

Theoretical isothermal equation of state of rhenium

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A first-principles computation of the zero-degree isotherm has been carried out for Re, employing a linear muffin-tin orbital electron-band theory technique. This computed isotherm departs significantly from the isotherm derived from shock-wave data, but is in reasonable agreement with those from empirical equations of states based on zero-pressure parameters. Consequently, it is suggested that the 200–250-GPa pressures achieved by Vohra, Duclos, and Ruoff in recent diamond-anvil-cell experiments are underestimated by about half a megabar.

Recently, there has been interest in the high-pressure behavior of Re ($Z = 75$). It has been used as a gasket material in high-pressure diamond-anvil-cell experiments.^{1,2} Because of its higher yield strength, it is expected to avoid “punchthrough” at the corners of the diamond until higher pressures are reached. Vohra, Duclos, and Ruoff³ have shown that this material is stable in its ambient-pressure crystal structure (i.e., hexagonal close packed, hcp) up to 216 GPa and the axial ratio (c/a) is independent of pressure within the experimental errors. More recently, they have used Re to calibrate the ruby fluorescence method for pressure determination using x-ray-diffraction methods. It has been suggested that above 200 GPa the extrapolation of the ruby sale, previously calibrated up to 180 GPa, is erroneous.⁴ In all these experiments, Vohra *et al.* used the isothermal equation of state (EOS) of Re, derived from shock-wave data.⁵ This is, in turn, based on shock-wave data up to 135 GPa. To check how far extrapolations of this EOS above 200 GPa are valid, we have carried out a first-principles computation of the zero-degree isotherm of Re. Comparisons are also presented with isotherms based on parameters derived from ultrasonic measurements.

For the first-principles calculation, based on an electron-band-theory method, the pressure was written as the sum of three terms,⁶

$$P(V) = P_{\text{LMTO}} + P_{\text{MT}} + P_{\text{core}} \quad (1)$$

Here, P_{LMTO} is the electronic pressure corresponding to the conduction electrons, evaluated in the atomic-sphere approximation (ASA) by the linear muffin-tin orbital (LMTO) method of Andersen.⁷ It is given by

$$3PV = \sum_l \int^{E_F} dE N_l(E) S \phi_l^2(E, S) \times [(D_l - l)(D_l + l + 1) + (E - \epsilon_{xc})S^2], \quad (2)$$

where $N_l(E)$ is the projected density of states of angular momentum l and $\phi_l(E)$ is the amplitude at the sphere radius S of the normalized radial wave function at energy E . $D_l(E)$ is the logarithmic derivative and ϵ_{xc} is the exchange-correlation energy density at the sphere radius

(S) in the local approximation. In our calculations, using Skriver’s programs,⁸ we included all relativistic contributions except spin orbit, employed the exchange-correlation potential of von Barth and Hedin,⁹ and retained angular-momentum components up to $l = 3$. The electron states corresponding to the Xe core in Re were kept frozen. However, at higher compressions, the pressure contribution due to $5p$ -core states was evaluated separately by the method of Sikka and Godwal¹⁰ [this is the P_{core} term in Eq. (1)]. This contribution is small. It ranges from 0.6 to 4 GPa for the compressions considered here.

P_{MT} in Eq. (1) is due to intercellular Coulomb interaction beyond ASA, commonly known as the muffin-tin (MT) correction¹¹ and is given by

$$P_{\text{MT}} = \frac{\alpha q_s^2(S)(1 - 2Sq'_s/q_s)}{3SV} \quad (3)$$

Here q_s is the charge per atom corresponding to electron density $n(S)$ and $\alpha = 8.25$ mRy for the fcc lattice, which was assumed for all the calculations in this paper.¹² P_{MT} increases from 12.3 to 18.0 GPa at $V/V_0 = 1$ to $V/V_0 = 0.725$ ($V_0 = 99.2$ a.u. is the low-temperature

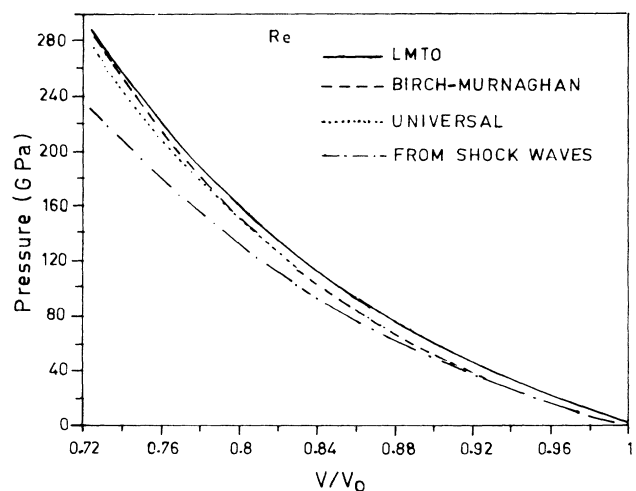


FIG. 1. Various zero-degree isotherms of Re.

TABLE I. Comparison of pressure values from different methods at the compression point ($V/V_0=0.734$) measured by Vohra *et al.* (Ref. 3).

	P (GPa)
Shock isotherm	216
Birch-Murnaghan fit ($B_0=372$ GPa and $B'_0=5.41$)	266
Universal EOS ($B_0=372$ and $B'_0=5.41$)	257
Our value	264

equilibrium volume¹³).

The calculated pressure at $S_{\text{expt}}=2.872$ a.u. corresponding to experimental V_0 is 1.3 GPa, and the calculated equilibrium radius is 2.875 a.u. The agreement between the two is remarkably close, considering that Re is one of the least compressible materials and a slight error in calculations will produce large changes in pressure. The theoretical P - V curve is presented in Fig. 1, where it is compared with shock-derived zero-degree isotherm from Ref. 3. The numerical values corresponding to the compression, $V/V_0=0.734$ ($S=2.591$ a.u.), obtained by Vohra *et al.* are given in Table I. These show that the theoretical and shock-derived isotherms differ systematically, and at higher compressions the deviations are outside the accepted limits (e.g., $\sim 10\%$) for the agreement between such first-principles theories and experiments.¹⁴

The reasons for the above deviations may be as follows. (i) Re is a spd transition metal and a LMTO calculation may not place correctly the s , p , and d bands with respect to each other because of approximations in the LMTO procedure such as the local-density approximation. A consequence of the error in the placement of bands of different angular momentum is that the pressure contribution is different. However, changes of exchange-correlation expressions to other forms in our calculations did not produce any significant difference in the pressure values. (ii) The extrapolation of the shock data is not appropriate due to some electronic-structure changes (e.g., $s \rightarrow d$ transition, leading to a softening of the P - V curve) which occur beyond the range of available shock data. We rule this out, as our LMTO results (see Fig. 2) show that the respective populations of sp and d bands are remarkably constant up to $V/V_0=0.72$. (iii) There are some systematic errors in shock-wave data or in reduction procedures to zero-degree isotherm.

In connection with the last point, it is interesting to note that the computed Hugoniot curve of Walzer,¹⁵ using a semitheoretic approach, is harder than the experimental data. Further, this calculation uses the experi-

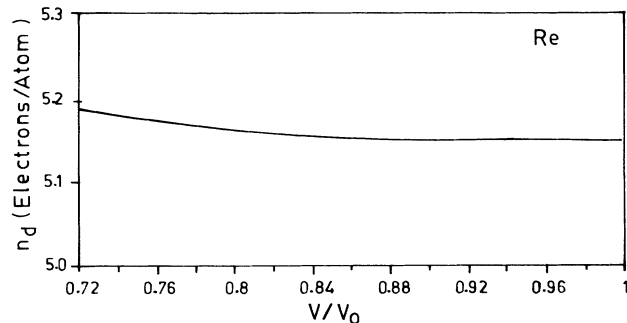


FIG. 2. d population vs V/V_0 of Re sp electrons at a given V/V_0 will be $7-n_d$.

mental value of the bulk modulus (B_0) at $V/V_0=1$ and predicts the value of the pressure derivative of the bulk modulus (B'_0). Walzer's value of $B'_0=5.388$ is in agreement with the ultrasonic measured value of 5.41, quoted by Steinberg,¹⁶ but differs from the value 4.05 from a Birch-Murnaghan fit¹⁷ to the shock isotherm. Again, Rose *et al.*¹⁸ have related B'_0 to other zero-pressure quantities, namely cohesive energy (ΔE_0), B_0 , and equilibrium Wigner-Seitz radius (r_{WS}),

$$B'_0 = 1 + \frac{2.3}{3} \frac{r_{\text{WS}}}{S_l}, \quad (4)$$

where

$$S_l = \left[\frac{\Delta E_0}{12\pi B_0 r_{\text{WS}}} \right]^{1/2}. \quad (5)$$

Using (4) and (5), they get $B'_0=5.72$. In view of the above, we accepted $B_0=372$ GPa and $B'_0=5.41$ and computed isotherms by Birch-Murnaghan fitting and use of the universal form¹⁹ of equations of state.²⁰ These are also included in Fig. 1 and Table I. These support our theoretical curve and strongly indicate that the use of the shock isotherm of Re underestimates the pressure, when used as a standard in diamond-cell-based x-ray-diffraction experiments. In fact, Vohra *et al.*^{3,4} might have achieved more than 300-GPa rather than 250-GPa pressures in their experiments—the highest so far in x-ray-diffraction experiments. Our study also suggests that (i) B'_0 be remeasured, and (ii) that shock Hugoniot points on crystal-density samples be measured above the currently available data up to 135 GPa.

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