

which gives the isothermal bulk modulus $K^T = 2060$ kbar as compared to the adiabatic value (Table II) of $K^S = 2090$ kbar. For the shear modulus we have, because of Eq. (6), the results $G^S = G^T$. This result is obvious, because there is no thermoelastic effect associated with the shear mode. However, the point is emphasized here, because it apparently has not been realized by all workers.⁹

To calculate the Voigt-Reuss-Hill isothermal Young's modulus we first make separate adiabatic to isothermal corrections for the Voigt and Reuss expressions then take the average value of the resulting isothermal moduli. We obtain the isothermal Young's modulus of 2204 kbar compared to the adiabatic value of 2207 kbar. (The value of 2210 kbar given in Table II was rounded off to three significant digits. This was not done for the present calculation because the adiabatic to isothermal correction is so small.) The smallness of the correction is due to the fact that the value of the shear modulus G dominates the value of E and, as discussed above, there is no adiabatic to isothermal correction for G . For Poisson's ratio we find, using a similar procedure to that used for E , the isothermal value $\sigma^T = 0.322$ compared to the adiabatic value of $\sigma^S = 0.324$.

Marlowe⁹ has published adiabatic to isothermal corrections for UO_2 based on the assumption (which he does not justify) that there is zero correction for σ . This procedure leads to a finite correction for G and a correction for E which is about three times larger than the one we have calculated. We believe that our procedure for calculating the adiabatic to isothermal corrections (zero correction for G) is better justified than Marlowe's. The corrections are, of course, quite small at room temperature.

D. Grüneisen constant, Debye temperature, and equation of state

Procedures for estimating the Grüneisen constant γ from single-crystal elastic-constant data have been extensively reviewed in the literature¹⁷ and will not be discussed here in any detail. These procedures generally involve some approximations which cannot be rigorously justified. We will use what is probably the simplest (and least justifiable) approach, which is to assume an isotropic model with the values of \bar{v}_l and \bar{v}_s which were computed above as the sound velocities. In this approach we expect γ to lie between the values of γ_{LT} and γ_{HT} defined by the following equations:

$$\gamma_{LT} = \frac{(\bar{v}_s/\bar{v}_l)^3 \gamma_l + 2\gamma_s}{(\bar{v}_s/\bar{v}_l)^3 + 2},$$

$$\gamma_{HT} = \frac{1}{3}(\gamma_l + 2\gamma_s). \quad (8)$$

In Eq. (8), γ_l and γ_s are defined as

$$\gamma_s = \frac{1}{3} + K^T \left(\frac{\partial \ln \bar{v}_s}{\partial p} \right)_T,$$

$$\gamma_l = \frac{1}{3} + K^T \left(\frac{\partial \ln \bar{v}_l}{\partial p} \right)_T \quad (9)$$

Using the values of \bar{v}_l , \bar{v}_s , and their pressure deriva-

tives given above we obtain $\gamma_s = 2.1$ and $\gamma_l = 2.4$, which yield $\gamma_{HT} = 2.2$ and $\gamma_{LT} = 2.1$. The values of the thermal Grüneisen parameter reported in the literature have a range of values, possibly because of sample-to-sample variations. Hall¹⁸ reports a room temperature value of 1.8 as calculated from data of Burdick and Parker¹⁹ (thermal expansion) and of Rand and Kubaschewski²⁰ (heat capacity). Using the value of α quoted above and the heat-capacity data of Moore and Kelley²¹ we obtain the same value of $\gamma_{th} = 1.8$. Marlowe and Kaznoff²² obtain values near 1.7, while Winslow⁶ uses a value of 2.0.

Elastic data can be used to estimate the Debye temperature θ . The appropriate equation, which again holds for an isotropic model, is¹⁷

$$\theta = \frac{h}{k} \left(\frac{9\rho N}{4\pi M} \right)^{1/3} \left(\frac{2}{\bar{v}_s^3} + \frac{1}{\bar{v}_l^3} \right)^{-1/3}, \quad (10)$$

where h is Planck's constant, k is Boltzmann's constant, and N is Avogadro's number. Using the values of \bar{v}_s and \bar{v}_l obtained above we obtain a Debye temperature of $\theta = 385$ °K. Marlowe and Kaznoff²² give a value of $\theta = 875$ °K computed from their elastic data. It is very difficult to understand this large discrepancy, since the elastic data are in reasonably good agreement. One possible explanation is that Marlowe and Kaznoff may have made an algebraic error in evaluating Eq. (10); in this regard note that the ratio of the two Debye temperatures is $875/385 \approx 10^{1/3}$. Jones *et al.*¹⁶ obtain a value of $\theta = 160$ °K from low-temperature specific-heat data. It has been pointed out previously,^{22,23} however, there is a magnetic contribution to the specific heat at low temperature due to the 31 °K antiferromagnetic transition which makes a reliable determination of the Debye temperature difficult. Dolling *et al.*²³ have fitted their neutron diffraction data on UO_2 to a shell model and have plotted the temperature dependence of the predicted Debye temperature between 0 and 500 °K. The 0 °K value for θ is $\theta = 395$ °K in good agreement with our value of $\theta = 385$ °K.

Anderson²⁴ has discussed the use of the pressure derivative of the isothermal bulk modulus dK^T/dp to estimate the high-pressure compression of solids via the Murnaghan equation of state. This equation is

$$\ln \frac{V}{V_0} = \left(\frac{dK^T}{dp} \right)^{-1} \ln \left(1 + p \frac{d \ln K^T}{dp} \right). \quad (11)$$

We have followed the procedure given by Anderson²⁴ to obtain dK^T/dp from our value of $dK^S/dp = 4.69$ (Table II). We obtain $dK^T/dp = 4.81$, which gives the following compression equation

$$V/V_0 = (1 + 0.00233p)^{-0.208}. \quad (12)$$

In summary, we have measured the elastic constants of UO_2 at high pressure, and these constants exhibit normal and linear increases with pressure up to 20 kbar. There is no evidence for a pressure-induced room-temperature phase transition up to this pressure. The data have been used to calculate various elastic properties of UO_2 and compared to other data and calculations where possible.

ACKNOWLEDGMENTS

Thanks are due to H. J. Anderson for supplying the excellent UO_2 samples and to J. E. Clickner for technical assistance.

*This work is supported by the U. S. Energy Research and Development Administration.

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