

Pressure and Temperature Dependence of the Single Crystal Elastic Moduli of the Cubic Perovskite KMgF_3

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Abstract. The elastic moduli (c) of single crystal KMgF_3 have been determined by the ultrasonic pulse superposition technique as a function of temperature from $T=298-550$ K, and as a function of pressure from $P=1$ bar – 2.5 kbar. Room temperature values of the elastic moduli and their temperature derivatives are consistent with Reshchikova's (1969) values. Comparison with the data for SrTiO_3 indicates that, for most of the moduli, $1/c(\partial c/\partial T)_p$ and $(\partial c/\partial P)_T$ are very similar for the fluoride-oxide analogue pair, KMgF_3 – SrTiO_3 . Values of $(\partial c/\partial P)_T$ for KMgF_3 are calculated from a simple central force model using parameters determined for KF and are in good agreement with the measured values. The bulk sound velocity-mean atomic weight relationship, $v_\phi \bar{M}^{1/2} = \text{constant}$, is well obeyed by the fluoroperovskites; comparison with the perovskite oxide data on a log-log plot of v_ϕ versus \bar{M} leads to a value of 70% for the relative effective charge of the oxides with respect to the fluorides.

1. Introduction

Perovskite-type compounds have received particular attention in solid-state physics in connection with a wide range of phenomena such as ferroelectricity, piezoelectricity, and low-temperature structural transformations. Experimental and theoretical studies have aimed at explaining such behaviour in terms of the lattice dynamics and crystallographic structure of the perovskite type (e.g., Cowley, 1964; Stirling and Cowley, 1972).

The perovskite structure attracted interest in earth sciences when Ringwood (1962) suggested that its intrinsic high density made it a possible candidate for the crystallographic structure of lower mantle silicates. Recently, Liu (1974, 1975a and b, 1976) demonstrated that ferromagnesian silicates with $\text{Fe}/\text{Fe} + \text{Mg} \leq 0.3$ transform to assemblages characterized by the presence of an orthorhombic perovskite

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structure for pressures in excess of 250 kbar. Corroboration of Liu's results was presented by Ito (1977). These experimental studies indicate that silicates with the perovskite structure are indeed a likely constituent of the lower mantle.

Unfortunately there are no elasticity data for silicate perovskites from which to construct mantle models for comparison with seismically-determined velocity-depth profiles. In the absence of direct elasticity measurements, the use of analogue compounds can yield valuable information. Liebermann et al. (1977) reported values for the elastic moduli of a suite of polycrystalline perovskites consisting of titanates, germanates, stannates and aluminates, and provided estimates for the bulk and shear moduli of the perovskite-polymorph of MgSiO_3 . To date, there is no information on the pressure and temperature derivatives of the elastic moduli for perovskite- MgSiO_3 . In fact, SrTiO_3 is the only perovskite oxide for which such data are available (Beattie and Samara, 1971; Bell and Rupprecht, 1963). An important experimental goal, therefore, is the measurement of the pressure and temperature dependence of the elastic moduli for those perovskites for which good specimens, preferably single crystal, can be obtained.

On the basis of Goldschmidt's (1927) crystal chemical considerations, Jones (1976a and b; 1977a and b) considered fluorides as models for the elastic behaviour of their oxide analogues. With the exception of the rocksalt structure, it was concluded that the fluorides could not be used directly to predict the elastic properties of the oxides. However, the study of almost completely ionic compounds, such as the fluorides, is a particularly useful one for the formulation and testing of lattice-dynamical models for the simpler case of ionic bonding. This consideration, as well as availability, prompted the study of the single crystal elastic moduli of the cubic perovskite KMgF_3 as a function of temperature to 550 K and as a function of pressure to 2.5 kbar, using the precise ultrasonic pulse superposition technique.

The purpose of this paper is to report new values for the elastic moduli and their pressure and temperature derivatives for KMgF_3 , to consider these values in terms of a central force model for fluoroperovskites, to compare them with the corresponding values for SrTiO_3 , and to examine elastic constant systematics for the fluoride and oxide perovskites.

2. Experimental Techniques

A single crystal of KMgF_3 was obtained from Atomergic Chemetals (Plainview, New York, U.S.A.) as a 0.2 inch cube with a pair of (110) faces and a pair of (001) faces. Back reflection X-ray techniques verified that the orientation was correct to within 0.5° for the [110] direction. The bulk density, ρ_0 , was determined hydrostatically and agrees with the X-ray density to within 0.03% (Table 1). The (110) faces were polished to a flatness of $5\ \mu\text{m}$ and a parallelness of 0.01° .

Measurements as a function of temperature to 550 K were performed in a small controlled atmosphere furnace (Jones, 1976a and b). A 10 kbar liquid medium apparatus (Harwood Engineering Company) was used for the room temperature measurements to 2.5 kbar, with silicone oil (Dow-Corning DC-200) as the pressure medium. The pressure was determined from a manganin pressure gauge with a

Table 1. Basic data for KMgF_3

Data	
Molecular Weight	120.41
Molar Volume, cm^3	38.23
Bulk Density, $\text{gm} \cdot \text{cm}^{-3}$	3.151 ± 0.003
X-ray Density, $\text{gm} \cdot \text{cm}^{-3}$	3.15^a
Length (in [110] direction), cm	0.492 ± 0.0005

^a Rosenberg and Wigmore (1967)

precision of 10 bars. The temperature was not controlled but was monitored; with each increase in pressure the temperature also increased, and time to reach equilibrium was allowed before measurements were made.

Propagation in the [110] direction of a compressional and two shear waves (polarized [1 $\bar{1}$ 0] and [001]) enabled the determination of the three independent elastic moduli, $c'' = 1/2(c_{11} + c_{12} + 2c_{44})$, $c' = 1/2(c_{11} - c_{12})$ and c_{44} respectively. The elastic wave velocities were determined by the pulse superposition technique (McSkimin, 1961). 20 MHz co-axial quartz transducers (X and AC-cut) were bonded directly to the sample with Dow-Chemical resin 276-V9 for the pressure runs and with Extemp 9901 (Frisillo and Barsch, 1972) for the temperature runs. The transducers were operated at the resonant frequency of the transducer-bond-sample assemblage, such that maximum amplitude of the echo signal was attained.

Davies and O'Connell (1977) have indicated that large errors due to phase shifts at the transducer-bond-sample interfaces can be introduced when the transducer is operated away from its free resonance frequency. These phase shifts are strongly frequency dependent and would cause the measured value of the pulse repetition frequency to vary as the operational frequency of the transducer was varied. Since we observed that such behaviour did not occur, we can conclude that any errors due to phase shifts were small in our experiments. For the purposes of a least squares analysis, the uncertainties are taken to be instrumental and all equal (in general, the relative error is 1×10^{-4}); the random errors in the measurement of temperature and pressure are neglected.

3. Results

3.1. Temperature Data

The pulse repetition frequency, f_R , measured during very slow heating, is plotted against temperature in Fig. 1, for the three modes for the [110] direction. The standard F -test, along with the χ^2 -test led to the conclusion that only a straight line fit to the $f_R - T$ data was statistically significant (Bevington, 1969; Jones, 1976a and b). The coefficients of these linear equations are given in Table 2.

The pulse repetition frequency, f_R , the elastic wave velocity, v , and the elastic modulus, c , are related by

$$c = \rho v^2 = 4\rho l^2 f_R^2. \quad (1)$$

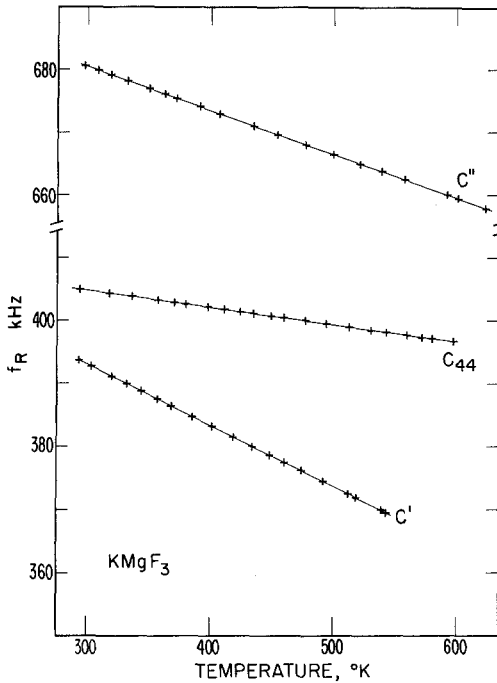


Fig. 1. Pulse repetition frequency, f_R , versus temperature for the modes c'' , c' , and c_{44} for KMgF_3 . For reasons of clarity, not all the data points used in the analysis were plotted. The solid lines are the straight lines fitted to the data

Table 2. Coefficients of the straight lines, $f_R = A + BP$ and $f_R = C + D(T - 298)$, fitted to the $f_R - P$ and $f_R - T$ data, respectively

	A (kHz)	B (kHz · kbar ⁻¹)	C (kHz)	D (kHz · deg ⁻¹)
c' ^a	393.40 (393.69)	1.13 (1.18)	393.29	-0.09708
c_{44} ^b	404.75 (404.71) (404.76)	0.44 (0.43) (0.43)	404.89	-0.02685
c''	680.59	1.60	680.61	-0.06976

^a The primary data are taken from run 2. Results for run 1 are listed in parentheses

^b The primary data are taken from run 3. Results for runs 1 and 2 are listed in order in parentheses

The room temperature values of the elastic moduli (Table 3) were calculated from (1) using the f_R evaluated from the $f_R - T$ equations at 298 K. The associated errors are determined from the uncertainties in the coefficients of the linear equations (Bevington, 1969, chapter 6-5, 8-1), together with the uncertainties in ρ_0 (0.1%) and in l_0 (0.1%). Errors due to misorientation from the [110] crystallographic axis are negligible (Waterman, 1959).

Table 3. Elastic moduli and their pressure and temperature derivatives at 298 K

Modulus, <i>c</i> (kbar)	$\left(\frac{\partial c}{\partial P}\right)_T$	$2\left(\frac{\partial \ln f_R}{\partial T}\right)_P$ (10 ⁻³ deg ⁻¹)	$\left(\frac{\partial c}{\partial T}\right)_P^a$ (kbar · deg ⁻¹)
<i>c'</i>	471.9 ± 1	2.94 ± 0.06	-0.4937 ± 0.0006
<i>c</i> ₄₄	500.1 ± 1	1.31 ± 0.03	-0.1326 ± 0.0003
<i>c''</i>	1,413.3 ± 3	7.3 ± 0.4	-0.205 ± 0.0008
<i>c</i> ₁₁	1,385 ± 5	8.93 ± 0.55	-0.4838
<i>c</i> ₁₂	441 ± 5	3.05 ± 0.55	+0.001
<i>K</i> _S	756 ± 4	5.01 ± 0.47	-0.161
<i>μ</i>	489 ± 1	1.98 ± 0.07	-0.146

^a Calculated from Eq. (2), using $\alpha = 2 \times 10^{-5} \text{ deg}^{-1}$. See also footnote on this page

In the absence of thermal expansion data for KMgF₃, it was not possible to determine the temperature derivatives of the elastic moduli as a function of temperature. The temperature dependence can be expressed in the following form

$$\left(\frac{\partial \ln c}{\partial T}\right) = -\alpha + 2\left(\frac{\partial \ln f_R}{\partial T}\right) \quad (2)$$

where α is the linear coefficient of thermal expansion. Equation (2) is obtained by taking the logarithmic derivative of Eq. (1) with respect to T . The temperature dependence of the elastic moduli at 298 K can be found directly from Eq. (2) by inserting a measured value for α when it becomes available. In Table 3 we have listed the values of $(\partial \ln f_R / \partial T)_P$ along with the appropriate errors. Also given in Table 3 are values of $(\partial c / \partial T)_P$ calculated at 298 K using an estimated value of $2 \times 10^{-5} \text{ deg}^{-1}$ for α ¹.

3.2. Pressure Data

The primary data for the pressure runs are the values of f_R measured as a function of pressure to 2.5 kbar under equilibrium and quasi-isothermal conditions, and corrected to 298 K using data for the temperature dependence of the f_R . The data for the *c*₄₄ mode are shown plotted in Fig. 2 as an illustration of the quality of the pressure data. For all the modes, only a linear fit to the data was justified for the small number of data points spanning a limited pressure range. In Table 2, we list the coefficients of these fitted straight lines. The runs providing the primary data were chosen on the basis of consistency and reproducibility. Measurements were limited to approximately 2.5 kbar, since at higher pressures it was not possible to obtain reproducible data, apparently due to bond effects.

¹ This is the value of the linear thermal expansion coefficient for KCoF₃ determined from graphical data presented by Julliard and Nouet (1975). KCoF₃ exhibits the cubic perovskite structure and its molar volume is close to that of KMgF₃ (see Table 7)

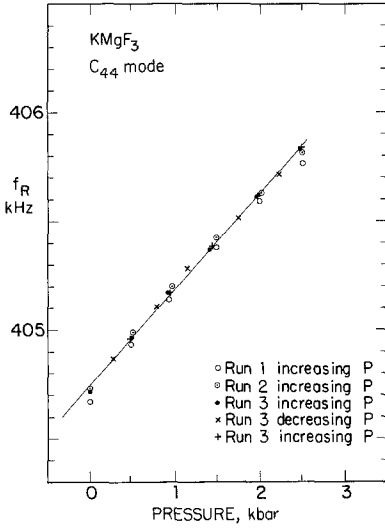


Fig. 2. Pulse repetition frequency, f_R , versus pressure for c_{44} for KMgF_3 . The solid line is the straight line fitted to the data for run 3

The linear relationship for $f_R - P$ simplified the application of Cook's (1957) formula for the relative length change with pressure

$$\left(\frac{l}{l_0}\right) = 1 + \frac{(1 + \alpha_V \gamma T)^P}{12 \rho_0 l_0^2} \int_0^P \frac{dP}{f_1^2 - f_2^2 - f_3^2/3} \quad (3)$$

where f_1, f_2 and f_3 are the pulse repetition frequencies corresponding to the moduli c'', c_{44} and c' ; α_V is the volumetric thermal expansion, and γ is the thermal Gruneisen parameter. For the purposes of this calculation, $(1 + \alpha_V \gamma T)$ can be replaced by unity, since this has a negligible effect on (l/l_0) . The integral in Eq. (3) reduces to a standard integral of the form

$$\int_0^P \frac{dP}{aP^2 + bP + c}$$

which can easily be evaluated explicitly (e.g., see Abramowitz and Stegun, 1965).

The relationship between elastic modulus and pulse repetition frequency in Eq. (1) can be expressed at any pressure as

$$c = 4 \left(\frac{l_0}{l}\right) \rho_0 l_0^2 f_R^2 \quad (4)$$

where ρ_0 and l_0 are the density and length, respectively, at atmospheric pressure. The elastic moduli were calculated at each value of pressure from Eq. (4), using the experimentally determined values of f_R and the values of (l/l_0) from Eq. (3). The pressure derivatives of the elastic moduli were determined from a least squares fit to the $c - P$ data. The errors in the elastic moduli and their pressure derivatives were estimated from the uncertainties in the coefficients of the fitted straight lines (taken as three standard deviations) (Bevington, 1969).

In Table 3 are listed values of the pressure derivatives of the elastic moduli at 298 K. The elastic moduli at 298 K determined from the pressure runs (not tabulated) agree to within 0.06 % of those determined from the temperature runs (Table 3), which is of the order of the uncertainty expected from the linear regression analysis. (The larger errors listed in Table 3 result from the incorporation of the measurement errors for ρ_0 and l_0 .) This close agreement is better illustrated in Table 2 for the coefficients A and C of the fitted straight lines, and further supports our statement that the bond effects are negligible, since the pressure and temperature measurements were performed with different bonding materials. It is also worth pointing out that the values of $(\partial c/\partial P)_T$ calculated from the less reliable runs for c' and c_{44} agree within the uncertainties listed in Table 3, even though there is a definite offset in the data in the case of c' (Table 2). These results would seem to suggest that any bond associated errors have a larger effect on the absolute value of the modulus than on the change as a function of pressure.

3.3. Comparison With Other Data

In Table 4, our values of the elastic moduli at 298 K for KMgF_3 are compared with those of other investigators. There is very good agreement between our values and those of Reshchikova (1969), while the values of Rosenberg and Wigmore (1967) all appear too low.

The values of $(\partial c/\partial T)_P$ at 298 K are also compared in Table 4. The agreement between our values of $(\partial c/\partial T)_P$ for c'' , c' and c_{44} , calculated neglecting thermal expansion, and those of Reshchikova (1969) who also neglected thermal expansion, is excellent. Table 4 also illustrates that the effect of neglecting thermal expansion completely is an error of approximately 5 % in all of the $(\partial c/\partial T)_P$ except for the smaller magnitude $(\partial c_{44}/\partial T)_P$ for which the error is approximately 15 %. This indicates that any errors in our estimate of α for KMgF_3 will have an even smaller effect on the temperature derivatives of the elastic moduli.

Table 4. Comparison of the room temperature values of c and $(\partial c/\partial T)_P$ for KMgF_3 from various investigators

c_{11}	c' (kbar)	c_{44} (kbar)	K_s (kbar)	Reference
1,385	472	500	756	This work
1,380.1	471.8	498.3	751.1	Reshchikova (1969)
1,320	462	485	704	Rosenberg and Wigmore (1967)
$\left(\frac{\partial c_{11}}{\partial T}\right)_P$	$\left(\frac{\partial c'}{\partial T}\right)_P$	$\left(\frac{\partial c_{44}}{\partial T}\right)_P$	$\left(\frac{\partial K_s}{\partial T}\right)_P$	
-0.48	-0.24	-0.076	-0.161	This work
-0.46	-0.23	-0.066	-0.153	This work neglecting thermal expansion
-0.47	-0.23	-0.061	-0.163	Reshchikova (1969)

4. Discussion

In an earlier section, we briefly mentioned the value of lattice dynamical studies on predominately ionic crystals where the bonding forces are simpler and presumably better understood. As an extension of this idea, the effect of the higher degree of covalent bonding for the oxides could be investigated by comparison of the elastic behaviour of the members of a fluoride-oxide analogue pair, where the ionic radii and consequently the interionic distances are very similar. For the perovskite structure, KMgF_3 and SrTiO_3 are members of such a fluoride-oxide analogue pair.

The fluoride-oxide modelling scheme is based on the crystal chemical considerations of Goldschmidt (1927). The central feature of this scheme is the similarity in the ionic radii for the fluorine and oxygen ions. The members of a fluoride-oxide analogue pair are characterized by similar ionic radii and a valence charge ratio of 1:2 for the corresponding cations. The fluorides are “weakened” models of the oxides in that the weaker bonding forces associated with the singly charged ions result in lower hardness, refractive index and melting temperature than for the oxides. Jones and Liebermann (1974) suggested extension of this concept to include the temperature dependence of the elastic moduli, which they postulated might be greater for the fluorides than for the oxides. This prompted evaluation of the fluorides as models for the high-temperature elastic behaviour of the oxides, analogous in some senses to the use of germanates to infer the physical properties of silicates at higher pressures (Ringwood, 1975; Liebermann, 1974, 1975).

4.1. Temperature Dependence of the Elastic Moduli

Jones (1976a) demonstrated that for rocksalt fluorides and oxides, the values of $[(\partial c/\partial T)_p]$ decrease with increasing interionic distance in a manner that can be described quantitatively by the application of semi-empirical results to the theoretical equations of Mitskevich (1965). Obvious or explicable trends were not in evidence for fluorides and oxides in either the fluorite or rutile structure (Jones, 1977a and b). For the perovskite structure, there is insufficient data to examine trends in the values of $(\partial c/\partial T)_p$ for either fluorides or oxides. Some available fluoride data were not used, since some of these compounds (e.g., KMnF_3 , Aleksandrov et al., 1966) undergo phase transitions at lower temperatures and the elastic moduli exhibit anomalous temperature dependence, even at room temperature. SrTiO_3 does undergo a structural phase transition at approximately 110 K, but at room temperature the elastic moduli exhibit typical “high-temperature” elastic behaviour (i.e., for temperatures greater than the Debye temperature, they decrease with increasing temperature in an approximately linear fashion). The existence of these low-temperature structural transitions cannot be ignored, as they reflect details of the lattice dynamical behaviour that are ultimately expressed in the temperature derivatives of the elastic moduli. However, for the present we shall confine ourselves to examining the behaviour of the elastic moduli in that region where they decrease linearly with increasing temperature, and to comparing and

Table 5. Extrinsic and intrinsic components of $(\partial c/\partial T)_P$ for the perovskites KMgF_3 , RbMnF_3 and SrTiO_3 at room temperature

			Intrinsic	Extrinsic	
		$-\left(\frac{\partial \ln c}{\partial T}\right)_P$ (10^{-3} deg^{-1})	$-\left(\frac{\partial \ln c}{\partial T}\right)_V$ (10^{-3} deg^{-1})	$\frac{\alpha_V K_S}{c} \left(\frac{\partial c}{\partial P}\right)_T^a$ (10^{-3} deg^{-1})	$\left(\frac{\partial c}{\partial P}\right)_T$
c_{11}	KMgF_3	0.349 ^b	0.0614	0.288	8.93 ^b
	RbMnF_3	0.358 ^c	0.025	0.333	10.19 ^c
	SrTiO_3	0.273 ^d	0.119	0.154	10.21 ^e
c'	KMgF_3	0.513	0.237	0.275	2.94
	RbMnF_3	0.562	0.160	0.402	3.95
	SrTiO_3	0.341	0.192	0.149	3.35
c_{44}	KMgF_3	0.152	0.036	0.116	1.31
	RbMnF_3	0.089	-0.001	0.09	0.75
	SrTiO_3	0.130	0.0826	0.0478	1.24
K_S	KMgF_3	0.213	-0.082	0.295	5.01
	RbMnF_3	0.206	-0.075	0.2804	4.92
	SrTiO_3	0.216	0.0586	0.1579	5.74

^a α_V for SrTiO_3 taken from Lytle (1964)

α_V for KMgF_3 estimated in footnote Page 5

α_V for RbMnF_3 calculated by Naimon and Granato (1973) from data of Teaney et al. (1966)

^b This work

^c Naimon and Granato (1973)

^d Bell and Rupprecht (1963)

^e Beattie and Samara (1971)

contrasting the behaviour of KMgF_3 and SrTiO_3 . It is, after all, the “high-temperature regime” that is of particular interest in a geophysical context.

In Table 5 we have listed values of the dimensionless quantity $(\partial \ln c/\partial T)_P$ for the moduli c_{11} , c' , c_{44} and K_S for KMgF_3 , RbMnF_3 and SrTiO_3 . In general, the values of $(\partial \ln c/\partial T)_P$ for a particular modulus are quite similar for these three compounds (much more so than the values of $(\partial c/\partial T)_P$). This is very different from the behaviour for the members of the rocksalt analogue pairs (in particular, LiF-MgO and NaF-CaO), where it is the values of $(\partial c/\partial T)_P$ that are very similar (Jones, 1976b). The similarity is very striking for $(\partial \ln K/\partial T)_P$ for the three perovskites. The assumption that $(\partial \ln K/\partial T)_P$ is approximately constant over a wide range of lattice parameters would lead to a value of $-0.54 \text{ kbar. deg}^{-1}$ for $(\partial K/\partial T)_P$ for MgSiO_3 perovskite, using the Liebermann et al. (1977) value of 2.5 Mbar for K_S . Such empirical estimates should nevertheless be treated with caution, particularly when there is, as yet, no theoretical basis.

The other interesting feature of Table 5 is the decomposition of the temperature dependence of the elastic moduli into intrinsic and extrinsic components; the extrinsic component results from the dependence of the moduli on volume, which in turn depends on temperature through thermal expansion. The dependence is

expressed as follows

$$\begin{aligned}
 \left(\frac{\partial c}{\partial T}\right)_P &= \underbrace{\left(\frac{\partial c}{\partial T}\right)_V}_{\text{intrinsic}} + \underbrace{\left(\frac{\partial c}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T}_{\text{extrinsic}} \left(\frac{\partial V}{\partial T}\right)_P \\
 &= \left(\frac{\partial c}{\partial T}\right)_V - \alpha_V K_T \left(\frac{\partial c}{\partial P}\right)_T \\
 &= \left(\frac{\partial c}{\partial T}\right)_V - \frac{\alpha_V K_S}{(1 + \alpha_V \gamma T)} \left(\frac{\partial c}{\partial P}\right)_T
 \end{aligned} \tag{5}$$

where α_V is the volumetric thermal expansion, K_T is the isothermal bulk modulus, and K_S is the adiabatic bulk modulus. Gruneisen's parameter, γ , is defined as $\gamma = \alpha_V K_S / \rho C_P$ where C_P is the specific heat at constant pressure. For the purpose of this calculation, the term $(1 + \alpha_V \gamma T)$ is taken as unity, which is a good approximation at room temperature. The results of this decomposition must be taken tentatively for KMgF_3 since only an estimated thermal expansion was used. However, it appears that the temperature dependence is predominately extrinsic for KMgF_3 and RbMnF_3 , while for SrTiO_3 the intrinsic contribution plays a much more important role.

4.2. Pressure Dependence of the Elastic Moduli

We will now examine more closely the values of the pressure derivatives of the elastic moduli for KMgF_3 , RbMnF_3 and SrTiO_3 . These are listed in Table 5 for the single crystal moduli c_{11} , c' , c_{44} , and K_S . There is a good correspondence between the values of $(\partial c / \partial P)$ for all the moduli for these compounds, particularly for RbMnF_3 and SrTiO_3 . Even though the fluorides are "weakened" models of the oxides, it is not surprising that the pressure derivatives are very similar. Theoretical equations for the elastic moduli and their pressure derivatives (e.g., O.L. Anderson and Liebermann, 1970) show that the $(\partial c / \partial P)$ are independent of ionic charge for several cubic lattices. We can probably infer that the effect of the more covalent bonding for the oxides ought to be a second order one. The available data does not allow separation of the effects of covalent bonding and interionic distance on the pressure derivatives.

The similarity of the pressure derivatives of the elastic moduli for KMgF_3 , RbMnF_3 , and SrTiO_3 seems to indicate that the values of $(\partial c / \partial P)_T$ for these perovskites are controlled primarily by crystallographic structure. Naimon and Granato (1973) pointed out a strong correspondence between the elastic constants (both second and third-order) for RbMnF_3 and SrTiO_3 , and were able to interpret the results for RbMnF_3 in terms of the relative geometrical arrangement of the closest ions. In view of this correspondence, it is of particular interest to determine whether the elastic moduli and their pressure derivatives can be calculated from a simple central force model for the fluoroperovskites for the simpler case of purely ionic bonding. A similar model to that used by Naimon (1974) for RbMnF_3 will be employed here for KMgF_3 and RbMnF_3 .

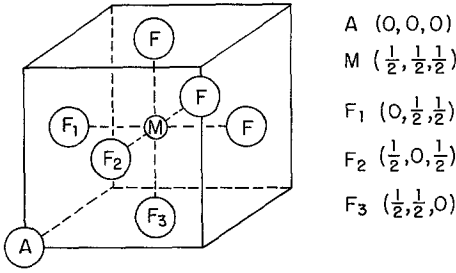


Fig. 3. Arrangement of the ions in the cubic perovskite structure. The basic repeat unit is AMF_3 , with positions of the ions as shown

The arrangement of the ions in the general fluoride perovskite AMF_3 is illustrated in Fig. 3. Each A^+ ion is surrounded by twelve F^- ions, while each M^{2+} ion is surrounded by six F^- ions; the F^- ions are six-fold coordinated. Following Cowley (1964) for the case of central forces, the force constants, A_i and B_i , associated with the short-range interaction are defined as

$$\frac{e^2 A_i}{2V} = \left(\frac{\partial^2 \phi_i}{\partial r_i^2} \right); \quad \frac{e^2 B_i}{2V} = \frac{1}{r_i} \left(\frac{\partial \phi_i}{\partial r_i} \right) \quad (6)$$

where ϕ_1, ϕ_2 and ϕ_3 are the repulsive potentials associated with each pair of nearest neighbour ions, $A-F$, $M-F$ and $F-F$ respectively. V is the volume of the unit cell, and r_1, r_2 , and r_3 are the interionic distances such that $r_1 = r_3 = \sqrt{2}r$ and $r_2 = r$, r being the nearest neighbour distance. With the assumptions of purely ionic bonding and negligible $F-F$ short-range interaction, Cowley's (1964) expressions for the elastic moduli reduce to the following equations, involving a Coulombic contribution and the short range force constants A_1, A_2, B_1 and B_2

$$\begin{aligned} c_{11} &= \frac{e^2}{rV} \left[\frac{1}{8} (2A_1 + 2B_1 + A_2) - 6.1850 \right] \\ c_{12} &= \frac{e^2}{rV} \left[\frac{1}{8} (A_1 - 5B_1 - B_2) - 1.03338 \right] \\ c_{44} &= \frac{e^2}{rV} \left[\frac{1}{8} (A_1 + 3B_1 + B_2) + 3.09254 \right]. \end{aligned} \quad (7)$$

From the requirement that $P = -\partial\Phi/\partial V$, where P is the pressure and Φ is the potential energy for a unit cell, the equilibrium constraint

$$8\alpha_M + 12B_1 + 3B_2 = - \left(\frac{24rV}{e^2} \right) P \quad (8)$$

can be obtained. In the above equation, $\alpha_M = 6.188785$ is the Madelung constant for the perovskite structure defined in terms of nearest neighbour distance. This value is determined by substituting the valence charges into Cowley's (1964) expression for the Madelung constant in terms of the lattice parameter. Applying the equilibrium constraint to Eq. (7) leads to the general Cauchy relation for non-zero

pressure,

$$c_{12} - c_{44} = 2P. \quad (9)$$

For the central A–F and M–F interactions, we assume that the functional form of the repulsive potential is given by the Born-Mayer expression

$$\phi_i = \lambda_i e^{-r_i/\rho_i} \quad (10)$$

where λ_i and ρ_i are the repulsive parameters, and r_i is the interionic distance. Using this functional form, the force constants defined in Eq. (6) can be evaluated

$$\frac{e^2 A_i}{2V} = \frac{\lambda_i}{\rho_i^2} e^{-r_i/\rho_i}, \quad \frac{e^2 B_i}{2V} = -\frac{\lambda_i}{r_i \rho_i} e^{-r_i/\rho_i} \quad (11)$$

It can be easily shown that the pressure derivatives of the elastic moduli are related to the derivatives with respect to r by

$$\left(\frac{\partial c}{\partial P}\right)_T = -\frac{r}{3K_T} \left(\frac{\partial c}{\partial r}\right)_T \quad (12)$$

Since the perovskite structure is centrosymmetric, we can obtain the pressure derivatives of the c_{ij} by taking the derivatives of Eq. (7) with respect to r , provided we do this before applying the equilibrium constraint. The result of this procedure is that the terms A_i and B_i in the expressions for the elastic moduli transform to $[1 + r_i/\rho_i]A_i/3K_T$ and $[2 + r_i/\rho_i]B_i/3K_T$ in the expressions for the pressure derivatives, where $r_i/\rho_i = -A_i/B_i$. The final expressions are:

$$\begin{aligned} \frac{\partial c_{11}}{\partial P} &= \frac{e^2}{3KrV} \left\{ \frac{1}{8} \left[2A_1 \left(1 + \frac{r_1}{\rho_1} \right) + 2B_1 \left(2 + \frac{r_1}{\rho_1} \right) + A_2 \left(1 + \frac{r_2}{\rho_2} \right) \right] - 4 \times 6.1850 \right\} \\ \frac{\partial c_{12}}{\partial P} &= \frac{e^2}{3KrV} \left\{ \frac{1}{8} \left[A_1 \left(1 + \frac{r_1}{\rho_1} \right) - 5B_1 \left(2 + \frac{r_1}{\rho_1} \right) - B_2 \left(2 + \frac{r_2}{\rho_2} \right) \right] - 4 \times 1.03338 \right\} \\ \frac{\partial c_{44}}{\partial P} &= \frac{e^2}{3KrV} \left\{ \frac{1}{8} \left[A_1 \left(1 + \frac{r_1}{\rho_1} \right) + 3B_1 \left(2 + \frac{r_1}{\rho_1} \right) + B_2 \left(2 + \frac{r_2}{\rho_2} \right) \right] + 4 \times 3.09254 \right\} \end{aligned} \quad (13)$$

where for the purposes of this calculation it does not matter whether we use the adiabatic or isothermal bulk modulus.

In order to calculate the values for $\partial c_{ij}/\partial P$, it is necessary to know the parameters ρ_i and λ_i for the A–F and M–F interactions for KMgF_3 and RbMnF_3 . To avoid the problem of using most of the experimental data merely to determine the four repulsive parameters, we took an alternative approach. We assumed that the A–F repulsive interactions in both AMF_3 and the rocksalt-structure fluoride AF can be described by the same repulsive parameters ρ_1 and λ_1 , thus enabling these parameters to be obtained from the rocksalt fluoride. It can be shown quite simply for the rocksalt structure that at the equilibrium position $P=0$

(e.g., Roberts and Smith, 1970a),

$$K = \frac{\rho \lambda_1 e^{-r/\rho_1}}{9V_0} \left[\left(\frac{r}{\rho_1} \right)^2 - 2 \left(\frac{r}{\rho_1} \right) \right] = \frac{\alpha_M e^2}{9V_0 r} \left(\frac{r}{\rho_1} - 2 \right) \quad (14)$$

where K is the bulk modulus, p is the coordination number, V_0 is the volume per molecule and α_M is the Madelung constant. With the values of ρ_1 and λ_1 thus determined, A_1 and B_1 can be obtained using Eq. (6). B_2 can now be found from the expression for the equilibrium constraint, Eq. (8); the final parameter A_2 is determined from the expression for the bulk modulus of AMF_3

$$K = \frac{e^2}{3rV} \left\{ \frac{1}{8} [4A_1 - 8B_1 + A_2 - 2B_2] - 8.25171 \right\}. \quad (15)$$

To arrive at these values for A_i and B_i we have used only the values of the bulk modulus and the nearest neighbour distance at equilibrium for AF and AMF_3 .

In Table 6 we list the basic data for KF, RbF, KMgF_3 and RbMnF_3 , as well as the values of A_i and B_i , and the elastic moduli and their pressure derivatives for KMgF_3 and RbMnF_3 . For both these compounds, A_2 is by far the largest force constant, indicating that the M–F interaction is responsible for the strength of these compounds. The dominant contribution to the pressure derivatives comes also from this interaction. The calculated values of the elastic moduli and their pressure derivatives are in good agreement with the experimental values. As is to be expected, the central force model predicts that $c_{12} = c_{44}$, and that $(\partial c_{12}/\partial P) - (\partial c_{44}/\partial P) = 2$. For KMgF_3 , the central force model appears to be more applicable than it is for RbMnF_3 .

Table 6. Parameters and calculated values for a central force model for fluoroperovskites

	KF	KMgF_3	RbF	RbMnF_3
K (kbar)	316 ^a	756	277 ^b	672 ^c
r (10^{-8} cm)	2.674 ^a	1.9865 ^c	2.826 ^b	2.1195 ^c
V (10^{-24} cm ³)	38.24 ^a	62.71	45.13 ^b	76.17
	KMgF_3	RbMnF_3		
A_1	11.0435	10.675		
B_1	-1.1408	-1.0174		
A_2	86.824	103.237		
B_2	-11.94	-12.434		
c_{11} (kbar)	1,323 (1385) ^d	1,305 (1174) ^c		
c_{12} (kbar)	473 (441)	356 (421)		
c_{44} (kbar)	473 (500)	356 (319)		
c'_{11}	7.4 (8.93) ^d	8.7 (10.19) ^f		
c'_{12}	2.68 (3.05)	2.49 (2.29)		
c'_{44}	0.68 (1.31)	0.49 (0.75)		

^a Roberts and Smith (1970a)

^b Roberts and Smith (1970b)

^c Rousseau et al. (1974)

^d This work

^e Melcher and Bolef (1969)

^f Naimon and Granato (1973)

This good agreement between theory and experiment is encouraging in view of the simplicity of the model and the fact that thermal effects have been ignored. Using the values of the parameters for KF and RbF from Smith and Cain (1975) for reduction to a static lattice affects the results of the calculation very little. It turns out that the parameters A_i and B_i are not particularly sensitive to the value of K employed in Eq. (14), probably since the K – F interaction is not the dominant one. In any case, for a complete static lattice treatment, we would require thermal expansion data for KMgF_3 and the temperature dependence of the pressure derivatives.

Inclusion of the F – F interaction, with the same values of ρ_1 and λ_1 as the K – F interaction leads to very poor results for KMgF_3 . This approach was used by Naimon (1974) in discussing RbMnF_3 . However, our calculations for RbMnF_3 , neglecting the F – F term, give better agreement for the elastic moduli, despite the fact that Naimon had corrected the data to a static lattice. There are some justifications for ignoring the F – F interaction. Firstly, Cowley's (1964) results for SrTiO_3 showed that A_3 and B_3 appear to be negligible for the perovskite structure. Secondly, consideration of the ionic radii for the appropriate coordination number given by Shannon and Prewitt (1969, 1970), $\text{K}^+ = 1.60 \text{ \AA}$, $\text{Rb}^+ = 1.73 \text{ \AA}$, $\text{Mg}^{2+} = 0.72 \text{ \AA}$, $\text{Mn}^{2+} = 0.82 \text{ \AA}$ and $\text{F}^- = 1.33 \text{ \AA}$, shows that the only overlap occurs between the cations and the anions, and not between the anions for KMgF_3 and RbMnF_3 .

This simple central force model is very successful with the inclusion of only two types of interaction for the case of purely ionic bonding. For the perovskite oxides, calculation of the pressure pressure derivatives presents a larger problem in that more parameters are required to characterize the model for the case of polarizable ions and possible departures from purely ionic behaviour. We can, however, make use of the empirical result that $(\partial K/\partial P)_T$ does not depend on cationic radius for the alkali halides and shows no systematic behaviour for oxides and silicates (Davies, 1976). This approach would predict a value between 5 and 6 for $(\partial K/\partial P)$ of MgSiO_3 -perovskite, on the basis of the results for KMgF_3 , RbMnF_3 and SrTiO_3 .

4.3. Systematics in Elastic Properties of Perovskite Oxides and Fluorides

The empirical result $KV = \text{constant}$ is well established for isostructural series of halides, sulphides, selenides and tellurides (O.L. Anderson and Nafe, 1965; D.L. Anderson, 1967; O.L. Anderson and Soga, 1967; D.L. Anderson and O.L. Anderson, 1970; and O.L. Anderson, 1972). An alternative representation of this result in terms of bulk sound velocity, v_ϕ , and mean atomic weight, \bar{M} , is $v_\phi \bar{M}^{1/2} = \text{constant}$ for isostructural compounds (Shankland, 1972). Liebermann et al. (1977) reported values of the elastic moduli for a suite of poly-crystalline perovskites consisting of ScAlO_3 , GdAlO_3 , SmAlO_3 , EuAlO_3 , YAlO_3 , CdTiO_3 , CaTiO_3 , CdSnO_3 , CaSnO_3 , and CaGeO_3 , and demonstrated that the perovskite oxides followed a linear trend of gradient $-1/2$ on a log-log plot of bulk sound velocity versus mean atomic weight. In Fig. 4, we have similarly

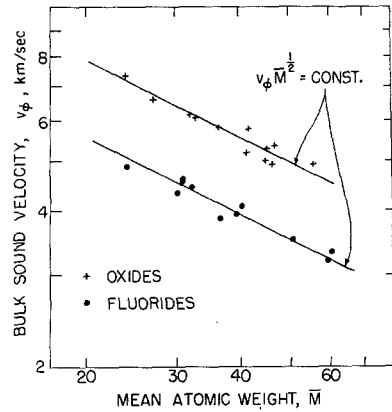


Fig. 4. Bulk sound velocity, v_ϕ , versus mean atomic weight, \bar{M} , for oxides and fluorides with the perovskite structure. The data for the perovskite fluorides are listed in Table 7. Data for the oxides were taken from Liebermann et al. (1977). The solid lines have gradient $-1/2$

Table 7. Elasticity data for perovskite fluorides

Compound	\bar{M}	P ($\text{gm} \cdot \text{cm}^{-3}$)	V_m (cm^3)	K_S (kbar)	v_ϕ ($\text{km} \cdot \text{s}^{-1}$)
KMgF ₃	24.08	3.15 ^a	38.23	756 ^b	4.899
KMnF ₃	30.21	3.42 ^c	44.16	649 ^d	4.356
KNiF ₃	30.96	3.985 ^e	38.84	851 ^f	4.621
KCoF ₃	31.00	3.82 ^e	40.58	787 ^f	4.539
KZnF ₃	32.29	4.023 ^e	40.13	800 ^{f,g}	4.459
RbCaF ₃	36.51	3.435 ^h	53.15	503 ⁱ	3.828
RbMnF ₃	39.48	4.317 ^j	45.73	672 ^j	3.945
RbCoF ₃	40.28	4.756 ^e	42.34	801 ^{f,k}	4.104
RbCdF ₃	50.97	4.971 ^l	51.27	614 ^m	3.514
TlCdF ₃	59.40	5.8109 ^l	51.11	599 ^m	3.211
CsCdF ₃	60.46	5.638 ^l	53.62	629 ^m	3.341

^a Reshchikova (1969)

^b This work

^c Beckman and Knox (1961)

^d Aleksandrov et al. (1966)

^e Calculated from the lattice parameters listed in Rousseau et al. (1974)

^f Rousseau et al. (1974)

^g Gesland et al. (1972)

^h Wyckoff (1963)

ⁱ Fischer et al. (1978)

^j Melcher and Bolef (1969)

^k Nouet and Plicque (1971)

^l Calculated from the lattice parameters listed in Rousseau et al. (1975)

^m Rousseau et al. (1975)

plotted the data for the perovskite fluorides (Table 7) as well as the perovskite oxides (Table 3, Liebermann et al., 1977). The fluorides also fall very closely about another line of gradient $-1/2$. A least squares analysis showed the gradient of the best fitting straight line to the data was actually -0.49 for the oxides and -0.46 for the fluorides; these lines are indistinguishable from the

lines $V_\phi \bar{M}^{1/2} = \text{constant}$. It is particularly interesting that the relationship $KV = \text{constant}$ is obeyed for the perovskite structure since, due to the presence of two types of cation-anion interactions, the expression for the potential energy is not nearly as simple as for the diatomic solids for which the relationship was first established.

The other noteworthy feature of Fig. 4 is the scaling of the respective lines for the oxides and the fluorides. It can be shown from simple theory (e.g., O.L. Anderson, 1972) that

$$K = \frac{2\alpha_M e^2}{9V_0 r_0} \left[1 + \frac{v''(r_0)r_0}{2v'(r_0)} \right] \quad (13)$$

where $v(r)$ is a general repulsive potential, V_0 is the molecular volume and α_M is the Madelung constant. Upon substitution in terms of the reduced Madelung constant, $A = 2\alpha_M/Z_c Z_a p$, where Z_c , Z_a are the valence charges of the cation and anion respectively, and p is the number of atoms per molecule, Eq. (13) becomes (O.L. Anderson, 1972)

$$\ln K = \ln \left(\frac{AZ_c Z_a}{\left(\frac{2M}{p\rho} \right)} \right) + \text{constant} \quad (14)$$

where $(2M/p\rho)$ is the molar volume per ion pair. Equation (14) demonstrates that the lines on a log-log $K - V$ plot ought to be scaled as $Z_c Z_a$ for isostructural diatomic compounds, since the reduced Madelung constant is almost independent of crystallographic structure (Johnson and Templeton, 1961). To account for the deviation from this behaviour, O.L. Anderson (1972) postulated that the lines were actually scaled as $S^2 Z_c Z_a$, where SZ is an effective charge in the Coulombic interaction. From Fig. 4, we can obtain a value of 70% for the relative effective charge of the perovskite oxides with respect to the fluorides. This is not very different from the value of 74% obtained from the then available data by Jones and Liebermann (1974), who also demonstrated that the relative effective charge seemed to be relatively independent of crystallographic structure for oxides and fluorides in the rocksalt, fluorite, rutile and perovskite structures.

However, the interpretation is not straightforward for the perovskite structure; the Madelung constant, α_M , is a function of the charges on three different ions, and thus the effective charge need not necessarily be 70% for each of the ions. Also, the above is only one definition of the effective charge. Other definitions lead to the conclusion that the behaviour for SrTiO_3 is almost purely ionic (e.g., Cowley, 1964). Perhaps the values of effective charge obtained from the lines for isostructural fluorides and oxides on a $K - V$ plot are a reflection of subtle differences in the repulsive potential parameters occurring in the bracketed term in Eq. (13).

5. Summary

Since the perovskite polymorph of MgSiO_3 is a probable lower mantle constituent (Liu, 1974; 1975a and b; 1976), it is of particular importance to obtain data on the elastic properties of compounds crystallizing in the perovskite structure, in order to better understand the relationship of elastic properties to crystallographic parameters and to estimate those for MgSiO_3 -perovskite. Accordingly, we have employed precise ultrasonic pulse techniques to determine the elastic moduli of the single crystal perovskite KMgF_3 as a function of temperature to approximately 550°K , and as a function of pressure to 2.5 kbar. Our room temperature values of the elastic moduli and their temperature derivatives are consistent with those of Reshchikova (1969), whose measurements were made below and up to room temperature.

Comparison of our data with that for SrTiO_3 indicates that, in general, the values of $1/c(\partial c/\partial T)_P$ for SrTiO_3 are similar to the corresponding values for its fluoride analogue KMgF_3 ; similarly, corresponding values of $(\partial c/\partial P)_T$ are not very different for KMgF_3 and SrTiO_3 . While there is no theoretical explanation for the values of the temperature derivatives, values of $(\partial c/\partial P)_T$ can however be calculated from a simple central force model. These results are in good agreement with the experimental values for KMgF_3 .

It was also demonstrated that the fluoroperovskites obey the bulk sound velocity-mean atomic weight relationship, $v_\phi \bar{M}^{1/2} = \text{constant}$. Comparison with the perovskite oxide data on a log-log plot of bulk sound velocity versus mean atomic weight leads to a value of 70% for the relative effective charge of the oxides with respect to the fluorides.

More data are required before the pressure and temperature derivatives of the elastic moduli can be estimated for the perovskite MgSiO_3 . Measurement of these derivatives, for either polycrystals or single crystals, for as many of these perovskites as possible would be of tremendous value in establishing empirical relationships. Tentatively, on the basis of the results for KMgF_3 and SrTiO_3 , we have estimated a value between 5 and 6 for $(\partial K/\partial P)_T$ for MgSiO_3 . Calculation of the pressure derivatives of the elastic moduli of perovskite- MgSiO_3 via Cowley's (1964) model would require data from Raman and neutron scattering experiments, as well as elastic data for a number of perovskite oxides, so that the variation of the force constants with lattice parameter could be obtained. A further complication is introduced by the fact that most perovskites (including MgSiO_3) are not cubic at room pressure and temperature. Apart from the empirical approach, a possible alternative method could involve the calculation of lattice energies from the wave-functions of the individual ionic species, an approach that has been used by Cohen and Gordon (1975) with great success for the alkali halides, and that has the advantage of no a priori assumptions about the nature of the interaction potentials. Until such calculations are performed, further experimental studies on available perovskites and their fluoride analogues will be particularly useful.

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