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# Accuracy of equation-of-state formulations

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(February 1, 2008)

The accuracy of equation-of-state formulations is compared for theoretical total energies or experimental pressure-volume measurements for H<sub>2</sub>, Ne, Pt, and Ta. This spans the entire range of compression found for minerals and volatiles in the Earth. The Vinet equation is found to be most accurate. The origin of the behavior of different equation-of-state formulations is discussed. It is shown that subtle phase transitions can be detected by examining the residuals from an equation-of-state fit. A change in the electronic structure of Ta is found at high pressures using this procedure, and a possible new transition in H<sub>2</sub>.

## I. INTRODUCTION

In geophysics and high-pressure research, experimental or theoretical data consisting of pressure, temperature, and volume triplets PVT are parameterized to a functional form for ease of interpolation and extrapolation. These equations of state are then used to compute phase diagrams, or are used in geodynamic or shock compression modeling, etc. A recent book by Anderson (1995) comprehensively reviews equation-of-state formulations, and comprehensive reviews and comparisons of equations of state are given by Hama and Suito (1996), Stacey et al. (1981), and Duffy and Wang (1998). The primary purpose of this paper is to discuss the reasons for the accuracy of the most-used formulation, based on the Birch equation of state (Birch 1978) and compare with the Vinet equation of state (Vinet et al. 1987). Jeanloz (1988) has previously shown that the Birch equation of state and the Vinet equation of state can be similar up to moderate compressions. Here we show that this breaks down at high compressions, and for highly compressible materials the Vinet equation of state is considerably more accurate. A logarithmic equation of state (Poirer and Tarantola 1998) and another exponential equation of state (Holzapfel 1996) are discussed and compared with the Vinet and Birch equations. Finally, we show how subtle transitions can be detected by deviations from an equation of state.

The above equations of state are appropriate for isothermal data. To include thermal expansivity there are three main approaches that have been used. The first is to fit isotherms, and then tabulate or fit the parameters  $V_0$ ,  $K_0$ , and  $K_0'$  as functions of temperature. Since experimental data are not always collected along isotherms, that method is most amenable to analysis of theoretical results. Secondly, one can assume Debye and Mie-Grüneisen theory, and fit parameters for  $\Theta_D$ ,  $\gamma$ , and  $q$  to include thermal effects. Thirdly, one can directly model the thermal pressure. See Anderson (1995), Hama and Suito (1996), and Duffy and Wang (1998) for further discussion of thermal equations of state.

In order to test equation-of-state formulations, it is important to study large compressions, because most common equations of state will work reasonably over small compression ranges. Thus we choose to study the very compressible materials, hydrogen and neon. We also consider tantalum and platinum, which are useful pressure standards.

## II. ISOTHERMAL OR STATIC EQUATIONS OF STATE

The Birch equation of state (Birch 1978) is based on a series expansion of pressure

$$P(f) = 3K_0f(1+2f)^{\frac{5}{2}} \left[ 1 + \frac{3}{2}(K_0' - 4)f + \dots \right] \quad (1)$$

in terms of the Eulerian strain  $f$ , where

$$f = \frac{1}{2} \left[ \left( \frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right]. \quad (2)$$

and  $V_0$ ,  $K_0$ , and  $K_0'$  are the zero pressure volume, bulk modulus, and bulk modulus pressure derivative. Truncated as written it is called the “third-order” Birch equation. The fourth-order Birch equation, which includes another term in  $f^2$  and  $K_0''$  is useful for theoretical equations of state, but when applied to experimental data, the added parameter usually induces severe correlations in parameters so that they lose physical significance.

The Vinet equation (Vinet et al. 1987) is derived from a scaled approximate form for the energy:

$$E(r) = -\Delta E (1 + a^*) \exp[-a^*]; \quad a^* = \frac{r - r_0}{l} \quad (3)$$

where  $\Delta E$  is the binding energy, and  $r$  is the length per electron. This gives:

$$P(x) = 3K_0 (1 - x) x^{-2} \exp\left[\frac{3}{2}(K'_0 - 1)(1 - x)\right] \quad (4)$$

where  $x = \left(\frac{V}{V_0}\right)^{\frac{1}{3}}$ . The energy can then be expressed as

$$E = E_0 + \frac{4K_0V_0}{(K'_0 - 1)^2} - 2V_0K_0(K'_0 - 1)^{-2}(5 + 3K'_0(x - 1) - 3x) \exp\left(-\frac{3}{2}(K'_0 - 1)(x - 1)\right). \quad (5)$$

The Holzapfel equation of state (Holzapfel 1996) is similarly given by

$$P(x) = 3K_0x^{-5}(1 - x) \exp[(cx + c_0)(1 - x)] \quad (6)$$

where  $c_0$  and  $c$  are chosen to give  $K'$  and the limiting Fermi gas behavior as  $x \rightarrow 0$ . If  $c = 0$ , one gets a 3 parameter ( $V_0$ ,  $K_0$ , and  $K'_0$ ) equation of state that behaves better at extreme compression (Hama and Suito 1996):

$$\begin{aligned} P(x) &= 3K_0x^{-5}(1 - x) \exp[c_0(1 - x)] \\ &= 3K_0x^{-5}(1 - x) \exp\left[\frac{3}{2}(K'_0 - 3)(1 - x)\right] \end{aligned} \quad (7)$$

Finally we consider the logarithmic equation of state recently proposed by Poirer and Tarantola (1998), derived similarly to the Birch equation, but where the strain is defined as  $\varepsilon = \ln \frac{V}{V_0}$ , rather than as in eq. 2, giving at third-order,

$$P = K_0 \left[ \ln \frac{V_0}{V} + \left(\frac{K'_0 - 2}{2}\right) \left(\ln \frac{V_0}{V}\right)^2 \right]. \quad (8)$$

Now we examine the application of these equations of state for several materials. First we consider the extremely compressible behavior of hydrogen. Hemley et al. (1990) showed in analyses of x-ray diffraction data for hydrogen that the Vinet equation of state is considerably more accurate than the Birch equation. The experimental equation of state, (room temperature data is corrected to 4 K), is shown in Figure 1 along with equation-of-state fits, and the fitted parameters and  $\chi^2$  are shown in Table I. For most of the fits,  $V_0$  was fixed at its known value, 23.0 cm<sup>3</sup>/mole (Silvera 1980). The best fit is given by the Vinet equation of state, with acceptable fits using Birch or Holzapfel, but the logarithmic equation of state fails completely. When the parameter  $V_0$  is relaxed for the Vinet equation there is no significant change in the fit, and the parameters become less well determined. Figure 1b shows the residuals of the fits (the logarithmic residuals go off scale as shown). Interestingly, there is a peak in the residuals at 40 GPa, which may be a subtle transition, or change in compression mechanism, previously undiscovered, or a small problem with a subset of the data. Note that this deviation is completely invisible on the P-V curve itself. This illustrates the usefulness of having a good equation-of-state formulation; even small deviations may indicate possible transitions that should be examined more closely. Secondly, it illustrates that one only expects equations of state to work well under compression with no underlying transitions. If there are even subtle electronic or structural transitions, these will affect the equation of state significantly.

One of the tests of an equation-of-state fit is the accuracy with which it reproduces known zero-pressure parameters. To this end, high-pressure static compression data can be compared with low-pressure elasticity measurements, including data from ultrasonic experiments, Brillouin scattering, or in some cases high-precision static compression data. Useful low-pressure static compression data exist for hydrogen because of its very high compressibility. Swenson and Anderson (1974) reported  $K_{0T} = 0.17 \pm 0.06$  GPa for n-H<sub>2</sub> from volumetric strain measurements to 2.5 GPa at 4.2 K. The results are in excellent agreement with those of Wanner and Meyer (1973), who obtained  $K_0 = 0.174 \pm 0.010$  GPa for single-crystal n-H<sub>2</sub> at 4.2 K using ultrasonic methods. The latter number provides the best comparison with the present analysis (e.g., for n-H<sub>2</sub>). These results are also close to zero-pressure Brillouin scattering results obtained at T=4 K for p-H<sub>2</sub> by Thomas et al. (1978); the latter obtained  $K_{0S} = 0.173 \pm 0.001$ , with  $K_{0T} = 0.162$  GPa (corrected for isothermal conditions). Udovidenko and Manzhelli (1970) performed accurate static compression (volumetric) measurements on p-H<sub>2</sub> from 0 to 18 MPa (down to 6 K) and obtained  $K_{0T} = 0.186 \pm 0.006$  GPa. The

neutron diffraction study of p-H<sub>2</sub> to 2.5 GPa by Ishmaev et al. (Ishmaev et al. 1983) gave  $K_{0T} = 0.186 \pm 0.03$  and  $K'_{0T} = 6.33 \pm 0.2$ . The Vinet  $K_0$  is close to that determined directly, but the Birch and Holzzapfel  $K_0$ 's are way too high. The deviation in  $K_{0,T}$  with the Vinet equation may be due to being thrown off by the equation of state glitch at 40 GPa, or may be due to insufficient flexibility in the Vinet equation over this large compression range. In order to examine this possibility, we considered the extended Vinet equation given by Moriarty (1995) and Vinet et al. (1989):

$$P = 3K_0(1-x)x^{-2} \exp \left[ \frac{3}{2}(K'_0 - 1)(1-x) + \beta(1-x)^2 + \gamma(1-x)^3 \dots \right], \quad (9)$$

where  $\beta = \frac{1}{24}(-19 + 18K'_0 + 9K_0'^2 + 36K_0K_0'')$  and fit the H<sub>2</sub> data varying  $\beta$  as well as  $V_0$ ,  $K_0$ , and  $K'_0$ . As shown in table I,  $K_0 = 0.15 \pm 0.02$ , now in excellent agreement with the ultrasonic bulk modulus. The peak in residuals survives this higher-order fit. Other extensions to the Vinet equation are possible, and it would seem more physical to add further terms to the prefactor of eq. 3, such as  $b(a^*)^{-c}$ , rather than terms in the exponential, but such extended equations of state will not be considered further here.

Secondly, we consider another soft material, Ne, from fitting theoretical Linearized Augmented Plane Wave (LAPW)(Singh 1994) local density approximation (LDA)(Hedin and Lundqvist 1971) results. Figure 2 shows the fitted equation of state, the residuals of the fit, and the resulting PV curves. equation-of-state parameters are shown in Table II. Only the Vinet and Birch equations are compared since the logarithmic equation of state fails above for H<sub>2</sub>, and the energy expression obtained from integrating the Holzzapfel PV equation is not closed form. The Vinet equation is superior to the Birch equation again, and does an excellent job simultaneously over the large energy scale of large compressions, and the small energy scale near the minimum. We also show results for the fourth-order Birch equation, which in spite of an additional parameter, is still not as good as the Vinet equation. As more parameters are added, the quality of the fit improves, but the correlations among individual parameters increases.

Next we consider equations of state of two stiff metals, Ta and Pt (tables IV and III and Figures 3 and 4). Energies were computed using the LAPW method and the Generalized gradient approximation [GGA-PBE, (Perdew et al. 1996)]. The Vinet equation fits better than the Birch equation for Pt, but for Ta the Birch equation fits better. However, examination of the residuals for Ta (Fig. 4c) shows that there is a peak in the residuals at  $\sim 10.5 \text{ \AA}^3$ , and closer study shows a change in the occupied bands (and thus the Fermi surface) around that volume, where the  $t_{2g}$  states at  $\Gamma$  move below the Fermi level,  $E_F$ , (Fig. 5) so the improved fit using Birch is a side effect of this anomaly. Fitting only the data above  $13 \text{ \AA}^3$  shows a greatly improved fit, and a better fit for Vinet than Birch. This again illustrates the utility of examining residuals from well founded equations of state such as the Vinet equation in order to find subtle transitions.

### III. DISCUSSION

We have considered a range of materials from very compressible to more incompressible, covering the entire range of compression of minerals and volatiles in the Earth. An equation of state reflects the underlying interactions potential among the ions and electrons that make up a crystal. Thus, a useful way to compare different equations of state is to compare the implied assumptions about the interaction potential. First we consider the Birch equation in some detail. As normally expressed, it is not obvious that the Birch equation in terms of Eulerian strain

$$E = \sum_{n=0}^N a_n f^n = \sum_{n=0}^N a_n \left[ \frac{1}{2} \left( \eta^{-\frac{2}{3}} - 1 \right) \right]^n, \quad (10)$$

where  $\eta = \frac{V}{V_0}$ , is actually a series for energy  $E$  in  $\left( \frac{V}{V_0} \right)^{-\frac{2n}{3}}$ . For example, if  $N = 3$

$$E = a_0 - \frac{1}{2}a_1 + \frac{1}{4}a_2 - \frac{1}{8}a_3 + \left( \frac{1}{2}a_1 - \frac{1}{2}a_2 + \frac{3}{8}a_3 \right) \eta^{-\frac{2}{3}} + \left( \frac{1}{4}a_2 - \frac{3}{8}a_3 \right) \eta^{-\frac{4}{3}} + \frac{1}{8}a_3 \eta^{-2} \quad (11)$$

The  $\frac{2}{3}$  powers arise from distance squared in finite strain theory, so one can think of the Birch equation as a series in "inverse length squared." The reason only even terms in length are included is in order to preserve rotational invariance in the strain energy expansion for general strains. Thus, the Birch equation assumes that the underlying potential can be represented as a series in  $(1/r^{2n})$ . The commonly used third-order Birch equation (with parameters

$V_0$ ,  $K_0$ , and  $K_0'$ ) includes  $n = 1, 2$ , and  $3$ . Now, it is well known that polynomials can behave poorly (wobble) and extrapolate poorly (go crazy outside the range of the fit), and this is in fact a problem with using the Birch equation to too high an order. Note also that it is not a convergent series (unless the coefficients obey  $\frac{a_n}{2a_{n-1}} < f$ , which is not expected in a fit). Under compression,  $\eta = V/V_0 < 1$  so that for larger  $n$  the terms  $\eta^{-\frac{2n}{3}}$  blow up. The truncated series may still do well, as it does up to moderate compressions, if the truncated series represents the interatomic potential accurately. However, there is no fundamental reason to expect  $(1/r^{2n})$  to well represent interatomic interactions, so it is not surprising that the Birch equation is not perfect. Indeed, the energy expression from the Birch equation has a non-physical hump at expanded volumes that then decays with increasing volume, whereas the Vinet and Holzapfel equations converge smoothly to a constant at large volumes, being consistent with physically based potentials. The logarithmic equation of state unphysically diverges with expansion.

Another question that often arises with regard to the Birch equation is why  $K_0' = 4$  often works so well. Note that for moderate compressions (say 10% or less) higher order terms in eq. 1 are quite small. For example, if  $\eta = 0.9$ , then  $f = 0.036$ , so that deviations from  $K_0' = 4$  are only reflected in a few percent or less of the pressure, and higher order terms, with factor  $f^2 = 0.0013$  are only affected at the 0.1% level.

The Lagrangian strain

$$\bar{\varepsilon}_L = \frac{1}{2} \left( \eta^{\frac{2}{3}} - 1 \right). \quad (12)$$

can be used instead of the Eulerian strain (Thomsen 1970), but the Lagrangian equation of state is not satisfactory at high pressures since it saturates with increasing density. The Lagrangian strain gives a series in  $E$

$$E = \sum_{n=0}^N a_n \bar{\varepsilon}_L^n = \sum_{n=0}^N a_n \left[ \frac{1}{2} \left( \eta^{\frac{2}{3}} - 1 \right) \right]^n = \sum_{n=0}^N b_n \eta^{\frac{2n}{3}} \quad (13)$$

which has the advantage that the series converges in  $\eta^{\frac{2n}{3}}$  for  $\eta < 1$ , but since  $\sum r^{2n}$  does not look like an interatomic potential, it does not work well compared with the Eulerian strain.

The Hencky (logarithmic) strain (Poirer and Tarantola 1998)

$$d\varepsilon_H = \frac{dl}{l}; \varepsilon_H = \ln \frac{l}{l_0} \quad (14)$$

shares a similar shortcoming. Though it looks reasonable as a measure of finite strain the effective potential,  $\sum (\ln r)^n$  is not very physical. The Hencky potential can be expanded to look like  $-a(1/r) + b(1/r)^{(3K_0'-7)}$  (Poirer and Tarantola 1998). The attractive part is long-ranged and ill-conditioned and the repulsive part is too soft.

In contrast, the Vinet equation is based on a potential at the outset (eq. 3). This potential was introduced by Rydberg (1932), who used it not for an equation of state (Stacey et al. 1981), but as a form for the *intramolecular* potential in  $H_2$  and other simple molecules for obtaining solutions to the anharmonic Schrodinger equation for fitting and comparison to molecular vibrational spectra. The Vinet equation of state works surprisingly well for a wide range of types of materials, and for compressions of up to  $\eta = 0.1$ , as has been discussed in detail (Hama and Suito 1996; Vinet et al. 1987). Note the sign errors in eq. 102 of Stacey et al. (1981).

One failure of the Vinet equation is that it does not give the proper behavior at even greater compressions, and does not merge into electron gas (Thomas-Fermi), or quantum-statistical (Kalitkin and Kuz'mina 1972) behavior at extreme compression. Holzapfel found expressions that do have the proper limiting form, such as eqs. 7 and 6 above. The underlying energy expression, however, of even the simplest Holzapfel equation is exceedingly complex

$$E(x) = \frac{1}{8} x^{-5} K_0 (9 \exp \left[ \frac{3}{2} (K_0' - 3) (1 - x) \right] (-4 + 2(-5 + 3K_0') x) \quad (15)$$

$$+ 3 \exp \left[ \frac{3}{2} (K_0' - 3) x \right] (15 - 14K_0' + 3K_0'^2) x^2 \text{Ei} \left[ -\frac{3}{2} (K_0' - 3) x \right]),$$

where

$$\text{Ei} = - \int_{-z}^{\infty} \frac{e^{-t}}{t} dt.$$

The fact that the Holzapfel equation works less well than Vinet for H<sub>2</sub> and other materials (Hama and Suito 1996) up to almost 10-fold compression suggests that this underlying potential does not accurately represent the interaction potential in solids, though it has the correct limiting behavior at extreme compressions.

An equation of state that agrees with the quantum statistical model (Kalitkin and Kuz'mina 1972) at extreme compression, which is obtained by assuming homogeneous compression of spherical atoms and expanding the Hartree-Fock equations in density and dropping terms of order  $\hbar^2$  and higher, was developed by Hama and Suito (1996). This should become accurate at lower pressures than Thomas-Fermi. We did not test this here, but in Hama and Suito's tests, it seems to work well from 0 to 10 fold compression or more for rare gases, simple metals, and ionic compounds. Further exploration of this approach is warranted for extreme compressions. Their equation of state is:

$$P = 3K_0x^{-5}(1-x)\exp[(\eta-3)(1-x) + (\xi-3/2)(1-x)^2] \quad (16)$$

where  $x = \left(\frac{V}{V_0}\right)^{\frac{1}{3}}$ , as above, and  $\xi$  is determined from the quantum statistical model (Kalitkin and Kuz'mina 1972).

Finally, in comparing equations of state, note that correlations among  $V_0$ ,  $K_0$  and  $K'_0$  are much lower for Vinet than Birch, so parameters are better determined. In the Vinet equation,  $K'_0$  is inside exponential, and  $K_0$  in the prefactor, whereas in the Birch equation  $K_0$  and  $K'_0$  appear as products. In any case, it is very difficult to resolve  $V_0$  from  $V$ - $P$  data, especially for a high-pressure phase unstable at  $P = 0$ . Data usually only extends to  $P = 0$  at best, and it is thus difficult to obtain good values of  $K_0$  and  $K'_0$  (if not for a robust equation-of-state formalism) since one is trying to find first and second derivatives from one-sided data. This is one advantage of theory; results are available at negative pressure and  $V_0$  can be well constrained.

For strains less than 30%, it probably doesn't matter what equation of state you use, as was emphasized by Jeanloz (1988), but parameters will still be better determined with the Vinet equation (see also Hemley et al. 1990). For large strains, the Vinet equation is best, and forms such as the Holzapfel equation are required at extreme compressions.

#### ACKNOWLEDGMENTS

This research was supported by NSF grants EAR-9418934 and EAR-9706624, the NSF Center for High Pressure Research, and the Academic Strategic Alliances Program of the Accelerated Strategic Computing Initiative (ASCI/ASAP) under subcontract no. B341492 of DOE contract W-7405-ENG-48. Computations were performed on the Cray J90/16-4069 at the Geophysical Laboratory, supported by NSF grant EAR-9304624 and the Keck Foundation. We thank Orson Anderson, T. Duffy, and D.G. Isaak and for helpful discussions.

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TABLE I. Fitted equation-of-state parameters for H<sub>2</sub> pressure-volume experimental data.

	$\chi^2$	$V_0$ (cm <sup>3</sup> /mole)	$K_0$ (GPa)	$K'_0$	$K_0 K''_0$
Vinet	0.1901	23.0	0.250±0.004	6.56±0.02	
Vinet	0.1895	22.4±2.6	0.279±0.15	6.49±0.35	
Birch 3	0.6554	23.0	0.694±0.009	3.990±0.007	
Birch 4	0.2356	23.0	0.28±0.02	5.7±0.2	-9.4±1.2
Birch 4	0.4033	23.0	0.162	7.77±0.03	-23.4±0.3
Holzappel	0.4126	23.0	0.47±0.01	4.95±0.03	
Logarithmic	13.98	23.0	0.08±0.36	64.3±292.4	
Ext. Vinet	0.1623	23.0	0.15±0.02	8.0±0.4	-21.±2.

TABLE II. Fitted equation-of-state parameters for Ne LAPW (LDA) energy (Ryd, 1 Ryd=13.605 eV)-volume results.

	Vinet	Birch 3	Birch 4
$\chi^2$	$1.02 \times 10^{-9}$	$1.35 \times 10^{-7}$	$3.03 \times 10^{-9}$
$V_0$ (cm <sup>3</sup> /mole)	8.641±0.008	8.598±0.074	8.592±0.013
$K_0$ (GPa)	8.94±0.06	11.2±0.8	9.24±0.18
$K'_0$	7.192±0.009	6.07±0.14	7.51±0.11
$K_0 K''_0$	(-16.0) <sup>a</sup>	(-10.2) <sup>a</sup>	-21.1±0.98
$E_0$ (Ryd)	-256.7593±0.00005	-256.7658±0.0002	-256.7654±0.00003

<sup>a</sup>Not varied, result of formulation.

 TABLE III. Fitted equation-of-state parameters for Pt LAPW (GGA-PBE) energy (Ryd)-volume results ( $V > 10\text{\AA}^3$ ).

	Vinet	Birch	exp. <sup>a</sup>
$\chi^2$	$1.47 \times 10^{-7}$	$3.51 \times 10^{-7}$	
$V_0$ (cm <sup>3</sup> /mole)	9.448±0.007	9.445±0.011	9.09
$K_0$ (GPa)	248.9±0.7	238.6±1.1	278
$K'_0$	5.43±0.02	5.474±0.03	5.6
$E_0$ (Ryd)	-36893.5648±0.0002	-36893.5641±0.0002	

<sup>a</sup>(Holmes et al. 1989)

TABLE IV. Fitted equation-of-state parameters for Ta LAPW (GGA-PBE) energy (Ryd)-volume results.

	Vinet	Birch	Vinet ( $V > 13\text{\AA}^3$ )	Birch ( $V > 13\text{\AA}^3$ )	exp. <sup>a</sup>
$\chi^2$	$9.32 \times 10^{-7}$	$2.71 \times 10^{-7}$	$8.08 \times 10^{-9}$	$1.31 \times 10^{-8}$	
$V_0$ (cm <sup>3</sup> /mole)	11.026±0.009	11.058±0.005	11.057±0.002	11.062±0.03	10.865
$K_0$ (GPa)	188.±1.8	188.±0.9	192.3±0.2	190.±0.3	195±5
$K'_0$	4.08±0.04	3.81±0.01	3.82±0.02	3.77±0.02	3.4±0.1
$E_0$ (Ryd)	-31252.3337± 0.0004	-31252.3339±0.0002	-31252.33425±0.00004	-31252.3342±0.00005	

<sup>a</sup>(Cynn and Yoo 1999)

#### IV. FIGURE CAPTIONS

Figure 1. Equation-of-state of hydrogen. (a) Experimental P vs. V. and equation-of-state fits. (b) Residuals of equation-of-state fits. Note that the logarithmic equation-of-state residuals go off scale.

Figure 2. Equation of state of neon from LAPW total energy computations within the LDA. (a) Energy versus volume and third-order Birch and Vinet fits. The inset (inset area is shaded in the larger figure) shows the fact that the Birch equation does not match the data at low pressures, whereas the Vinet works at both low and high compressions. (b) Pressure volume relations from the fits shown in (a) as well as a fourth-order Birch fit. In spite of the fact that all fits look good to the eye at high pressures in figure (a), the derived pressures differ by over 150 GPa at extreme compression. (c) Residuals for the fits. Note the large and systematic deviations in the third-order Birch fit. The fourth-order Birch is almost as good as Vinet, but with one additional fitting parameter.

Figure 3. Static equation of state for Pt to extreme compressions computed using LAPW and GGA. (a) Energy versus volume and Vinet, third- and fourth-order Birch fits. The “low P” Vinet fit is to volumes greater than  $10 \text{ \AA}^3$ . (b) Pressure versus volume from the fits. The Vinet and fourth-order Birch give similar results over the extreme pressure range. A Vinet fit to a smaller pressure range gives better constrained equation of state parameters and smaller residuals, but the pressures are very close to those computed using the large data range. (c) Residuals of the Vinet fits, and the lower pressure third-order Birch fit. Note that there are no systematic deviations.

Figure 4. Static equation of state for Ta computed using LAPW and GGA. (a) Energy versus volume. Note that to the eye both fits appear perfect. (b) Pressure versus volume. In spite of the apparently excellent fits in (a), the pressure is significantly different under extreme compression. (c) Residuals of the fits. An electronic transition was hidden under the apparently smooth equation of state. There is a peak in the residuals at  $10.5 \text{ \AA}^3$ . When data is fit at  $V > 13 \text{ \AA}^3$ , the fit greatly improves and the residuals are much smaller.

Figure 5. Band structures of Ta at (a)  $V = 12.66 \text{ \AA}^3$  (5 GPa) and (b)  $V = 9.3 \text{ \AA}^3$  (460 GPa). There is a major change in the occupied states as the  $t_{2g}$  states move below the Fermi level  $E_F$  at high pressures, crossing at a volume of  $11.67 \text{ \AA}^3$  (200 GPa). This change is responsible for a glitch in the equation of state.