Al as a Simple Solid: High Pressure Study to 220 GPa (2.2 Mbar)

Raymond G. Greene, Huan Luo, and Arthur L. Ruoff

Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

The static equation of state of Al has been measured to 220 GPa, corresponding to a compression of $V/V_0 = 0.50$. No phase transformation from the fcc to hcp phase was observed. The equation of state fits the H11 form for a simple solid as defined by W. B. Holzapfel [Phys. Rev. B **48**, 767 (1993)] with no free parameters. These results are also consistent with recent shock data on Al to a pressure of 1 TPa ($V/V_0 = 0.30$) [Phys. Rev. Lett. **60**, 1414 (1988)]. The ultrasonic, static, and shock equations of state of Al are reconciled and compared to theoretical predictions.

There is considerable interest in the high pressure study of solids. Comparison of observed to predicted crystal structures continues to stimulate both theory and experiment [1,2]. As a metallic element with no d shell electrons, a relatively low atomic number, and a simple structure, aluminum is especially amenable to theoretical modeling. The results of such modeling have then been used to predict structural phase transformations vs pressure and the equation of state (EOS) of Al, both of which can then be compared to experiment.

Transition pressures from fcc to hcp have been predicted at 120, 220, and 360 GPa by the linear muffin-tin orbital, *ab initio* pseudopotential, and generalized pseudopotential methods, respectively [3,4]. Modern diamond anvil cell (DAC) technology routinely achieves 100 GPa scale pressures for sample volumes of about 4 μmm^3, and the use of synchrotrons to provide the intense x-ray sources for energy-dispersive x-ray diffraction (EDXD) has also become standard practice. Nevertheless, 100 GPa scale experimental structural studies of Al remain quite difficult because of its relatively low atomic number and shear modulus.

There have also been theoretical predictions of the EOS of Al [5,6]. Holzapfel and co-workers have recently proposed an EOS for "simple" solids based on semiempirical considerations combined with the EOS of a solid line in the Thomas-Fermi limit and successfully applied this model to experiments on In to a pressure of 67 GPa ($V/V_0 = 0.62$) [7,8]. It is of interest to test this model to higher compression on lower atomic number materials. The present results indicate that Al is such a simple solid.

Al has also been the subject of numerous shock-type experiments [9–13]. An ultrahigh pressure of 2 TPa has been reached by Ref. [9], and the EOS has been measured to 1 TPa [10]. However, limited structural information is obtained, compared to static DAC experiments which are isothermal. Previously published DAC work on Al achieved a pressure of 12 GPa [14,15]. Unpublished work in our laboratory observed no structural phase transformation from the fcc structure to 150 GPa, as discussed in [16]. This experiment extends that result and

the static EOS of Al from 12 to 219 GPa. It has also yielded a positive result as a consistency check between shock, static, and ultrasonic EOS data of Al and between shock and static EOS's of Al and Pt.

A commercial aluminum powder of 99.99% purity was used as the sample. A DAC of the controlled displacement type was used as the pressure vessel [17]. Two separate experiments were performed at room temperature.

In the first experiment single-beveled diamond anvils with 50 μm flats were used. The sample chamber was a 50 μm diameter hole drilled in a spring steel gasket preindented to 50 μm thickness. A small flake of platinum powder to be used as a pressure marker was placed across the top of the sample chamber after the loading and compaction of the Al powder into the hole. This experiment reached 219 GPa. In the second experiment the anvils had 35 μm flats, and a 20 μm diameter hole was drilled in a tungsten gasket preindented to 8 μm. Only Al was loaded into the sample chamber. This experiment reached a pressure of 207 GPa. No pressure medium was used in either experiment.

Energy-dispersive x-ray diffraction experiments were performed at the Cornell High Energy Synchrotron Source (CHESS) to measure the EOS and structure of the Al sample. Further details of the experimental techniques and apparatus are given in [17,18]. The size of the incident x-ray beam into the DAC was collimated to 20 μm × 20 μm with a set of tungsten apertures. This aperture set is important to minimize both gasket diffraction and pressure gradient effects [19]. Also the slit downstream of the DAC which defines the diffraction angle was moved as close to the sample as possible, about 35 mm, to minimize Compton scattering from the diamonds. This effect is important for experiments over 100 GPa where the sample becomes quite thin.

The diffraction angle was calibrated with a gold foil; 2θ was 18.144° for experiment 1 and 14.282° for 2. Typical collection time for a spectrum was over 1 h. The pressure for the spectra of experiment 1 was determined from the isothermal EOS of platinum by Holmes *et al.* [20] and from the x-ray measured Pt cell volume. The pressure

for the spectra of experiment 2 was determined using the shock EOS data on Al of Nellis *et al.* [10] from the x-ray measured Al cell volume.

In all spectra of experiment 1 the Al indexed well to the original fcc phase, even at the highest pressure of 219 GPa corresponding to an Al compression of $V/V_0 = 0.50$. Figure 1 shows a spectrum taken at 176 GPa. Experiment 2 (only Al in the sample chamber) was undertaken to hopefully research higher pressures and to observe a phase transformation from the fcc phase. However, failure occurred on loading above 207 GPa, no transition was observed.

Figure 2 is a plot of the measured Al EOS data of experiment 1 and the shock data of Nellis *et al.* [10]. The static and shock results are in good agreement. Since the pressure measurements for our static work are based on Pt shock EOS, the static and shock EOS's of Al and Pt are mutually consistent.

Also displayed in Fig. 2 is the dashed curve generated by fitting our experimental data to the simple solid H11 EOS from Ref. [7]:

$$P = P_{FG_0} x^{-5}(1 - x)e^{-cx}, \tag{1}$$

with $x = (V/V_0)^{1/3}$, $P_{FG_0} = a_{FG}(Z/V_0)^{5/3}$, and $c = \ln(P_{FG_0}/3K_0)$. P is pressure, and P_{FG_0} is the pressure of a free-electron gas (Fermi gas) with an electron density of Z electrons in the volume V_0 at ambient conditions of the solid. $a_{FG} = [(3\pi^2)^{2/3}/5]\hbar^2/m_e = 2.337 \times 10^{-2}$ GPa $(nm)^5$, and K_0 is the isothermal bulk modulus at zero pressure. This EOS form depends on zero pressure measurements of only two quantities: the volume (V_0) and the bulk modulus (K_0). Our fitted value of $K_0 = 7.2 \pm 1$ GPa is in good agreement with the true value of $K_0 = 72.7 \pm 0.2$ GPa (to be discussed below). Thus, our data fit the H11 EOS with no adjustment of parameters. The small deviation of the curve from the
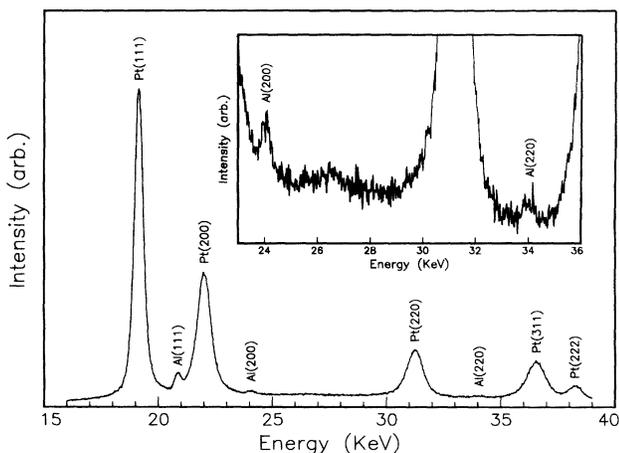

FIG. 1. EDXD diffraction spectra of Al at a pressure of 176 GPa. Peaks labeled Al are from the aluminum sample, and those labeled Pt are from the platinum pressure marker.
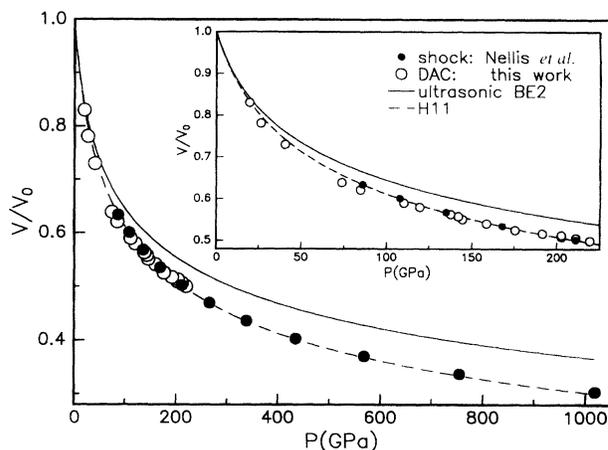

FIG. 2. Plot of reduced atomic volume V/V_0 of Al vs pressure P. V is the measured atomic volume and V_0 is the atomic volume at zero pressure. The shock data are from Ref. [10]. The BE2 curve is generated from the two-parameter Birch EOS using values of K_0 and K'_0, calculated from the ultrasonic data of Refs. [22–24], as discussed in the text. The curve labeled H11 is generated from the simple solid EOS from Ref. [7] using the same K_0 value as the BE2.

data in the inset of Fig. 2 in the 30–80 GPa is due to the nonuniform distribution of the data points in the fit. The density of points at high pressure (HP) is much higher (ten points above 100 GPa vs five below) so the HP region is weighted more heavily, particularly when one notes that the HP range corresponds to only a small variation of ρ/ρ_0. This curve is also an excellent representation of the shock data to 1 TPa. A fit of both the static and shock data sets to the H11 gives $K_0 = 74.2 \pm 0.8$ GPa, which is quite reasonable considering the possibility of some error in the TPa shock data.

Also displayed in Fig. 2 and labeled as ultrasonic BE2 is the curve generated from the two-parameter Birch EOS:

$$P = \frac{3}{2} K_0(x^{7/3} - x^{5/3})\left[1 + \frac{3}{4}(K'_0 - 4)(x^{2/3} - 1)\right], \tag{2}$$

where $x = V_0/V$, and K'_0 is the pressure derivative of the isothermal bulk modulus evaluated at zero pressure [21]. $K_0 = 72.7 \pm 0.2$ GPa was used and is the average of the ultrasonic values (corrected to isothermal) of Refs. [22–24], namely 72.92, 72.72, and 72.6. $K'_0 = 5.17 \pm 0.04$ was used and is the average of the ultrasonic values of Refs. [22,23], namely 5.15 and 5.19. We believe these ultrasonic-type measurements obtain the thermodynamically correct values of K_0 and K'_0. This BE2 curve starts deviating from the data at about 50 GPa and gets progressively worse with increasing pressure, i.e., this BE2 does not well represent the EOS of Al for $V/V_0 < 0.75$. The BE2 equation can be reasonably fit to our data with $K_0 = 72.7$ GPa, and $K'_0 = 4.14$. However, because K'_0 differs so greatly from the thermodynamic value, this

form must be viewed as a parametrized interpolation formula for the EOS (rather than a representation in terms of the Taylor series of the bulk modulus), since K_0' does not have its thermodynamic value.

Another issue to be addressed is the low-pressure region of the H11 vs previous EOS studies [14,15]. The results of these diffraction based EOS measurements were a BE2 fit with $K_0' = 4.30$, i.e., also much less than the true value. A comparison of the H11 with these BE2 results is virtually indistinguishable for pressures below 15 GPa and demonstrates that the H11 EOS gives equivalent results even at the low-pressure region to these two-parameter fits.

Comparison is also made between the H11 result of the present study and the previous theoretical studies of Ashcroft, Cohen, and co-workers [4,5]. This is displayed in Fig. 3 and shows that both predictions are good for pressures less than 150 GPa, but slightly stiffer than the measured EOS for higher pressures. The theoretical predictions are quite close to the measured data, compared to the BE2 result shown in Fig. 2. It is interesting to note that the theoretical predictions which neglect thermal contributions are closer to the measured data than the BE2 curve based on room temperature (ultrasonically measured) K_0 and K_0' which, of course, do include thermal contributions. From the H11 EOS it follows that $K_0' = 3 + 2c/3 = 4.31$ in the present case. This is close to our BE2 fitted value of 4.14 and significantly less than the ultrasonic value of 5.17, a fact that we and others have observed before for various materials.

The fitting of P-V data to the BE2 [Eq. (2)] yields parameters useful for interpolation only, but is of no physical significance if the volume range is large, i.e., the fit gives neither the correct K_0 nor the correct K_0'. In the three-parameter EOS (BE3) equation [21] if the true values of K_0 and K_0' are used and the density at 200 GPa is used to obtain K_0'' (a parameter, not a physical quantity), it will be found that a serious divergence exists. As
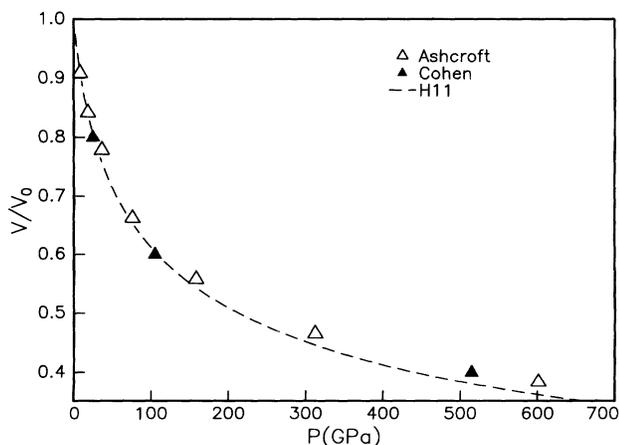
an example, at $\rho/\rho_0 = 3.2895$, the shock based isotherm gives 1018 GPa while the extrapolated BE3 curve gives 81 GPa. This erratic behavior for the BE3 equation has been noted earlier [25] and has been discussed for several second-order equations more recently [7,26]. The BE2 equation does not exhibit such erratic behavior, but if it is based on the true K_0 and K_0' it is always too stiff, a point discussed previously [7,26].

The H11 equation in which only quantities measured at atmospheric pressure are used (K_0 and V_0) has neither of these deficiencies and fits the data to 1000 GPa remarkably well.

FIG. 3. Comparison of theoretical predictions of Refs. [4,5] vs H11 Al EOS.

[1] A. L. Ruoff, in *Materials Science and Technology: A Comprehensive Treatment*, edited by R. W. Cahn, P. Haasen, and E. J. Kramer (VCH, New York, 1991), Chap. 8.

[2] A. Jayaraman, in *Shock Waves in Condensed Matter*, edited by S. C. Schmidt (Plenum, New York, 1985), p. 13.

[3] A. K. McMahan and J. A. Moriarty, Phys. Rev. B **27**, 3235 (1983).

[4] P. K. Lam and M. L. Cohen, Phys. Rev. B **27**, 5986 (1983).

[5] C. Friedli and N. W. Ashcroft, Phys. Rev. B **12**, 5552 (1975).

[6] P. K. Lam and M. L. Cohen, Phys. Rev. B **24**, 4224 (1981).

[7] O. Schulte and W. B. Holzapfel, Phys. Rev. B **48**, 767 (1993).

[8] W. B. Holzapfel, Europhys. Lett. **16**, 67 (1991).

[9] Th. Löer, R. Sigel, K. Eidmann, I. B. Földes, S. Hüller, J. Massen, G. D. Tsakiris, S. Witkowski, W. Preuss, H. Nishimura, H. Shiraga, Y. Kato, S. Nakai, and T. Endo, Phys. Rev. Lett. **72**, 3186 (1994).

[10] W. J. Nellis, J. A. Moriarty, A. C. Mitchell, M. Ross, R. G. Dandrea, N. W. Ashcroft, N. C. Holmes, and R. G. Gathers, Phys. Rev. Lett. **60**, 1414 (1988).

[11] V. A. Simonenko, N. P. Voloshin, A. S. Vladimirov, A. P. Nagibin, V. N. Nogin, V. A. Popov, V. A. Vasilenko, and Yu. A. Shoidin, Zh. Eksp. Teor. Fiz. **88**, 1452 (1985) [Sov. Phys. JETP **61**, 869 (1985)].

[12] A. V. Bushman, I. K. Krasyuk, P. D. Pashiniy, A. M. Prokhorov, V. Ya. Ternovoi, and V. E. Fortov, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 341 (1984) [JETP Lett. **39**, 411 (1984)].

[13] A. C. Mitchell and W. J. Nellis, J. Appl. Phys. **52**, 3363 (1981).

[14] K. Syassen and W. B. Holzapfel, J. Appl. Phys. **49**, 4427 (1978).

[15] L. C. Ming, D. Xiong, and M. H. Manghnani, Physica (Amsterdam) **139&140B**, 174 (1986).

[16] A. L. Ruoff and C. A. Vanderborgh, Phys. Rev. Lett. **66**, 754 (1991).

[17] M. Baublitz, Jr., V. Arnold, and A. L. Ruoff, Rev. Sci. Instrum. **52**, 1616 (1981).

[18] K. E. Brister, Y. K. Vohra, and A. L. Ruoff, Rev. Sci. Instrum. **57**, 2560 (1986).

[19] A. L. Ruoff, H. Luo, C. L. Vanderborgh, H. Xia, K. Brister, and V. Arnold, Rev. Sci. Instrum. **64**, 3462 (1993).

[20] N. C. Holmes, J. A. Moriarty, R. G. Gathers, and W. J. Nellis, J. Appl. Phys. **66**, 2962 (1989).

[21] F. Birch, J. Geophys. Res. **83**, 1257 (1978).

[22] P. S. Ho and A. L. Ruoff, J. Appl. Phys. **40**, 3151 (1969).

[23] R. E. Schmunk and C. S. Smith, J. Phys. Chem. Solids **9**, 100 (1959).

[24] J. L. Tallon and A. Wolfenden, J. Phys. Chem. Solids **40**, 831 (1979).

[25] L. C. Chhabildas and A. L. Ruoff, J. Appl. Phys. **47**, 4182 (1976).

[26] W. B. Holzapfel, in *Molecular Systems Under High Pressure,* edited by R. Pucci and G. Piccitto (Elsevier, Amsterdam, 1991), p. 61.