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LETTER TO THE EDITOR

The high-pressure, high-temperature equation of state of calcium fluoride, CaF_2

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Abstract. The behaviour upon compression of fluorite, CaF_2 , has been determined to pressures of 9 GPa at room temperature by single-crystal x-ray diffraction. The room temperature isothermal bulk modulus, K_T , is 81.0 ± 1.2 GPa, and $K' = 5.22 \pm 0.35$. These data are combined with other thermodynamic data to provide a high-pressure, high-temperature equation of state for fluorite.

Fluorite, CaF_2 , is used as an internal pressure standard in high-pressure, high-temperature experiments for the variety of reasons described by Hazen and Finger (1981). They therefore developed an equation of state (EOS) for fluorite which they believed to be valid to pressures of 4 GPa in the temperature range 300 K to 800 K. Recent and on-going developments in the capabilities of high-pressure, high-temperature diamond-anvil pressure cells has necessitated a re-evaluation of this EOS, especially in the light of disagreements in the literature regarding the value of the bulk modulus of fluorite (e.g. Jones 1977, Katrusiak and Nelmes 1986, Gerward *et al* 1992) and its temperature derivative (Jones 1977), issues not addressed by Hazen and Finger (1981). In this letter a new high-precision determination of the room pressure isothermal bulk modulus of fluorite and its pressure derivative are reported. Thermodynamic data for fluorite from the literature are also critically evaluated, and a high-pressure, high-temperature EOS suitable for use for pressure calibration is calculated.

Unit-cell volumes of fluorite were obtained at high pressure and ambient temperature by single-crystal x-ray diffraction, the centring of the 220 reflections by the method of King and Finger (1979) being used to eliminate diffractometer aberrations. The precision in the volumes derived from these measurements is $\sim 0.05\%$. Two types of diamond-anvil cell were used; initial experiments to 4 GPa were performed with a standard Merrill-Bassett-type cell (Hazen and Finger 1982), later experiments to ~ 9 GPa employed a DXR4 cell (Angel *et al* 1992). The pressure medium used in both cases was a 4:1 methanol:ethanol mixture which remains hydrostatic to pressures in excess of 10 GPa. Pressure measurement was by the ruby fluorescence technique (Forman *et al* 1972, Angel *et al* 1992), using the calibration of Mao *et al* (1986) to calculate the pressure from the wavelength shift. This calibration has a reported accuracy in this pressure range of ± 0.03 GPa, while the precision of our pressure measuring system is better than ± 0.03 GPa.

Data were obtained at 32 pressures between ambient pressure and 7.74 GPa from three different crystals and are displayed in figure 1. Further pressure increase from 7.74 GPa to 9.2 GPa resulted in the loss of diffraction intensity. Recent studies by Gerward *et al* (1992) show that this is due to the fluorite undergoing a phase transition from the low-pressure CaF_2 structure type to a high-pressure phase with a PbCl_2 -type structure. On subsequent pressure release broadened diffraction maxima, due to the low-pressure phase, appeared indicating that the high-pressure phase reverted to the fluorite structure, but that the original single crystal was not recovered.

The volume–pressure data obtained were fitted by least squares to the Murnaghan equation

$$V/V_0 = (1 + (K'/K_T)P)^{-1/K'} \quad (1)$$

to obtain the isothermal bulk modulus, $K_T = 81.0(1.2)$ GPa, and $K' = 5.22(35)$, with $R_{\text{fit}} = 0.027$ (figure 1). The values of K_T and K' are in excellent agreement with the values of $K_T = 81.7$ GPa and $K' = 5.0$ obtained from the ultrasonic measurements between 10^{-4} GPa and 0.4 GPa by Wong and Schuele (1968). The EOS parameters ($K_T = 87(5)$ GPa, $K' = 5(1)$) derived by Gerward *et al* (1992) from a combined dataset of x-ray powder and single-crystal data are also consistent with these results, but are of significantly lower precision. By contrast, the values of $K_T = 82.6$ GPa and $K' = 4.0$ obtained from the ultrasonic measurements to 1.2 GPa of Brielles and Vidale (1975), and those of $K_T = 82.5$ GPa and $K' = 5.97$ from Ho and Ruoff (1967), are not compatible with the new determination. The single-crystal diffraction data of Katrusiak and Nelmes (1986) are in error by a considerable margin (figure 1); a fit of the Murnaghan EOS to their data yields $K_T = 133(5)$ GPa and $K' = -5.4(2.6)$.

The development of the high-pressure, high-temperature EOS requires knowledge of the variation of K_T and K' with temperature, together with the ambient pressure volume thermal expansion coefficient, α_V . The various determinations of α_V were reviewed by Schumann and Neumann (1984), and their recommended polynomial for the variation of α_V with temperature (table 1) is employed here. There are no direct determinations of the isothermal bulk modulus at high temperatures, but K_S , the adiabatic bulk modulus, has been measured to 1100 K by ultrasonic techniques. These data are reviewed by Jones (1977), who found that there is good agreement on the value of $(\delta K_S/\delta T)$ between her own work and that of Nikanorov *et al* (1968), resulting in

$$(\partial K_S/\partial T)_{P=0} = -0.0165 - 0.117 \times 10^{-4}T \quad (2)$$

The Anderson–Grüneisen parameter, $\delta_S = (-1/\alpha_V K_S)(\partial K_S/\partial T)_P$, calculated from these data remains constant at 4.0 ± 0.05 between 300 and 900 K (figure 2). By contrast, the high-temperature determination of K_S by Vidale (1974) yields the unrealistic value of δ_S of ~ 2 .

The variation of K_T with temperature was derived with the relationship $K_T = K_S(1 + \alpha_V \gamma T)^{-1}$, where γ is the Grüneisen ratio, $\alpha_V K_S/\rho C_P$. The expression for C_P was taken from Robie *et al* (1978). The variation of K_S (equation (2)) with $H_T - H_{298}$ derived from the C_P data is linear within the experimental uncertainties, providing an independent check of the reliability of these two data sources (Anderson 1989). The Grüneisen ratio γ is found to be essentially constant at 1.77 ± 0.05 between

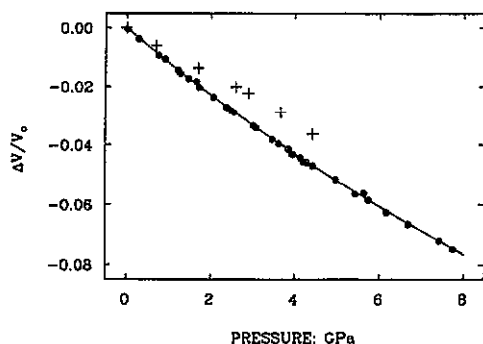


Figure 1. The variation of unit-cell volume of CaF_2 with pressure. Solid circles: this work. Crosses: Katrusiak and Nelmes (1986). The line is the Murnaghan EOS reported in table 1.

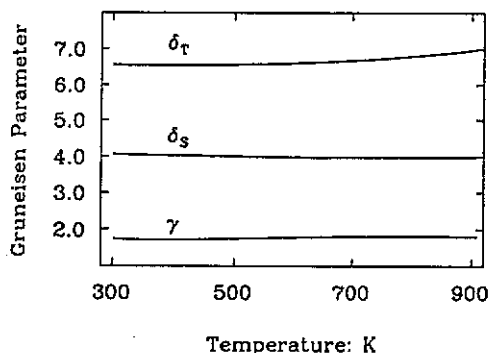


Figure 2. The variation with temperature of the macroscopic Grüneisen and Anderson-Grüneisen parameters of fluorite.

Table 1. Thermodynamic expressions for CaF_2 .

$$\alpha_V (\text{K}^{-1}) = 4.41 \times 10^{-5} + 4.411 \times 10^{-8}T + 1.65 \times 10^{-11}T^2$$

$$C_p (\text{J mol}^{-1} \text{K}^{-1}) = -24.692 + 5.8095 \times 10^{-2}T + 1870.6T^{-0.5} - 2.8774 \times 10^6T^{-2}$$

$$K_T (\text{GPa}) = 89.51 - 0.0264T - 7.2 \times 10^{-6}T^2$$

$$K' = 5.22 \text{ (lower bound)}$$

$$K' = 4.61 + 0.00204T \text{ (upper bound)}$$

300 K and 900 K (figure 2), and the resulting polynomial for the variation of K_T with temperature is given in table 1.

The variation of K' with temperature is less well constrained, the only reliable measurements being those of Wong and Schuele (1968) who give $K' = 4.77$ at 195 K and 4.98 at 298 K, or $(\partial K'/\partial T) = 0.002 \text{ K}^{-1}$. This slope provides an upper bound on K' at higher temperatures because $\partial^2 K'/\partial T^2$ must be negative in order to meet the constraint $K' \leq \delta_T$ at all temperatures ($\delta_T = (-1/\alpha_V K_T)(\partial K_T/\partial T)_P$). The isothermal Anderson-Grüneisen parameter δ_T rises from 6.6 to 7.0 over the temperature interval 300 K to 900 K (figure 2). An absolute, but unrealistic, lower bound on K' is provided by assuming that it remains constant at its value at 300 K, 5.22.

The equations used to describe the volume variation of fluorite at temperatures to 900 K and pressures of 8 GPa are:

$$V(T, 0) = V(298, 0) \exp\left(\int_{298}^T \alpha_V(T) dT\right)$$

$$V(T, P) = V(T, 0)(1 + (K'/K_T)P)^{-1/K'} \quad (3)$$

the parameters for which, having been discussed above, are given in table 1. Note that two expressions are provided for K' ; the true value of K' at any temperature must lie between these two bounds. Better constraints cannot be provided through the usual assumptions made in deriving the equations of state of other materials. For example, it is clear from the available data that $\alpha_V K_T$ is not invariant. Neither can

the relation

$$K' = (-1/\alpha_V K_T)(\partial K_T/\partial T)_V + \delta_T \quad (4)$$

be used with the assumption that $(\partial K_T/\partial T)_V$ is invariant with temperature since it can be shown to result in a value of $(\partial K'/\partial T)_P$ at 300 K that is inconsistent with the data of Wong and Schuele (1968). Further constraints on the variation of K' at high temperature must therefore await either its direct determination, or the measurement of α_V at elevated pressure. It is this lack of constraint on the value of K' that is the major source of uncertainty in the new EOS for fluorite presented here. The EOS with constant K' predicts lower pressures than that using the upper bound for K' , by as much as 1.1 GPa for $V/V_0 = 0.925$ at 900 K. At lower compressions and lower temperatures the comparison is better; the discrepancy is less than 0.1 GPa for the regime $V/V_0 - 0.00015 \cdot T > 0.86$.

There are three points worthy of note in the comparison of the pressures predicted by these EOS for a given volume and temperature with those predicted by the EOS of Hazen and Finger (1981). The latter underestimates pressures at high compressions and low temperatures due to the use by Hazen and Finger (1981) of a polynomial function to describe the variation of volume with pressure which underestimates pressures by 0.1 GPa at $V/V_0 = 0.97$ and by 0.7 GPa at $V/V_0 = 0.92$. By contrast, at high temperatures the Hazen and Finger EOS overestimates pressures due to their use of thermal expansion data from Sharma (1950) which appear to be anomalously high (Schumann and Neumann 1984). At high pressures and temperatures these two effects tend to cancel, providing good agreement with the EOS employing constant K' .

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