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Linear Bulk Modulus Approximation for Sapphire

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If the pressure dependence of the bulk modulus is linear, ultrasonic measurements of the bulk modulus and the pressure derivative of the bulk modulus accomplished at pressures of a few kilobars can be used to predict compressions to pressures of hundreds of kilobars. The linear bulk modulus approximation for synthetic single-crystal Al_2O_3, sapphire, is examined by comparing extrapolations of ultrasonic data to shock compression data obtained in the range of 175 to 1500 kb. It is observed that shear strength effects influence the interpretation of the shock data to an extent at least as large as higher-order bulk modulus theories, and that shear strength corrections cannot be unequivocally applied to the shock data. When the shock data are corrected for a constant volume offset due to shear strength effects, the linear bulk modulus approximation is found to give an accurate fit to the shock data. Ultrasonic values for the pressure derivative of the bulk modulus are found to have a value about 15% higher than the modulus measured under shock conditions. This difference may be a consequence of changes in the properties of shock loaded sapphire induced by the large shear stresses accompanying the unusually large shear strength of sapphire.

Anderson [1966] has proposed that precise measurements of the bulk modulus and its pressure derivative determined at low pressures with ultrasonic techniques can provide the basis for accurately predicting compressions at very high pressures. This proposal is based on the assumption that the isothermal bulk modulus $B(P)$ is linear with pressure P; i.e.,

$$B(P) = B_0 + B_0'P \qquad (1)$$

where B_0 is the isothermal bulk modulus at atmospheric pressure and B_0' is the first pressure derivative of the bulk modulus. In testing this proposal Anderson obtained reasonable agreement between states extrapolated from ultrasonic data and states obtained in shock-compression experiments. General agreement with the linear bulk modulus approximation was obtained for a wide variety of solids ranging from compressible solids like NaCl to relatively incompressible solids like Al_2O_3. In spite of the general agreement, systematic differences were sometimes noted; in particular a difference of about 1 to 2% in relative volume was observed between ultrasonic and shock data for polycrystalline and single-crystal Al_2O_3.

Chung and Simmons [1968] compared more recent ultrasonic data [*Gieske and Barsch,* 1968] on synthetic single-crystal Al_2O_3 (sapphire) with shock data on sapphire (R. G. McQueen and S. P. Marsh as reported by *Anderson* [1966]; see also *van Thiel* [1967] and *Clark* [1966]) and found a difference of about 1% in relative volume between 500 and 1500 kb. To account for the discrepancy between extrapolated states based on ultrasonic data and the shock data, *Yu* [1968] proposed that the bulk modulus should include terms employing the second pressure derivative of the bulk modulus. In spite of the improved fit to the shock data with the quadratic bulk modulus approximation, it appears that other effects should be considered before the linear bulk modulus approximation is dismissed. In particular, these investigators neglected the effects of the shear strength of sapphire in comparing the shock data with hydrostatic data. Sapphire exhibits the largest shear strength observed for any solid [*Brooks and Graham,* 1966] and the shear strength can cause a systematic difference between the hydrostatic and shock response that may be large enough to account for the different compressions predicted by the linear bulk modulus and the quadratic bulk modulus theories.

As a part of an extensive study of oxides, *Ahrens et al.* [1969] improved the agreement between ultrasonic and shock data on Al_2O_3 by

including a shear strength correction to the single-crystal shock data. This correction to the single-crystal data was based on shear strengths measured in shock compression experiments on polycrystalline Al_2O_3 and interpretations based on the elastic-plastic model of the deformation of solids. Isothermal, isotropic compression data derived from the single-crystal shock data were compared with extrapolations of polycrystalline ultrasonic data. A recent study of the shock compression of sapphire [*Graham and Brooks,* 1971] obtained new high-pressure data between 175 and 420 kb and also evaluated the shear strength of sapphire without assuming that the elastic-plastic model is valid.

It is the purpose of this article to utilize the recent shock data between 175 and 420 kb [*Graham and Brooks,* 1971], the ultrasonic data [*Gieske and Barsch,* 1968], and the very-high-pressure shock data between 500 and 1500 kb (R. G. McQueen and S. P. Marsh as reported by *Anderson* [1966]) to test the linear bulk modulus approximation for sapphire.

COMPRESSION EQUATIONS

If it is assumed that the isothermal bulk modulus is linear in pressure, the expression for compression can be obtained by integrating (1) to obtain the Murnaghan equation,

$$P = \frac{B_0}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'} - 1\right] \qquad (2)$$

where V is the specific volume at pressure P and V_0 is the specific volume at atmospheric pressure. Thus, to the extent that the linear bulk modulus approximation is valid, the results of ultrasonic measurements can be used in (2) to construct an isothermal equation of state to very high pressure.

Even though (2) describes compressions over a wide pressure range, it is computationally more convenient to use polynominal expansions of relative volume about the initial volume to obtain bulk modulus values from compression measurements. For moderate pressures, the salient features of compression can be described by a cubic polynomial expansion,

$$\frac{V}{V_0} = 1 - A_1P + A_2P^2 - A_3P^3 \qquad (3)$$

Anderson [1966] pointed out that in the linear bulk modulus approximation the coefficients of (3) are not arbitrary constants to be empirically determined, but should be expressed in terms of the bulk modulus and its pressure derivative. In particular,

$$A_1 = 1/B_0 \qquad A_2 = \tfrac{1}{2}(1 + B_0')/B_0^2$$

$$A_3 = \tfrac{1}{6}(1 + 3B_0' + 2(B_0')^2)/B_0^3$$

Graham and Brooks [1971] were able to fit their shock data with (3) to obtain shock compression values for B_0'. This value of B_0', which is independent of that obtained ultrasonically, can be confirmed by comparison to the very-high-pressure shock measurement of McQueen and Marsh. However, before proceeding with this comparison, the shear strength effects must be considered. Only a brief summary of these considerations will be presented; more extensive discussions can be found in *Jones and Graham* [1971] and *Graham and Brooks* [1971].

SHEAR STRENGTH EFFECTS

If the shear strength of a solid is nonzero, the state of stress achieved in the plane-wave shock experiment will be anisotropic. Accordingly, the high-pressure shock experiment will show a stress or volume offset from the isotropic compression curve. Many solids exhibit offsets that are proportional to the yield strength of the solid. Yield strengths of shock-loaded solids, called Hugoniot elastic limits, are now routinely measured, and a recent summary of these measurements [*Graham and Jones,* 1968] showed many solids with typical values from a few kilobars to several tens of kilobars.

Hugoniot elastic limit values for sapphire depend on the crystallographic orientations of the samples; values as large as 210 kb have been observed [*Brooks and Graham,* 1966]. Thus, shear strength offsets potentially as large as 3% in volume at a given stress are possible above the Hugoniot elastic limit. However, the recent shock compression study of sapphire [*Graham and Brooks,* 1971] examined these shear strength effects in the region above the Hugoniot elastic limit and found that sapphire exhibits a substantially lower shear strength in the high-pressure region than predicted from the Hugoniot elastic limit measurements. These shock compression data show that a relative volume correction, η_0, of $0.0118V_0$, corresponding to a stress offset, σ_τ, of 30 kb, must be applied to the shock data up to 420 kb to correct for the anisotropic component of the compression. Furthermore, various crystallographic orientations showed a common high-pressure compression curve. This latter observation is particularly important since the data of McQueen and Marsh were obtained on samples with unknown crystallographic orientations.

Although this shear strength correction is characteristic of pressures up to 420 kb, the correction cannot be extrapolated to the shock data at pressures as high as 1500 kb unless the pressure dependence of the shear strength is known. Various forms of the pressure dependence of the shear strength can be assumed; a constant shear strength or an increasing shear strength is usually assumed, but a decrease in shear strength cannot be unequivocally ruled out. Even though there is no quantitative guide for selecting the most appropriate shear strength model, shear strengths are generally thought to increase with increasing pressure. Thus, the constant volume offset assumption will be used to correct the shock data since it has the effect of applying an increasing shear strength correction with increasing pressure. Other shear strength models are not precluded; in fact, the various models serve to emphasize the uncertainties involved in evaluating shear strength effects in shock-loaded solids.

COMPARISON OF SHOCK AND ULTRASONIC DATA

Considerable information is now available to test the linear bulk modulus approximation for sapphire. The bulk modulus and its pressure derivative have been accurately determined ultrasonically and two independent shock-compression investigations provide data from 175 to 1500 kb. Furthermore, the effects of shear strength have been evaluated, and, since the thermal pressure correction due to shock heating is small, uncertainties in the details of the equation of state are not significant.

Various isothermal compression parameters for single crystal Al_2O_3 are shown in Table 1. Values for high-density polycrystalline Al_2O_3 are shown for comparison. The linear bulk modulus approximation can be tested in several independent ways. For example, the ultrasonic values from Table 1 can be used in (2) and the calculated compression curve compared with the isotropic, isothermal compression curve calculated from shock compression data. On the other hand, the modulus values determined from the low-pressure shock work can be used in (2) and the calculated compression curve compared with the very-high-pressure shock results. It should be noted that the shear strength values obtained on single-crystal Al_2O_3, as shown in Table 1, are less than the polycrystalline values previously observed.

The shock data are corrected to isothermal conditions by calculating the thermal pressure resulting from the shock compression. Fortunately, the thermal pressure is small for sapphire, amounting to only 40 kb at a shock pressure of 1000 kb. Since the thermal pressure is small, errors in thermal pressure calculation are not significant and uncertain details of the equation of state cause uncertainties in thermal

TABLE 1. Isothermal Compression Parameters for Al_2O_3

			Modulus Values		Shear Strength Values	
Source	Technique	Material	B_0, kb	B_0'	σ_τ, kb	η_0
Schreiber and Anderson [1966]	Ultrasonic	Polycrystal	2504	4.00		
Gieske and Barsch [1968]	Ultrasonic	Crystal	2526	4.35		
Ahrens et al. [1969]	Shock	Various	2901	3.24	52	
Graham and Brooks [1971]	Shock	Crystal	(2526)*	3.72	30	0.0118

Conversion of adiabatic to isothermal parameters was accomplished with the thermodynamic values reported by *Anderson* [1966]. B_0 is the isothermal bulk modulus, B_0' is the pressure derivative of the isothermal bulk modulus, σ_τ is the shear stress offset, and η_0 is the relative volume offset due to the shear strength effects.

* Independent value was not obtained in the shock experiments. The fit to the shock data was assumed to have a value equal to the ultrasonic value.

pressure corrections that are less than shear strength corrections for pressures up to about 1 Mb. The thermal pressure calculations were made with a Mie-Grüneisen equation of state. The calculated values are in good agreement with values reported for high-density polycrystalline Al_2O_3 by *Ahrens et al.* [1968].

The ultrasonic and low-pressure shock modulus values for sapphire are used in (2) to determine the 300°K isothermal compression curve shown in Figure 1. The shock-compression data are corrected for shear strength effects and for the thermal pressure. The static isothermal compression data of *Hart and Drickamer* [1965] are also shown. Agreement between the ultrasonic extrapolation based on (2) and the shock data is better than that noted in previous comparisons. For pressures greater than 1250 kb the shock data show a discontinuous change that cannot be fit by a smooth curve. Even though the ultrasonic and shock data are in good agreement the shock compressions are systematically larger than those predicted from the ultrasonic data.

When the B_0' value obtained from the shock data between 175 and 350 kb is used in (2), the calculated isothermal compression curve is in significantly better agreement with the shock data of McQueen and Marsh from 500 to 1250 kb than that obtained from the ultrasonic moduli. In effect, the higher-pressure shock data confirm the B_0' value measured under shock at lower pressures. The pressure range of the shock data is large enough that higher-order pressure derivatives of the bulk modulus, if significant, should affect the compressions significantly. However, the results show that higher-order bulk modulus values are not needed to describe the data.

There appears to be a significant difference between the ultrasonic and shock values for B_0'. It is possible that the large shear stresses resulting from the large Hugoniot elastic limit alter the properties of the sample. In the yielded state the material could possibly have a different character than the unstressed crystal. In fact, the B_0' value obtained from single-crystal shock data is in better agreement with the polycrystalline value of B_0' obtained ultrasonically than with the single-crystal ultrasonic value.

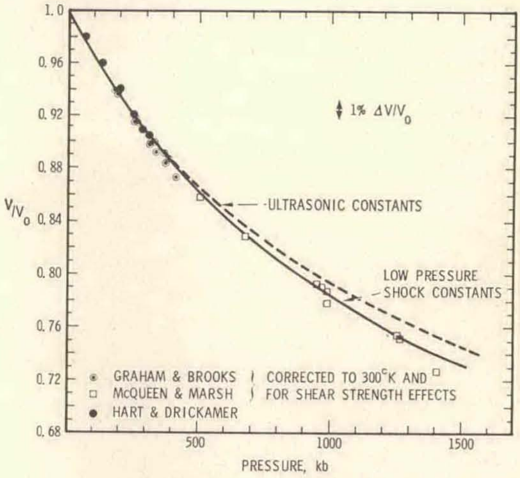

Fig. 1. High-pressure isothermal compression curves for sapphire. The dotted and solid lines are the relationships predicted by the Murnaghan equation with constants derived ultrasonically [*Gieske and Barsch,* 1968] and with constants derived from the low-pressure shock data of *Graham and Brooks* [1971]. The shock data are corrected for thermal pressure and shear strength offsets. The static isothermal compression data of Hart and Drickamer are also shown. The extent to which the data agree with the Murnaghan relations provides a direct measure of the adequacy of the linear bulk modulus approximation for sapphire. The agreement between all experimental points and the isothermal compression curve is thought to be within the experimental error of the measurements.

In any event, when the B_0' value derived from shock data is used in the Murnaghan equation, systematic differences between experimental observations and extrapolations of lower-pressure data are eliminated. The shock compression data to 1250 kb scatter randomly by about $\pm\frac{1}{2}\%$ in relative volume about the Murnaghan equation. Thus, the linear bulk modulus approximation is confirmed within the accuracy of the shock data and the shear strength correction. Although there is a difference between the ultrasonic and shock values for B_0' the basic assumption of a linear bulk modulus from 175 to 1250 kb is confirmed. The present work emphasizes the importance of the shear strength correction; uncertainties in the degree to which this effect can be described unequivocally limit the value of higher-order bulk modulus descriptions of the compression of sapphire.

CONCLUSION

Recent shock compression data permit an evaluation of shear strength effects encountered in the shock compression of sapphire. When this effect is accounted for, the extrapolation of ultrasonic data based on a linear bulk modulus approximation shows good agreement with shock compression data confirming the validity of the model for Al_2O_3. The Murnaghan equation gives even better agreement with shock data if the pressure derivative of bulk modulus obtained from shock data is used. The linear bulk modulus approximation gives a precise fit to the shock data from 175 to 1250 kb.

The pressure derivative of the bulk modulus determined from the shock data is about 15% lower than the ultrasonic value and in better agreement with ultrasonic values for polycrystalline than single-crystal Al_2O_3. This result may be indicative of changes in the properties of shock compressed Al_2O_3 caused by the unusually large shear stresses in the shock compression experiments.

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