

Effect of hydrostatic pressure on the elastic constants of cubic PbF_2

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The adiabatic elastic stiffness moduli of fluorite-structure PbF_2 have been determined at hydrostatic pressures up to 3 kbar by means of ultrasonic velocity measurements at 296 K. All moduli increase linearly with pressure indicating that the impending transformation to the orthorhombic structure at 4 kbar is not due to softening of long-wavelength acoustic modes. It is found that a simple lattice-dynamical shell model fails to account for the pressure dependences of the moduli. Possible reasons are suggested.

I. INTRODUCTION

The cubic, fluorite-structure polymorph of PbF_2 exhibits many interesting properties. Among these are a transition to a highly ionic-conducting (superionic) state at moderately elevated temperatures (between 600 and 800 K),¹ a pressure-induced, nonreversible, first-order transition to an orthorhombic structure at 4 kbar,² and an anomalous temperature dependence of its dielectric constant below room temperature which is attributed to an incipient ferroelectric transition.²

Softening of the acoustic modes^{3,4} involving the C_{11} and $C_S = \frac{1}{2}(C_{11} - C_{12})$ elastic stiffnesses is known to accompany the superionic transition. In addition a soft, long-wavelength, transverse optic phonon is associated with the anomalous behavior of the dielectric constant.²

Recent specific-heat measurements⁵ have revealed that the pressure-induced, orthorhombic phase of PbF_2 undergoes a nonreversible transition at 633 K which has a latent heat of 1.9 kJ/mol. After this transition takes place, the heat capacity is the same as that of cubic, fluorite-structure PbF_2 . In order to elucidate further the lattice stability of PbF_2 , we have studied the effect of hydrostatic pressures up to 3 kbar on the elastic constants of the fluorite-structure polymorph of PbF_2 .

II. EXPERIMENTAL

The elastic constants were determined from ultrasonic velocity data obtained using the pulse-echo-overlap method of Papadakis.⁶ A single crystal of PbF_2 , grown by the Stockbarger technique, was purchased from the Harshaw Chemical Co. The crystal was oriented to within $\frac{1}{2}^\circ$ using Laue back reflection and polished so as to have pairs of faces perpendicular to the fourfold [001] and to the twofold [110] axes. The faces were flat to within 2 wavelengths of Na light and parallel to within 0.01° . These orientations permit all three

elastic constants, C_{11} , C_{12} , and C_{44} , to be determined.

The appropriate longitudinal and shear waves were produced, respectively, by X-cut quartz and X-cut LiNbO_3 transducers plated coaxially with chrome-gold. The transducers were 0.63 cm in diameter and had a fundamental frequency of 30 MHz. Dow Corning 276-V9 resin was used to bond the transducer to the crystal.

The sample holder and high pressure apparatus are described elsewhere.⁷ Pressure was measured using a commercial (Harwood) calibrated manganin coil and a Bourdon gauge. Lightweight motor oil was used as the pressure medium. Sufficient time was allowed after each pressure change to allow the sample to reach thermal equilibrium.

III. RESULTS

The effect of hydrostatic pressure on the longitudinal and shear elastic constants is shown in Figs. 1 and 2, respectively. Measurements were made up to only 3 kbar to insure that the nonreversible structural transformation would not take place, since we wanted to be able to make further investigations of the cubic phase. (Investigation of ultrasonic velocities through the transition is the subject of work now underway in our labora-

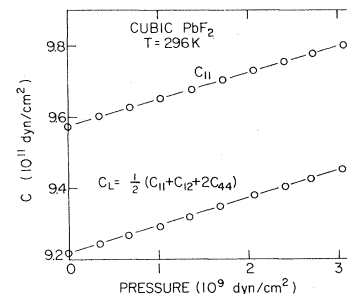


FIG. 1. The longitudinal elastic stiffness moduli of cubic PbF_2 .

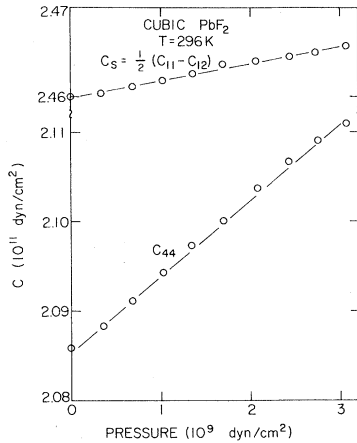


FIG. 2. The shear moduli of cubic PbF_2 . C_{44} was measured with \vec{k} , the wave vector, parallel to $[110]$ and \hat{e} , the polarization vector, parallel to $[001]$. C_S was measured with $\vec{k} \parallel [110]$ and $\hat{e} \parallel [1\bar{1}0]$.

tory.) The 1 bar values of the elastic constants reported here agree with those obtained by Hart⁸ from his own compliance data and from his re-analysis of results obtained by Wasilik and Wheat.⁹ As can be seen, all the elastic moduli increase with increasing pressure. Moreover, they show no softening in anticipation of the impending 4 kbar structural transformation. That this transformation actually occurs in the PbF_2 employed herein was verified by the milky white² appearance of a sample after it had been subjected to 4.5 kbar of hydrostatic pressure.

IV. DISCUSSION

Traditionally, structural phase transitions have been predicted to occur at those pressures and/or temperatures where the Born criteria are violated.¹⁰ More recently, Demarest and coworkers¹¹ proposed a model in which the difference in the Gibbs free energy between phases depends on the ratio of a certain shear elastic constant C_t to the bulk modulus B . When C_t/B reaches a certain critical value α , where typically $0 < \alpha < 0.2$, it is energetically favorable for the lattice to distort. In the case of the fluorite-structure fluorides, $C_t = C_S$. Extrapolation of C_S/B for CaF_2 ,¹² BaF_2 ,¹² and PbF_2 to the respective transition pressures¹³ yields values of α between 0.3 and 0.6. Thus the Demarest *et al.* criterion is not satisfied and the transition is not driven by a long-wavelength acoustic phonon. This is consistent with Samara's proposition^{2,14} that the transition is the result of a soft TA phonon near the zone boundary.

The pressure dependences of elastic moduli in cubic PbF_2 are similar to those found in fluorite-

structured CaF_2 , SrF_2 , BaF_2 , and CdF_2 .¹⁵ Since some of the elastic behavior of the latter three compounds has been accounted for fairly well using shell models,¹⁵ it is appropriate to determine if such models can account for our PbF_2 data.

An early shell-model calculation¹⁶ for PbF_2 yielded much smaller pressure derivatives dC_{ij}/dP than those measured in the present investigation. (A negative value was even calculated for dC_{44}/dP .) Since that calculation employed incorrect values for the C_{ij} , we repeated the calculation using our own C_{ij} values and obtained improved dC_{11}/dP and dC_{44}/dP values. As can be seen from Table I, the calculated pressure derivatives are still much smaller than the experimental ones.

Recently,¹⁷ phonon dispersion relations have been determined for PbF_2 using inelastic neutron scattering. Several models, fitted to these results, have resulted in C_{11} , C_{12} , and C_{44} values close to those determined ultrasonically at ambient conditions. These models contain interactions in addition to those in the simple shell model^{18,19} for which expressions¹⁹ to calculate pressure derivatives of the C_{ij} are available at present. Thus we do not attempt to calculate dC_{ij}/dP values using the models of Ref. 17.

Failure of a simple shell model to account for the pressure dependences of the elastic moduli in cubic PbF_2 , might be due to limitations imposed by the approximations made in the model. For example, the only interionic interactions considered are between lead and adjacent fluorine ions, and between fluorine ions on two different sublattices. Alternatively, the failure might be due to the use of a too simple interanionic potential (i.e., a $1/r^n$ form). Another reason for the shell model failing to account for the dC_{ij}/dP in PbF_2 might be that the specific nature of the Pb^{+2} ion needs to be taken into account. This is because, in contrast to the electronic configuration on the metal ions

TABLE I. Comparison of the observed pressure dependences of the elastic constants of cubic PbF_2 at 296 K with those calculated using a simple shell model like that in Refs. 16 and 19 but employing correct C_{ij} values at 1 bar.

	Observed	Calculated
$\frac{dC_{11}}{dP}$	7.4	3.9
$\frac{dC_{12}}{dP}$	7.0	5.3
$\frac{dC_{44}}{dP}$	0.94	0.3

of the other fluorites, the outermost electronic shell on the Pb^{+2} ion contains two electrons in s orbitals.

From the foregoing discussion it should be evident that in order to explain the elastic behavior of PbF_2 under pressure a number of things need to be done. First of all, theoretical expressions have to be developed which are appropriate for calculating pressure derivatives in the more complicated shell models. Then one might proceed empirically by choosing values for the parameters in a given model which fit the measured pressure derivatives. The validity of this procedure would be checked by determining if the chosen parameters yield correct values for the elastic constants and optical properties at 1 bar.

Alternatively, one might try to use an idea that has been applied to alkali halide crystals, namely: Each ion has a compression energy which is a function of its size.²⁰ The size depends in turn on the numbers and types of near neighbors so that there is one set of effective "radii" in the directions of the unlike, nearest neighbors and another set of radii in the directions of the like, next-nearest neighbors. That spatial considerations are important for the fluorites is suggested by a correlation between the fractional amount of void space and the pressure at which transformation to the orthorhombic structure takes place. This correlation can be seen in Fig. 3 where the fraction of unoccupied space per unit cell is plotted versus transition pressure.¹³ The volume occupied by ions was calculated assuming spherical ions with Goldschmidt radii,²¹ and the cell volume was calculated from lattice parameters^{15,22} as indicated in Ref. 18.

V. CONCLUSIONS

The second-order elastic constants of cubic PbF_2 have been determined at 296 K using hydro-

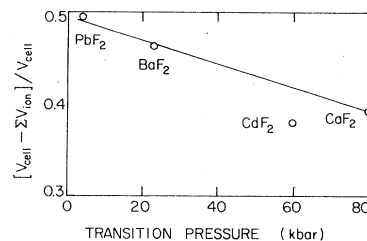


FIG. 3. The fraction of void space per unit cell versus the transition pressure (measured while increasing pressure).

static pressures up to $\frac{3}{4}$ of that where a structural transformation is known to occur. No softening of long-wavelength acoustic modes was found. This is consistent with the proposition of Samara that a soft TA mode near the zone boundary drives the transition. A shell-model calculation fails to yield correct values for the pressure derivatives of the elastic constants of cubic PbF_2 , even though such models have been moderately successful for some fluorite-structure fluorides. Possible reasons for this are proposed and new modeling approaches suggested.

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