Reprinted from THE PHYSICAL REVIEW, Vol. 138, No. 1A, A129–A133, 5 April 1.
Printed in U. S. A.

Melting and High-Temperature Electrical Resistance of Gold under Pressure*

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(Received 2 November 1964)

The electrical resistance of gold was measured over the temperature range 30°C to the melting point and over a pressure range 0–70 kbar. At constant pressure, a sudden twofold increase in resistance sharply indicated the melting point and was used to determine the solid-liquid phase line to 70 kbar. The experimental melting curve has an initial slope, 5.91°C/kbar, in very good agreement with Clapeyron's equation, and has a form satisfying a Simon's equation with a coefficient $c=2.2\pm0.1$. The electrical resistance data show a decrease in the temperature coefficient of resistivity at higher pressures, while the resistance at the melting point appears to be a constant independent of pressure.

I. INTRODUCTION

IN many high-pressure high-temperature experiments it would be convenient to use the electrical resistance of a material as an indication of its temperature. There have been occasions where the resistance of noble metals has been used for this purpose.[1,2] In these cases it was assumed that the increase of resistance with temperature is independent of pressure; thus measurements at atmospheric pressure were used as the temperature calibration. One object of this experiment is to determine the temperature dependence of the electrical resistance of gold as a function of pressure. Resistance measurements were made from room temperature to the melting point for the pressure range 0–70 kbar. At the melting point there is an abrupt resistance increase; thus the melting temperature was also determined as a function of pressure.

Gold is ideal for this type of study. First it is chemically inert which is of prime importance to the experimentalist, for in high-pressure studies the materials are in intimate contact with their surroundings. The electronic and thermodynamic properties of gold however give rise to more fundamental reasons for studying this material. The conduction electrons in gold behave as nearly free electrons with an isotropic effective mass and there are no isomorphic phase transitions to pressures as high as 100 kbar.[3] Thus one might expect the resistance and melting curves to be accurately represented by a simple semiclassical model of an ideal metal.

1. Electrical Resistance

The theory of the electrical resistance of metals at atmospheric pressure has met with considerable success,[4] especially for metals in which the Fermi surface is nearly spherical and lies entirely within one Brillouin zone. The extension of this theory to the range of high pressures is discussed by Lawson.[5] In the region where the temperature is greater than approximately twice the Debye temperature θ, one can write a simple expression for resistance as a function of pressure P and temperature T. Starting from a formula for the pressure coefficient of resistance, derived by Lennsen and Michels[6] for nearly free electrons, we arrive at the equation

$$R(P,T)=CT[V(P,T)]^{2\gamma-4/3}, \quad (1)$$

where C is a constant, $V(P,T)$ is the volume and γ is the Grüneisen constant. We now define the ratio

$$r_p(T,T_0)\equiv R(P,T)/R(P,T_0) = T/T_0[V(P,T)/V(P,T_0)]^{2\gamma-4/3}. \quad (2)$$

The accuracy of this equation at atmospheric pressure was determined by comparing the measured resistance ratio[7] with that calculated from Eq. (2) using experimental thermal-expansion data[8,9] and $\gamma=3.00$.[10] Calculated and measured values agree to better than 0.5% from room temperature to the melting point. Another check on Eq. (1) is possible using compressibility measurements at room temperature[11,12] and calculating $R(P,T_0)/R(0,T_0)$. These values agree with Bridgman's high-pressure resistance measurements[3] to better than 1.5% up to 50 kbar. For high pressure and temperature effects it is convenient to write

$$r_p(T,T_0)/r_0(T,T_0) = [V(P,T)V(0,T_0)/V(0,T)V(P,T_0)]^{2\gamma-4/3}. \quad (3)$$

All quantities on the right-hand side are known except $V(P,T)$. Even without an exact knowledge of the equation of state, it is obvious that (3) predicts a very small negative effect of pressure on $r_p(T,T_0)$. This is

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most easily recognized by noting that the right-hand side of (3) is the ratio of the thermal expansion at pressure P to that at atmospheric pressure, thus a quantity slightly less than unity. It is possible to estimate the initial decrease of $r_p(T,T_0)$ with pressure by differentiating Eq. (3) with respect to P and evaluating at $P=0$:

$$dr_p(T,T_0)/dP|_{P=0}=r_0(T,T_0)[2\gamma-\tfrac{4}{3}][K_{T_0}-K_T], \quad (4)$$

where K_T is the isothermal compressibility at temperature T.

2. Melting

The present theories of melting are only first-order approximations[13] which yield a form known as Simon's equation[14] for normal materials, i.e., those with a melting curve monotonically increasing with pressure. Simon's equation,

$$P_m/A+1=(T_m/T_{m,0})^c, \quad (5)$$

is an empirical relation containing two parameters, A and c. T_m is the melting temperature at pressure P_m and $T_{m,0}$ is the melting temperature at atmospheric pressure. Gilvarry[13] has derived an expression for c using some simple assumptions about melting and his results are carried somewhat further by Babb.[15] In the latter's article, c is given by the formula

$$c=(f+\mu)/(f-1). \quad (6)$$

If f is assumed to be constant along the melting curve Babb shows that $f=2\gamma_{m,0}+\frac{1}{3}$. The quantity μ is to be obtained from the volume dependence of the Grüneisen constant using a relation proposed by Gilvarry:

$$(\gamma-\tfrac{1}{3})/(\gamma_0-\tfrac{1}{3})=(V/V_0)^\mu. \quad (7)$$

In order to determine μ and $\gamma_{m,0}$ one must know how γ varies with volume. Using the Dugdale-MacDonald formula[16] and shock compression data[17] the value of μ is estimated to be 7.99 for gold. Assuming that γ is a function of volume only and employing the expansion of gold to the melting point[18] one obtains $\gamma_{m,0}=4.43$. These values substituted into Eq. (6) predict $c=2.10$.

The parameter A can be written in terms of c by using the Clapeyron equation. Differentiating Eq. (5) with respect to T_m and evaluating the result at $T_m=T_{m,0}$ it follows that

$$dP_m/dT_m|_{T_{m,0}}\equiv P_0'=Ac/T_{m,0}=(L/T_{m,0}\Delta V), \quad (8)$$

where L is the latent heat and ΔV is the volume change at fusion. Therefore $A=L/c\Delta V$ and Simon's equation becomes

$$P_m=(L/c\Delta V)[(T_m/T_{m,0})^c-1]. \quad (9)$$

Experimental results for $T_{m,0}$, L,[19] and ΔV,[20,21] at atmospheric pressure, are used in Eq. (9) thus leaving only one arbitrary parameter c to be empirically determined.

II. METHOD OF MEASUREMENT

The measurements were accomplished using a 600-ton tetrahedral anvil press[22] with a sample container of pyrophyllite in the form of a regular tetrahedron $1\frac{1}{4}$ in. on an edge. The gold was supplied by Nesor Alloy Products Company in the form of 99.999% pure wire 3 mils in diameter. The sample was constructed as shown in Fig. 1. The distance between the potential contacts was about 1 mm and the leads to these contacts were brought out of the pressure cell through 13-mil stainless-steel tubing. Pyrophyllite sleeves were put around the steel tubing and the thermocouple wire to keep them from breaking while the gaskets were forming. The BN served to insulate the gold and the thermocouple from the heater and also to spread the heat to make the temperature more uniform.

Measurements were made at a fixed ram loading while increasing the current through the heater strip and simultaneously recording the thermocouple emf and the resistance between the potential leads. A Kepco 100 A, 8 V, dc regulated power supply served as a source of heater power. The resistance between the potential leads was measured with a four-lead Keithley milliohm meter, the output of which was fed to one axis of a Moseley X-Y recorder. The other axis of the recorder monitored the thermal emf from the thermocouple junction. At the melting point the resistance of

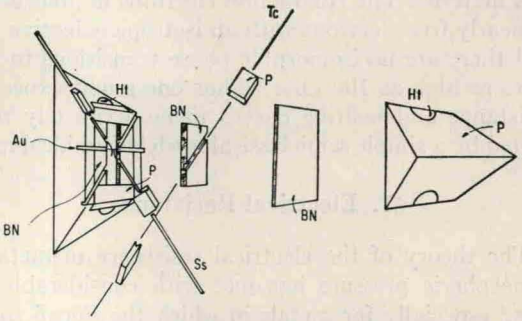

FIG. 1. High-pressure high-temperature sample chamber for resistance measurements in the tetrahedral anvil press. The lettered parts are: P, pyrophyllite; BN, boron nitride; Tc, thermocouple; Ss, stainless-steel tubes; Ht, heater tabs; Au, gold current leads.

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