it comes about I will discuss the electronic band structure of bismuth I and the effect of pressure on the Fermi surface.

Bismuth I (as well as the Group V elements) has a type A7 rhombohedral crystal structure with two atoms per unit cell. The rhombohedral angle $\alpha = 57.14^\circ$. The first atom is located at (0,0,0) and the second along the trigonal axis at (u,u,u) where $u = 0.474$. It turns out that if $\alpha = 60^\circ$
Fig. 12. Resistance of bismuth vs pressure at room temperature.
and \( u = 0.5 \) the rhombohedral structure becomes a simple cubic structure which is equivalent to two interpenetrating f.c.c. lattices as in NaCl. The fact that the second atom is not exactly half-way along the trigonal axis implies that it is closer to the three near neighbors below than to the three above it. Thus, bismuth has a structure of corrugated layers in which each atom is bonded to three others. The properties of bismuth are highly anisotropic. Bismuth I is very brittle and is similar to graphite on the ease of cleavage between these layer planes and the fact that the electrical conductivity with the current in the plane of the layers is much higher than the conductivity along the trigonal axis.\(^1\)

The Brillouin zone of the Group V semi-metals Bi, Sb, and As is shown in Fig. 13 showing the general shape of a truncated octahedron (which is the B.Z. of the f.c.c. lattice), however, it is squashed along the trigonal axis. This trigonal compression in reciprocal space of the B.Z. corresponds to the rhombohedral stretching along the body diagonal caused by the distortion of the simple cubic lattice whereby the angle goes from 60° to 57°. The effect of the distortion is to eliminate the symmetry equivalency of points T and L. There are two T points (centers of regular hexagons) and six L points (centers of "pseudo hexagons") on the B.Z. boundaries.\(^28\)

The electronic energy bands in Bi I as calculated by the pseudo-potential method\(^29\) are given in Fig. 14. It should be observed that at points T there is a band gap at the Fermi level whereas at points L there is an overlap into the next band. Since bismuth has a total of ten electrons per unit cell the first five zones are filled and there is a small overlap into the 6th zone at points L on the surface of the B.Z.
Fig. 13. Brillouin zone of bismuth.
Fig. 14. Calculated electronic band structure of bismuth. After Golin.29
The detailed shape of the Fermi surface of Bi I near the B.Z. was determined by Jain and Koenig after careful review of all the data given by experiments like cyclotron resonance, De Haas van Alphen effect, and the Hall effect. It was determined that there are six electron half-ellipsoids centered on the "pseudo hexagonal" faces at points L and two hole half-ellipsoids on the hexagonal faces at points T. Total carrier concentration is $10^{-5}$/atom with equal numbers of holes and electrons.

This band structure and overlap of bismuth is consistent with Bi I being a semi-metal at room pressure.

It was first observed by Souers and Jura that Bi I becomes a semiconductor with pressure by discovering a negative temperature coefficient of the resistance below $120^\circ$K at pressures higher than 15 Kbar. My results in Fig. 15 show the behavior of $R$ vs. $T$ among the different phases. Figure 16 shows the reduced thermal coefficient $R'/R$ vs. $P$ at room temperature. Figure 17 gives $R'$ vs. $T$ in the different phases from $90^\circ$K to room temperature. As can be seen, the resistance at 18 Kbar has a minimum at around $105^\circ$K. Souers was able to use the exponential resistance formula to measure the band gap of Bi I as a function of pressure. The band gap increases with pressure and is of the order of 0.010 eV. Because the gap is so small Bi I shows a positive temperature coefficient of the resistance at higher temperatures in this semi-conducting region due to thermal excitation.

There have been several experiments under pressure that support a decrease in the number of carriers for Bi I. Itskevich et al. measured the effect of pressure on the extremal cross-sectional areas of the electron and hole ellipsoids by the De Haas van Alphen effect at $1.5^\circ$K.
Fig. 15. The resistance of bismuth vs temperature and pressure.
Fig. 16. $R'/R$ of bismuth vs pressure at room temperature.
Fig. 17. $R'$ of bismuth vs temperature.
They found a surface decrease of 60% for the holes and 73% for the electrons up to 15 Kbar and they extrapolated the disappearance of the ellipsoids at about 25 Kbar.

Vaisnys and Kirk\textsuperscript{34} measured the Hall coefficient and magnetoresistance of Bi I with pressure. Assuming a two band model with equal electron and hole concentrations they found a 50% reduction in the number of carriers from 7 to 20 Kbar.

In summary, the shrinking of the different parts or ellipsoids of the Fermi surface and the decrease of the number of carriers with pressure is consistent with the semi-metal/semi-conductor transition of Bi I measured by Souers and observed in this work under pressure. Pressure brings about a separation of the bands which overlap at room pressure at points L on the pseudo hexagonal faces of the Brillouin zone.

The temperature behavior of $R$ in phases III and V show a positive temperature coefficient in the temperature range measured. The pressure behavior of the resistance is also normal as mentioned earlier since there is a decrease with pressure. Phases III and V appear to be more metallic than phase I, however the strong concave curvature of $R$ in Bi III is very puzzling. We should remember from the Bloch–Gruneisen equation that at low temperatures $T < \theta$, $R \propto T^5$, and at $T > \theta$, $R \propto T$. An upper limit of 200°K for $\theta$ can be assigned to these phases as will be discussed later from the heat capacity results. Thus, the normal temperature behavior of $R$ should be linear, or in the case of a curvature it should be convex, completely opposite from Bi III. The resistance in Bi V is quite linear as can be observed.

Bi III is not alone in the concave behavior of $R$. McWhan\textsuperscript{35} measured
the resistance of Sb at 45 and 60 Kbar from liquid helium to 200°K and
the resistance also shows a strong concave curvature. Other transition
metals such as Pt, Ta, and Pd\textsuperscript{10} show a much milder concave curvature at
higher temperatures up to their melting points. The reasons for this
behavior are not clearly understood.

Some attempts have been made to elucidate the crystal structures of
the high pressure phases of Bi II, Bi III, and Bi V. Brugger et al.\textsuperscript{36}
using time-of-flight neutron diffraction measurements report for Bi II a
base centered monoclinic structure \(\text{C}_{2h}^3\) with four atoms/unit cell at
\((0,0,0), (\frac{1}{2},\frac{1}{2},0), (0,\frac{1}{2},\frac{1}{2}), (\frac{1}{2},0,\frac{1}{2})\). The cell parameters are
\(a = 6.674 \text{ Å}, b = 1.117 \text{ Å}, c = 3.304 \text{ Å},\) and \(\beta = 110.33°\).

At \(P = 35 \text{ Kbar},\) Vereschagin et al.\textsuperscript{37} using x-ray molybdenum radia-
tion have compared the high pressure phases of Sb III and Bi III and claim
they are isomorphous. They have also compared the x-ray pattern of SnS
and Sb III and have found some similarities. The structure of SnS is
orthorhombic. Their proposed Bi III structure is a monoclinically
distorted SnS with \(\beta = 85°20, a = 6.65 \text{ Å}, b = 4.20 \text{ Å}, c = 4.65 \text{ Å}.\)
They found four atoms/unit cell but could not clearly locate them within
the unit cell.

Schaufelberger et al.\textsuperscript{38} determined Bi V to be b.c.c. with two
atoms/unit cell at \((0,0,0)\) and \((\frac{1}{2},\frac{1}{2},\frac{1}{2})\). \(a = 3.80 \text{ Å} \) at \(P = 90 \text{ Kbar}.\)

The electronic band structures of these high pressure phases has
not been calculated, partly because of the complexities of the crystal
structures and partly because of the lack of experimental data on the
Fermi surface at these high pressures. There is also some controversy
concerning the high pressure crystal structures. None of those reported
crystal structures have been confirmed independently. Professor John Jamieson, a pioneer on high pressure x-ray crystal structure determination in this country, feels that due to the short wave length Mo radiation employed in many of the experiments there is not enough angular resolution to make an unambiguous assignment of these complex structures. He has recently developed a high pressure technique with a Cu target of longer wave length and we expect more crystal structure data on high pressure bismuth in the future.

B. Heat Capacity Results

Figure 18 presents the results of $C_p/R'$ vs. $P$ in phases III and V at room temperature. As described in the experimental section there are results for two different experiments; one using the Fabritek 1070 digital recorder and the other using a PDP8 minicomputer equipped with the Lab 8 basic averager. All results are normalized at $P = 50$ Kbar at room temperature in order to compare results from different samples since with our experiments it is not possible to determine the mass between the current leads.

In order to obtain $C_p$ we must multiply $C_p/R'$ in Fig. 18 by $R'$ in Fig. 16. The result is given in Fig. 19.

Unfortunately, no results can be given for phase I for the following reasons. It should be recalled from the section on heat capacity analysis that the results were only valid if a plot of $dE/dt$ vs. $E$ would yield an interval in $E$ where $dE/dt$ were linear. A plot for phase III was given in Fig. 7 and it was shown that such a linear region existed. A plot for phase V is given in Fig. 20 and it can also be seen that such an interval exists. A similar plot for phase I is given in Fig. 21 for two
Fig. 18. $C_p/R'$ of bismuth vs pressure at room temperature.
Fig. 19. Heat capacity of bismuth vs pressure at room temperature.
Fig. 20. $\frac{dE}{dt}$ vs $E$ for bismuth V at 95 Kbar.
Fig. 21. $\frac{dE}{dt}$ vs $E$ for bismuth I at 18 Kbar.
different currents. Here we can see that such a linear region does not exist for phase I and consequently the results depend upon the arbitrary interval in $E$ on which the calculations are performed. The results on this phase also show a very strong current dependence which is absent on phases III and V. These inconsistencies render the data in phase I completely useless.

No satisfactory explanation can be given for this odd behavior. It would seem that rise time effects extend for a considerably longer period of time in Bi I. We must keep in mind the very peculiar electronic band structure of Bi I already discussed. At the beginning of the pulse there are very high frequency Fourier components of the current which could have a very strong frequency effect on the reactance resulting in these distortions.

Also no $C_p$ data are available for phase II because due to the narrowness in $P$, $T$ space over which it exists, no $R'$ was obtained there.

In Fig. 19 I have also introduced the high pressure heat capacity results of Dzhavadov. He used a 2 kHz a.c. current of duration up to 1 sec with larger mass samples (by a factor of $10^3$) which enabled him to measure the temperature rise directly with a thermocouple. There is very good agreement in the 15% increase in $C_p$ on the III-V transition at 88 Kbar, however my results in phase III show a reproducible drop of $C_p$ of about 12% going from 40 to 80 Kbar, whereas his data shows no pressure dependence within his experimental error ($\pm 5\%$) up to 80 Kbar. The experimental error in this work is estimated to be $\pm 3\%$ for $C_p$.

The heat leakage constant $K$ of the medium AgCl is given as a function of pressure in Fig. 22. Here, again, the low pressure results
Fig. 22. Heat leakage constant $K$ of AgCl vs pressure at room temperature.
are not very reliable, however, the general increasing trend towards a constant value at around 50 Kbar is easy to understand. At very low pressures the contact between the wire and the AgCl is very poor so the conduction losses are small. In the limiting case as \( P + 1 \) atm, \( K \) will depend mainly on the heat conductivity of the air which is very small. At high pressures \( K \) will be proportional to the heat conductivity of AgCl which is, of course, much higher than that of air. Since the AgCl medium is also being compressed it is likely that its thermal conductivity also increases with pressure. The discontinuity at around 90 Kbar is consistent with a well known polymorphic transformation of AgCl at the same pressure.\(^{41}\)

\( C_p \) as a function of temperature from 90°K to room temperature is given in Fig. 23 for two pressures: \( P = 52 \) Kbar and \( P = 95 \) Kbar. The room pressure values as tabulated by Hultgren et al.\(^{42}\) are introduced for comparison. It is first apparent that there is a stronger linear contribution to \( C_p \) at these higher pressures that shows for Bi III from 290°K down to 100°K. For phase V there is a linear region down to about 200°K and a curvature begins to appear below this temperature.

The Debye temperature \( \theta \) of Bi I is 60 - 100°K.\(^{10}\) From my experiments with Bi III and Bi V the data is insufficient to obtain a \( \theta \) at these high pressures because of the limited temperature range, and because the dilation contribution \( C_p - C_v \) and the electronic term \( C_v^e \) are not known. \( \theta \) seems to be higher for Bi V because of the curvature. A very rough upper limit of \( \theta \leq 200\)°K for Bi V and \( \theta \leq 150\)°K for Bi III can be estimated.

Both the dilation term \( C_p - C_v = VT a^2/\theta \) and the low temperature expression for the electronic heat capacity \( C_v^e = \gamma T \) can give linear
Fig. 23. Heat capacity of bismuth vs temperature and pressure.
contributions; in the first case if we assume that $V$, $\alpha$, and $\beta$ are approximately constant over the temperature range, in the second case if $T < T_F$ as discussed in the theory section. At room temperature the dilation term \( \left( C_p - C_v \right)/C_v \) can be as high as 6.7% for Pb and 10.0% for K.\(^{10}\) $\gamma$ terms can be relatively high for the transition metals because of the high density of electronic states associated with the sharp $d$ and $f$ bands. For Nb and V at room pressure $\gamma = 7.8$ and 9.3 mJ/K$^2$-mole, respectively.\(^{43}\) For these two metals at room temperature the extrapolated $\gamma_T$ contribution is 0.57 and 0.68 cal/mole-K or roughly about 10% of the lattice term. High pressure/low temperature heat capacity studies of the insulator/metal transitions in Sm\(^{44}\) and $V_2O_3$\(^{45}\) show very dramatic increases in the $\gamma$ value for these compounds. The first order transition in Sm\(^{46}\) at 6.5 Kbar results in a change of $\gamma$ from $\gamma < 7$ mJ/K$^2$-mole to $\gamma = 145$ mJ/K$^2$-mole at 15 Kbar. For $V_2O_3$, $\gamma = 0$ at zero pressure and $\gamma = 18.2$ mJ/K$^2$-mole at 25 Kbar.

For Bi I, $\gamma < 0.08$ after the data compiled by Phillips\(^{43}\) at room pressure. This phase has been shown to be non-superconducting down to 0.005°K.\(^{46}\) Bi III and V, on the other hand, are superconducting with superconducting transition temperatures of $T_c \approx 7^\circ$K at 30 Kbar and $T_c \approx 8^\circ$K at 100 Kbar.\(^{47}\) The onset of superconductivity of Bi with pressure is indirect evidence of a higher $\gamma$.

Electron-positron annihilation experiments on Bi at high pressures by Przybylinski\(^{48}\) of this group show an increase in the density of states in phase III by about a factor of two, despite a large scatter in the data. He also shows an increase of 1.5 in the number of annihilating electrons from phase I to III which he attributes to the 5d core electrons.
In summary, the temperature behavior of $C_p$ in phase III and $V$ is consistent with a predominant lattice contribution of a low Debye temperature (less than 200°K) and a smaller linear term which is probably due to a combination of dilation and electronic contributions.

At room temperature in phase III my data show a decrease of $C_p$ with pressure, something which is consistent with theory, however, the large magnitude of this decrease (12% drop from 40 to 80 Kbar) is very puzzling. We can estimate approximately the effect of pressure on the lattice term $C_v^L$ by calculating the change in $\theta$ with pressure from the Gruneisen expression $-3 \log \theta / 3 \log V = \gamma_G$, where $\gamma_G = 2$ for most elements. Using the compressibility data from Giardini and Bridgman, we obtain a volume change from $0.82 V_0$ to $0.78 V_0$ at those two pressures which correspond to $\theta_2 / \theta_1 = 1.12$. Using $\theta_1 = 150°K$ we get $\theta_2 = 168°K$. At room temperature this would correspond to a decrease in $C_v$ of 0.3% which is much smaller than the observed 12%. There is also a reproducible low $C_p$ point at 30 Kbar which cannot be disregarded within experimental error. It would seem almost as if $C_p$ had a maximum at around 35 or 40 Kbar. This is very hard to explain at this point. It is possible that in Bi III there could be a continuous electronic transition of the type found in Cs at around 45 Kbar and in Yb at around 37 Kbar. No one has performed published heat capacity experiments vs. pressure on these metals, however, one would expect high values of $C_p$ near the pressure of the electronic transformation.

The 15% increase of $C_p$ on the III - V transition at room temperature is also hard to understand in terms of a lattice $C_v^L$ change since the Debye temperatures on both phases seem to be less than 200°K. This increase is also observed in Dzhavadov's work. It is possible that since the
measurements in phase V are very close to the transition there might be some Bi III still untransformed with part of the heat input going into the ΔH of transition, and, therefore giving an apparently high heat capacity. If, on the other hand, this increase is real it could also be explainable in terms of another electronic change accompanying the III-V transition.

The heat leakage constant K is shown in Fig. 24 vs. T for the two pressures 52 and 95 Kbar. K remains constant within an experimental error of ±15%. K depends mainly on the heat conductivity k of the medium, AgCl. We know that in general k goes through a maximum at around $T_m = \theta/20$; below $T_m$ k falls with the $T^3$ dependence of the lattice heat capacity, above $T_m$ and around $\theta$ k falls with a $T^{-1}$ dependence since the phonon mean free path is inversely proportional to the number of phonons. The Debye $\theta$ for AgCl is $183^\circ K$ so we predict a slow drop of K with T. The fact that K is fairly constant within the temperature range measured agrees roughly with the theory.

In none of the physical properties of Bi III measured as a function of pressure at room temperature, including $R, R', C_p/R', \text{ and } C_p$, was there any evidence within experimental error of the phase transitions at 45 and 64 Kbar observed by Bridgman as volume discontinuities and recently reported by Zeitlin et al. and Nichols as discontinuities in the electrical resistance. These findings are in accordance with the general consensus among high pressure experimentalists that those transitions do not exist.
Fig. 24. Heat leakage constant $K$ of AgCl vs temperature and pressure.
VI. SUMMARY

In this work heat capacity data have been obtained on Bi III and Bi V as a function of pressure and temperature from liquid nitrogen to room temperature and from 0 to 100 Kbar. The heat leakage constant of the pressure medium AgCl has also been obtained.

There are many unanswered questions concerning the physical properties of bismuth at high pressures. If real, what is the nature of the $C_p$ maximum on bismuth at around 40 Kbar at room temperature? What is the cause of the 15% increase of $C_p$ in the III-V transition? What is the cause of the linear temperature behavior of the heat capacity?

In order to gain an understanding of these phenomena on bismuth and other substances many more high pressure experiments will have to be performed at low and high temperatures on the heat capacity, the crystal structure, electronic properties, magnetic properties, superconductivity, etc.

There are some experiments that can be done with our present setup; more isobars on Bi III and Bi V as well as isotherms at CO$_2$ and liquid N$_2$ temperatures; the measurement of $C_p$ on ytterbium and iron near their high pressure transitions.

More precise data could have been obtained with the use of the 12-bit AD converter (instead of the 9-bit AD) that was installed in the PDP8 averager two months before finishing this work; unfortunately, it was faulty and had to be returned twice to the manufacturer for repairs. This increase in the resolution of the recording instrumentation will allow better heat capacity and equation of state studies in the near future.
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