

Uniaxial Pressure Dependence of the Debye Temperature in Metals

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The electrical resistance and its temperature coefficient have been measured for a platinum foil as a function of uniaxial pressure over the pressure range 0 to 60 MPa. The measurements were performed at room temperature using the transient hot-strip method. The data are analyzed using the electrical resistivity formula within the Block-Grüneisen approximation. The pressure dependence of the Debye temperature was directly obtained from an expansion of this formula and using the basic definition of the temperature resistivity coefficient. The reliability of the experimental data was then verified using the basic definition of Grüneisen constant. Within the investigated pressure range, the analysis supports the interpretation that the change in resistance of platinum under pressure is mainly due to the change in the amplitude of the atomic vibrations that are directly related to the change in Debye temperature. The pressure dependence of resistance and the Debye temperature of the platinum were reasonably good in spite of the approximations involved.

KEY WORDS: Debye temperature; electrical resistivity; high pressure.

1. INTRODUCTION

The effect of pressure on electrical resistance has been extensively investigated and the high-pressure investigation on electrical resistivity and other physical properties by Bridgman [1] is an outstanding source of information in this field.

According to Lawson [2], the effect of hydrostatic pressure on the electrical resistance of metals may be divided into four broad categories. First, the interaction between the conduction electrons and the lattice waves changes. This change is caused by the stiffening of the lattice induced by the external pressure. It is always present and often most predominant. Second, the Fermi energy varies under pressure. Third, as the experimental

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pressure range is extended, there is an abrupt appearance of new, more dense, crystallographic forms. Fourth, a further extension in the pressure range may lead to changes in the band structure arising from the changes in overlap between various bands or from more radical changes in the electronic structure of the atoms. The latter two effects have been more profound in soft (compressible) metals that undergo large volume changes as the pressure is increased.

In this work, we have investigated the electrical resistance of a platinum foil under moderate pressure (< 100 MPa). In such a pressure range, we may expect that the most predominant effect of pressure on the resistance of platinum (hard metal) is confined to the first two categories. In fact, it is shown that for platinum the change in resistance under pressure is due mainly to the change in the amplitude of the atomic vibrations, which is directly related to the change in Debye temperature (see Section 4). Regarding this effect, there are numerous studies investigating the pressure dependence of Debye temperature in metals and metallic compounds [3–8]. In the present study, we have used the transient hot-strip (THS) method [9] to investigate the effect of uniaxial pressure on the electrical properties and on the Debye temperature of platinum foil (strip). This method has been applied for studying thermal properties of insulating solids and liquids [9–12]. It also offers the possibility to measure both the resistivity (ρ) of the metal strip and its temperature coefficient (α) simultaneously, if the thermal conductivity of the solid sample (the substrate) with low electrical conductivity is known. Measuring the electrical properties of the metallic thin foil (the strip) when the latter possibility is used is similar to the arrangement in the four-probe technique. The transient voltage variations are monitored across the strip, while its temperature is raised by about 1 K using a constant-current pulse. This possibility has been used to measure the electrical properties of thin metallic films at room temperature and atmospheric pressure [13].

In this work it is shown that, even at moderate pressures within the range (0.1 to 60 MPa), by measuring the uniaxial pressure dependence of the resistance and its temperature coefficient, it is possible to deduce directly the uniaxial pressure dependence of the Debye temperature (θ_D).

2. EXPERIMENTS

The sample, consisting of a platinum foil strip, is mounted between two circular fused quartz plates. The strip was cut from 99.99% platinum foil supplied by Johnson Matthey AB in Stockholm and its dimensions were 30 mm in length, 1.67 mm in width, and $12.5 \mu\text{m}$ in thickness. These dimensions were carefully determined using a Nikon measurescope. It should be

noted that according to these dimensions the ratio of the free surface area of the strip to the total surface area under the uniaxial pressure is less than 1%, this may regard the strip condition under the uniaxial pressure to be nearly approximated by a hydrostatic pressure condition.

The sample arrangement with all the necessary constituents and wiring connections was placed inside a pressure cell surrounded by a loosely packed cotton wool to achieve homogeneous temperature around the sample. The precise temperature of the sample was determined using both a chromel–alumel thermocouple and a Pt-100 resistance thermometer. The uniaxial pressure on the sample was generated by a piston-and-cylinder device using a 25-ton hydraulic press operated by means of a two-stage hand-pump and equipped with a calibrated pressure gauge. More details on the sample arrangement and the apparatus used are given elsewhere [14]. The resistance (R) and its temperature coefficient (α) of platinum were measured using the THS method at ambient temperature of the sample ($T=293\text{ K}$), between atmospheric pressure (0.1 MPa) and 60 MPa. The THS method is used in a similar manner as in measuring TCR of thin films [13]. The measurements are performed by pressing the metal strip between the fused quartz plates to the desired pressure, then passing a constant-current pulse and simultaneously monitoring the voltage variation between the end points of the strip. In this configuration the strip is used simultaneously as a heat source and temperature sensor. The height of the current pulse should be enough only to increase slightly the temperature of the strip by about 1 Kelvin, and the time of the transient recording should be less than the time required for the thermal pulse to penetrate the surrounding plates. The evaluation procedures of the THS recording with the necessary equations are given by Gustafsson et al. [10–12]. It should be noted that in the THS method it is possible to determine both R and α at the same temperature from one single transient recording, with an accuracy estimated to be better than 0.1% for R and 0.5% for α , while it is not possible to do this using the conventional method. In the conventional method, α is determined from the resistivity at different temperatures, which may lead to structure changes due to annealing as the temperature is increased. Furthermore, in this particular case the area of the strip is about 13 times less than the area of the quartz plates, which means that a pressure of about 5 MPa on the quartz plates is sufficient to produce 60 MPa on the platinum strip. Within this pressure range, the thermal conductivity of fused quartz is reported to be constant [15], which makes it even more simpler to use this method to monitor the TCR variations under pressure. The mean value of the thermal conductivity of the fused quartz used in these calculations was obtained from a series of measurements made on the same plates by the conventional way of using the THS

method to measure the thermal properties of solids, at room temperature and atmospheric pressure.

3. RESULTS

Two series of measurements with Pt strips were performed under uniaxial pressure ranging from 0.1 to 60 MPa. The discrepancy between the values of the two runs at the same pressure is within 2%. The results are depicted in Figs. 1, 2, and 3. All data were collected while increasing the pressure and the values of R_0 , α_0 , and Θ_{D_0} are obtained by extrapolation to zero pressure. Figure 1 shows the relative resistance variations with uniaxial pressure for both runs. Within this small pressure range, the value of $\Delta R/(R_0 \Delta P)$, the pressure coefficient of resistance (PCR), is negative, and as a first approximation within the experimental error, it may be approximated by a linear pressure-dependent variation. A least-squares fit to the data is also shown by the solid line; the slope of this line is $\approx -2.9 \times 10^{-5} \text{ MPa}^{-1}$. This value is not very far from the value reported for platinum sheet ($-2.2 \times 10^{-5} \text{ MPa}^{-1}$) at higher hydrostatic pressures [1]. However, it should be noted that the change in resistance of platinum over a relatively larger hydrostatic pressure range is not linear with pressure, but as the pressure increases the change becomes less [1], i.e., the resistance decreases with a normal upward curvature, which implies that the PCR value should be higher at lower pressures.

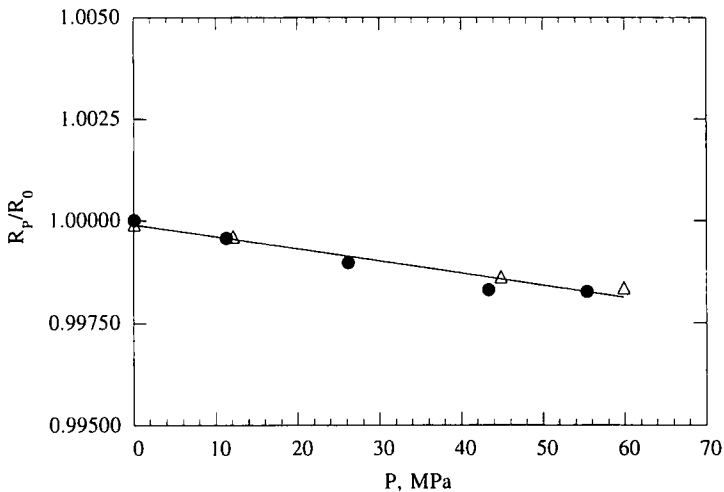


Fig. 1. The uniaxial pressure dependence of the relative resistance R_p/R_0 for the platinum strip at the sample ambient temperature (293 K). Two runs were performed, corresponding to the filled circles and open triangles, respectively.

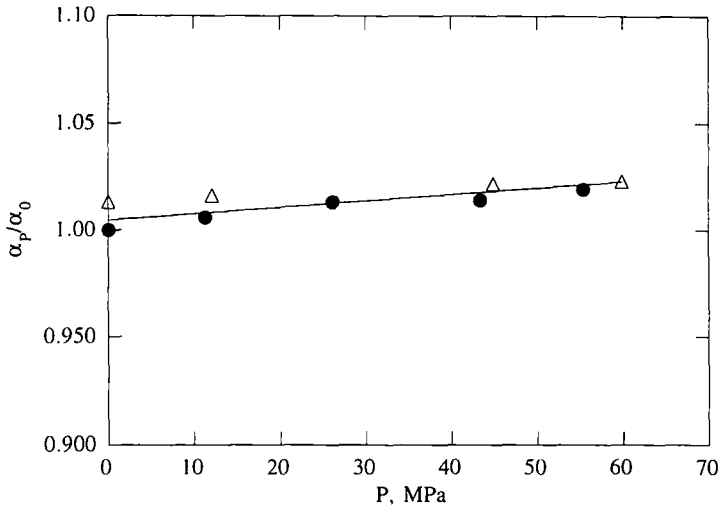


Fig. 2. The measured relative values α_p/α_0 of TCR as a function of the uniaxial pressure. The solid line is a least-squares fit to the data; the symbols correspond to the two runs as indicated in the legend to Fig. 1.

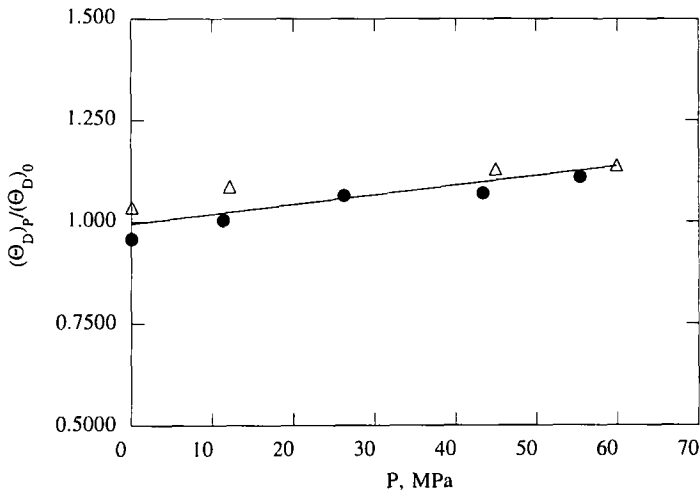


Fig. 3. The calculated $(\Theta_D)_p/(\Theta_D)_0$ as a function of uniaxial pressure from TCR data using Eq. (5). The symbols correspond to the two runs as indicated in the legend to Fig. 1. More details are given in the text.

The relative values of TCR for both runs as a function of uniaxial pressure are shown in Fig. 2. Using a least-squares fit, the pressure dependence of TCR can be expressed as $\alpha/\alpha_0 = A + (0.30 \pm 0.05) \times 10^{-3} P$, where $A = 1.0016$, P is the pressure in MPa, and α_0 is the TCR of the Pt strip at 293 K and zero pressure.

In order to check the accuracy of the THS recording, the TCR was measured at atmospheric pressure with the conventional four-probe method, using a very small current over a certain temperature range. Very good agreement was obtained between the two recordings. The calculated Debye temperatures (see discussion) are presented as a function of pressure in Fig. 3. The scatter of the calculated values of Θ_D follows the scatter of the experimental TCR values. However, the Θ_D at atmospheric pressure and room temperature (293 K) is in agreement with the data given in the literature [16] that are based on entropy data at room temperature. The variation of the Debye temperature within the investigated pressure range is estimated from a least-squares fit to the data. The estimated value is $(d\Theta_D/dP)_T = (2.3 \pm 0.05) \times 10^{-3} K(\text{MPa})^{-1}$. To our knowledge, there is no data for platinum to compare with, however, a rough estimation can be made by considering the pressure dependence for similar metals. Our estimated value is reasonably good and lies close to the range of numbers [3–4] for these metals $[(2.32\text{--}4.9) \times 10^{-3} K \cdot \text{MPa}^{-1}]$ in spite of the difference between the compressibility values and other related pressure-dependent properties of such metals.

4. DISCUSSION

The electrical resistivity (ρ) as a function of temperature (T) and pressure (P), within the Block-Grüneisen approximation, is given by [17]

$$\rho_{\text{BG}}(T, P) = \frac{K}{\Theta_D} \left[\frac{T}{\Theta_D} \right]^5 \int_0^{\Theta_D/T} dz \frac{z^5 e^z}{(e^z - 1)^2} \quad (1)$$

where K , which is independent of Θ_D , can be expressed in terms of a collection of elementary constants as

$$K = \frac{3\pi h}{4k_B e^2} \frac{R_D^6 C(0)^2}{MNR_V^4 V_V^2} \quad (2)$$

Here h , k_B , e , M , and N are Planck's constant, Boltzmann's constant, elementary charge, ionic mass, and number of unit cells per unit volume, respectively. $R_D = (6\pi^2 N)^{1/3}$ is the radius of Debye sphere, V_V is the

harmonic mean velocity of electrons at the Fermi surface, $R_F = (3\pi^2 n)^{1/3}$ is the Fermi radius, where n is the number of electrons per unit volume, and $C(o)$ represents the phonon–electron interaction energy.

The main pressure dependence for some of the above-mentioned parameters in Eq. (2) can be elucidated as follows. First, R_F changes because of the change in size of the unit cell under pressure. Second, $C(o)$ is an essential part of the matrix elements, and it is proportional to $n/N(E_F)$ for N -process, where $N(E_F)$ is the density of electronic states at the Fermi level. Thus we can see the implicit pressure dependence of this parameter in $N(E_F)$ or E_F , which depends on the band structure and mainly the ratio of electron density to energy level density at the Fermi surface. Equation (1) is an approximation within the Debye limit neglecting Umklapp processes, and it consists exclusively of contributions from electron–phonon scattering. Other contributions from electron–electron scattering may influence the dependence of $\rho_{BG}(T, P)$. However, such contributions are more dominant only at sufficiently lower temperatures [18]. Furthermore, in order to investigate the pressure and temperature dependence of the electrical resistivity of platinum on the above parameters, we may rewrite Eq. (1) in the following general expression: $\rho_{BG}(T, P) = (K/T) f(T/\Theta_D)$. In this expression, including the contributions from Umklapp processes will change the form of $f(T/\Theta_D)$, but not its functional dependence on the ratio T/Θ_D . It thus follows, by logarithmic differentiation of Eq. (1), that one may write the following [19]:

$$\frac{\partial \ln \rho_{BG}}{\partial \ln V} = \frac{\partial \ln K}{\partial \ln V} + \gamma_G \left[1 + \frac{\partial \ln \rho_{BG}}{\partial \ln T} \right] \quad (3)$$

where V is the sample volume, and $\gamma_G = -[\partial \ln \Theta_D / \partial \ln V]$ is the lattice Grüneisen constant. At relatively high temperatures $T > \Theta_D$, the first term of the expansion of Eq. (1) applies (see next section), and if we allow the pressure to vary at constant temperature, then Eq. (3) will give

$$\frac{\partial \ln \rho_{BG}}{\partial \ln V} = \frac{\partial \ln K}{\partial \ln V} + 2\gamma_G \quad (4)$$

which implies that the dependence of resistivity on pressure can be broken into two parts, the first giving the change under pressure of the Fermi surface and the electron–phonon matrix elements and the second describing the extent to which the phonon system entropy is lowered (lattice stiffening). The rightmost term in Eq. (4) can be obtained from the thermal expansion coefficient and compared with the experimental value of

$[\partial \ln \rho_{BG}/\partial \ln V]$; deduced from division of the PCR by compressibility. These values for platinum are given by Mott and Jones [20] as

$$2 \frac{\partial \ln \Theta_D}{\partial \ln V} = 5.08, \quad \frac{\partial \ln \rho_{BG}}{\partial \ln V} = 5.6 \quad (5)$$

Thus, from Eq. (4) we get $[\partial \ln K/\partial \ln V] = 0.52$. Using our PCR data and the data at room temperature given by Hanneman and Gatos [21] for the compressibility and γ_G of platinum, we get $[\partial \ln \rho_{BG}/\partial \ln V] \approx 6$, then from Eq. (4) we obtain $[\partial \ln K/\partial \ln V] \approx 0.7$. From these two independent calculations [see Eq. (4)], the two relatively low values obtained for the term $[\partial \ln K/\partial \ln V]$ imply that the decrease in resistance of platinum with pressure originates predominantly from $2\gamma_G$ or the "lattice stiffening" term. According to Mott and Jones [20], this means that the atoms of a metal under pressure, being closer together, are held in position by stronger forces and therefore, at given temperatures, vibrate with a lower amplitude than at atmospheric pressure. Nevertheless, since for $T > \Theta_D$ the resistance is proportional to the mean square of the atomic vibrations, it follows that the resistance is lowered.

In other words, the change in resistance under pressure of platinum is due mainly to the change in the amplitude of the atomic vibrations, which is proportional to the change in Debye temperature [20]. Furthermore, Bundy and Strong [22] have found that, in many simple metallic systems at ordinary temperatures, the major cause of resistance is due to the scattering of electrons by lattice waves. Their view is supported by a comparison between two formulas for the pressure coefficient of resistance. The two formulas are based on a rigid ion model, respectively, with and without conjunction to the tight-bonding approximations. In either case, they have concluded that the effect of pressure on Debye temperature is the predominant term and the resistance of such metals is expected to decrease with increasing pressure, as the disorder arising from lattice vibration is decreased. In the investigated pressure range, our analysis support this interpretation and verify the resistivity pressure dependence for such metals.

4.1. Pressure Dependence of Θ_D

In order to associate the pressure dependence of the Debye temperature with the pressure dependence of the electrical resistivity, we use a series expansion of the integral given by Eq. (1). This expansion is in agreement

with the integral to within 0.6% for $T \geq \Theta_D/2$. The resistivity ρ_{BG} can then be given by the following expression [18]

$$\rho_{BG}(T, P) = \frac{KT}{4\Theta_D^2} \left[1 - \frac{1}{18} \left(\frac{\Theta_D}{T} \right)^2 + \frac{1}{480} \left(\frac{\Theta_D}{T} \right)^4 \right] \tag{6}$$

where Θ_D and K are expected to contribute to the pressure dependence of ρ_{BG} , with a different strength. At any desired pressure value, the experimental TCR data can be directly related to the Debye temperature by using the basic definition of the TCR(α). Then from Eq. (6) we obtain

$$\alpha(T, P) = \frac{1}{\rho} \frac{d\rho}{dT} = \frac{1}{T} + \frac{1}{T} \left[\frac{\left(\frac{1}{9} \left(\frac{\Theta_D}{T} \right)^2 - \frac{1}{120} \left(\frac{\Theta_D}{T} \right)^4 \right)}{\left(1 - \frac{1}{18} \left(\frac{\Theta_D}{T} \right)^2 + \frac{1}{480} \left(\frac{\Theta_D}{T} \right)^4 \right)} \right] \tag{7}$$

The interesting aspect of Eq. (7) is that an accurate determination of α as a function of pressure will directly reveal the pressure dependence of the Debye temperature without involving K , which contains a large number of parameters. Equation (7) is used to determine the isobaric Θ_D values from the experimental isobaric values of α (see Figs. 2 and 3). The implicit pressure dependence of Θ_D for platinum was estimated from Fig. 3 to be $\approx 2.3 \times 10^{-3} \text{ K(MPa)}^{-1}$. The reliability of this result can be roughly verified by using the basic definition of γ_G , i.e.,

$$\gamma_G = - \frac{\partial \ln \Theta_D}{\partial \ln V} = \frac{B_T}{\Theta_D(P, T)} \left(\frac{d\Theta_D}{dP} \right)_T$$

or

$$\left(\frac{d\Theta_D}{dP} \right)_T = \frac{\Theta_D(P, T) \gamma_G}{B_T} \tag{8}$$

where $B_T = -V(dP/dV)$, is the isothermal bulk modulus and equals the inverse of the compressibility (β). Using Eq. (8) and the corresponding values for platinum at room temperature that are given in the literature [21, 16], i.e., $\Theta_D = 228 \text{ K}$, $\gamma_G = 2.66$, and $\beta = 3.6 \times 10^{-6} \text{ MPa}^{-1}$, we obtain for the pressure dependence of Θ_D a value $\approx 2 \times 10^{-3} \text{ K(MPa)}^{-1}$, which is in good agreement with the estimated result from our experimental data. We have used the above analysis just to illustrate the dominant role of pressure on the behavior of Θ_D . At this point, it should be noted that, in this analysis, we have used expressions derived for hydrostatic pressure as

the best alternative to examine our data and as the closest approximation to adapt a condition of relatively thin metallic foil under uniaxial pressure. Moreover, there are many approximations involved in our analysis such as neglecting possible contributions from Umklapp processes, electron-electron scattering, Fermi energy variation, and/or variation of any of the band structure quantities, etc. Furthermore, the variations of the thermal properties of fused quartz under pressure might not be negligible as it was postulated. However, our measurements may still exhibit the dominant features of the pressure dependence of the investigated properties for platinum and possibly for other similar fcc cubic metals as well [21].

5. CONCLUSIONS

Within the investigated pressure range, our analysis supports the interpretation that the change in resistance of platinum under pressure is due mainly to the change in the amplitude of the atomic vibrations, which is directly proportional to the change in Debye temperature.

The results were reasonably good in spite of the many approximations involved either by using expressions derived for, hydrostatic pressure or by neglecting possible contributions from various physical processes. As a consequence, the analysis cannot be regarded as highly precise but it almost certainly reflects the expected general behavior accurately.

Finally, this work demonstrates how the THS method can be used for studying the electrical properties of metals as a function of both temperature and pressure. When measuring the TCR by this method, the rather difficult experimental problem of establishing isothermal conditions for series of temperatures at each pressure is avoided. Furthermore, in conventional studies to obtain the TCR with the same accuracy, one would have to cover a quite substantial temperature interval.

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