

## Elastic constants of cubic lead fluoride from 300 to 850 K

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Measurements of ultrasonic velocity in single-crystal cubic  $\text{PbF}_2$  have been made over a temperature range from 300 to 850 K. Values of the three independent, adiabatic elastic constants over this temperature range are obtained from  $C_{11}$ ,  $(C_{11} + C_{12} + 2C_{44})/2$ ,  $(C_{11} - C_{12})/2$ , and  $C_{44}$ . The results are anomalous at the Faraday temperature of 711 K for  $\text{PbF}_2$ , which is well below its melting temperature of 1158 K. A large decrease in the elastic constant  $C_{11}$  and much smaller decrease in  $C_{12}$  and  $C_{44}$  are observed near 711 K in addition to the nearly linear decrease in the elastic constants with temperature.

## INTRODUCTION

A class of materials exists in which ionic conductivity is comparable to that in molten salts. These solids are called solid electrolytes, superionic conductors, or fast-ion conductors. Faraday<sup>1</sup> reported that the conductivity of  $\text{PbF}_2$  increased dramatically when its temperature was increased above a particular temperature,  $T_c$ , which was below the melting temperature. The alkaline-earth fluoride crystals exhibit broad specific-heat anomalies<sup>2</sup> as well as anomalies in many other properties at the Faraday temperature  $T_c$ . These phenomena are generally assumed to be associated with the development of extensive Frenkel disorder in the anion sublattice with the disorder giving rise to the fast-ion behavior.<sup>3</sup>

A heat-capacity peak<sup>4,5</sup> in  $\text{PbF}_2$  has been observed near a  $T_c$  of 711 K.<sup>5</sup> The effect of the high-temperature disorder on neutron scattering by  $\text{PbF}_2$  has been investigated by Dickens *et al.*<sup>6</sup> Catlow *et al.*<sup>3</sup> describe an experimental study of the effect of the disorder on the elastic constants of  $\text{PbF}_2$  as well as some other fluorite crystals by using the Brillouin scattering method. Elliott *et al.*<sup>7</sup> have studied the effect of anharmonicity and high-temperature disorder on Raman scattering in fluorite crystals, including  $\text{PbF}_2$ . In this study, we report experimental results of the effect of the disorder on the elastic constants of  $\text{PbF}_2$  using ultrasonic techniques.

## THEORY

The classical theory of elasticity shows that the number of independent adiabatic elastic constants of a cubic crystal is three.<sup>8</sup> Values of these elastic constants  $C_{ij}$  can be obtained from the relationship  $C_{ij} = \rho v^2$ , where  $\rho$  is the density and  $v$  is the velocity of sound. The crystals were cut along [100] and [110] directions to allow measurements of two longitudinal and two transverse velocities. The relations of elastic constants to density and velocity used in this work were  $\rho v_L^2 = C_{11}$ ,  $\rho v_L'^2 = (C_{11} + C_{12} + 2C_{44})/2$ ,  $\rho v_T^2 = C_{44}$ , and  $\rho v_T'^2 = (C_{11} - C_{12})/2$ , where  $v_L$  is the longitudinal ultrasonic velocity of the wave propagated in the [100] direction, and  $v_L'$ ,  $v_T$ , and  $v_T'$  are the ultrasonic velocities of waves propagated in the [110]

direction for the longitudinal wave and transverse waves polarized in the [001] and  $[1\bar{1}0]$  directions, respectively.

In order to calculate the elastic constants as a function of temperature, it is necessary to correct the crystal specimen's density and length using the thermal-expansion coefficient. Since the elastic constants are proportional to the crystal length squared divided by the volume, the correction due to thermal expansion appears reciprocally as a length correction to the first power. If one knows the density  $\rho_0$  and the crystal length  $L_0$  at some temperature  $T_0$ , and the thermal-expansion coefficient  $\alpha(T) = d(\ln L)/dT$ , it can be shown that an elastic constant is calculated from the pulse round-trip transit time  $\Delta t$  at any temperature  $T$ , by the expression

$$C_{ij}(T) = \frac{4\rho_0 L_0^2}{(\Delta t)^2} \exp\left[-\int_{T_0}^T \alpha(T) dT\right], \quad (1)$$

where  $\rho_0$  is the density at  $T_0 = 300$  K and is taken to be  $7.755 \times 10^3$  kg/m<sup>3</sup> for  $\text{PbF}_2$ .<sup>3</sup> The thermal-expansion coefficient in units of K<sup>-1</sup> was taken to be  $\alpha(T) = 2.73 \times 10^{-6} + 7.03 \times 10^{-8} T$  for  $\text{PbF}_2$ .<sup>9</sup>

## EXPERIMENT

A cylindrical single-crystal unorientated specimen of  $\text{PbF}_2$  approximately 1.5 cm in diameter and 2.5 cm in length was obtained from the Harshaw Chemical Company.<sup>10</sup> X-ray diffraction by using back-reflection Laue photography was used to orient this sample to within 7.5° of the [100] direction. For 7.5° misalignment, the error in the longitudinal velocity was determined<sup>11</sup> to be  $\Delta v/v = 0.05\%$ . The end faces of this sample were parallel to within 1 part in  $10^2$ . This single-crystal  $\text{PbF}_2$  crystal was difficult to orientate due to x-ray absorption and to polish due to its susceptibility to cracks.

Another cylindrical, single-crystal specimen of  $\text{PbF}_2$  approximately 2.5 cm in diameter and 0.85 cm in length, previously used in low-temperature heat-capacity measurements,<sup>12</sup> was oriented by using back-reflection Laue photography to within 2° of the [110] direction. For 2° misalignment, the error in the elastic constants was negligible. The end faces of this second sample were parallel

to within 2 parts in  $10^3$ . Laue photography confirmed that both crystals were cubic  $\text{PbF}_2$ .

The electronic equipment has been described previously.<sup>13</sup> Measurements of the round-trip transit time of the ultrasonic pulse were made using the pulse superposition method with the McSkimin criterion for the correct cycle-for-cycle overlap of two pulse echoes assuming the thin bond or no bond limit.<sup>14,15</sup> A DuPont model no. 9770,<sup>16</sup> a platinum and silver conductor composition ordinarily used to provide thick-film conductors for microcircuits, has been previously used as an effective acoustic bond at high temperature for compressional<sup>17</sup> and shear<sup>18</sup> waves. The transducers<sup>19</sup> used for longitudinal and transverse sound-velocity measurements were 16 MHz,  $36^\circ$  y cut and 10 MHz,  $41^\circ$  x cut lithium-niobate transducers, respectively. The temperature was measured using a type-K Chromel-Alumel thermocouple with an Omega-CJ (cold-junction) compensator and a Keithley model no. 171 digital multimeter. A Marshall furnace, Varian model no. 1023, was used in this work.

The relatively small scatter of data of a particular run is an indication of the precision of the data. The estimated accuracy for the measured  $\rho v^2$  is approximately  $\pm 0.5\%$  near the room temperature increasing to  $\pm 0.9\%$  at high temperature due to possible thermocouple errors.

## RESULTS

Figure 1 shows the temperature dependence of the measurements presented as  $\rho v^2$ . Figure 2 shows the dependence of the three independent elastic constants on temperature. As the temperature is increased from 300 K, all of the elastic constants show a nearly linear decrease, but in the vicinity of Faraday temperature,  $C_{11}$ ,  $(C_{11} - C_{12})$ , and  $(C_{11} + C_{12} + 2C_{44})/2$  undergo an additional sharp decrease. This is remarkable for  $C_{11}$  which decreases in

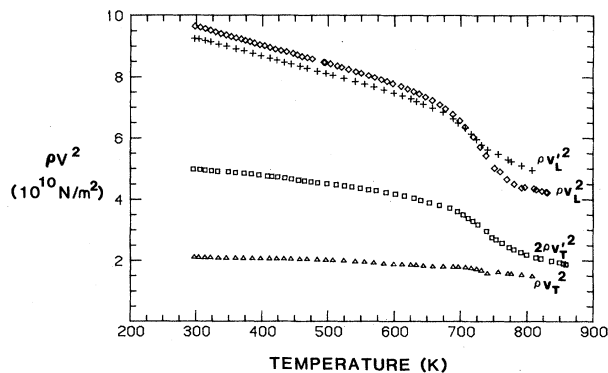


FIG. 1. Temperature dependence of the measured quantities  $\rho v_L^2 = C_{11}$  (diamonds),  $\rho v_L^2 = (C_{11} + C_{12} + 2C_{44})/2$  (crosses),  $2\rho v_T^2 = C_{11} - C_{12}$  (squares), and  $\rho v_T^2 = C_{44}$  (triangles).

value by almost a factor of two between 600 and 800 K while a much smaller change is observed in  $C_{12}$ , and the effect on  $C_{44}$  is only slight. A second linear region is apparently reached above  $T_c$ . There is good consistency between  $C_{11}$  calculated from  $\rho v_L^2$ ,  $\rho v_T^2$ ,  $\rho v_T^2$  (all in the [110] direction), and  $C_{11} = \rho v_L^2$  in the [100] direction. The agreement of the  $C_{11}$  data from the two different specimens is 0.1% at 298 K increasing to 3.7% at 808 K.

Examination of Table I shows that the values of  $C_{44}$  obtained in the different ultrasonic experiments<sup>20-22</sup> and a composite oscillator experiment<sup>23</sup> agree to within about 1%, and agree within experimental error with the Brillouin and neutron scattering measurements.<sup>3,6</sup> Agreement between present measurements, the ultrasonic measurements of Rimai *et al.*,<sup>20,21</sup> and the ultrasonic measurements of Wasilik and Wheat<sup>22</sup> (as corrected by Hart<sup>23</sup>) for  $C_{11}$  and  $C_{12}$  are within 0.9% and 1.2%, respectively.

TABLE I. Elastic constants of single-crystal lead fluoride at room temperature (unless noted) measured by different techniques are given. The density is taken to be  $7.755 \times 10^3 \text{ kg/m}^3$ . All units are  $10^{10} \text{ N/m}^2$ .

	$C_{11}$	$C_{11} - C_{12}$	$C_{12}$	$C_{44}$	$(C_{11} + C_{12} + 2C_{44})/2$	Technique
Present work (300 K)	$9.637 \pm 0.048$	$4.973 \pm 0.050$	$4.663 \pm 0.070$	$2.104 \pm 0.011$	$9.237 \pm 0.046$	Ultrasonic
Rimai and Sladek <sup>a</sup> (296 K)	9.57	4.92	4.654	2.086	9.217	Ultrasonic
Ramai, Chao, and Sladek <sup>b</sup>	9.548	4.900	4.648	2.080		Ultrasonic
Dickens <i>et al.</i> <sup>c</sup> (300 K)	$8.51 \pm 0.17$	$4.37 \pm 0.10$	$4.14 \pm 0.17$	$2.08 \pm 0.02$	$8.41 \pm 0.16$	Neutron
Catlow <i>et al.</i> <sup>d</sup> (300 K)	$9.30 \pm 0.14$	$4.90 \pm 0.08$		$2.06 \pm 0.03$		Brillouin
Hart <sup>e</sup>	9.34		4.40	2.10		Composite oscillator
Wasilik and Wheat <sup>f</sup> (27 °C)	9.63		4.72	2.08		Ultrasonic

<sup>a</sup>Reference 20.

<sup>b</sup>Reference 21.

<sup>c</sup>Reference 6.

<sup>d</sup>Reference 3.

<sup>e</sup>Reference 23.

<sup>f</sup>Reference 22.

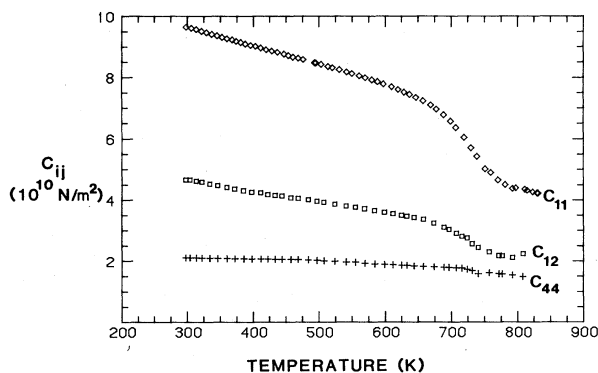


FIG. 2. Temperature dependence of the independent elastic constants  $C_{11} = \rho v_L^2$  (diamonds),  $C_{12} = \rho v_L^2 - 2\rho v_T^2$  (squares), and  $C_{44} = \rho v_T^2$  (crosses) for cubic  $\text{PbF}_2$ .

The agreement between the present measurements of  $C_{11}$  and  $C_{12}$  and the composite oscillator measurements of Hart,<sup>23</sup> and the Brillouin and neutron scattering measurements<sup>3,6</sup> is less satisfactory.

### DISCUSSION

The temperature dependence of the elastic constants can be explained by assuming it to have three contributions: One contribution from normal-lattice anharmonicity<sup>24</sup> which is the dominant effect at temperatures up to 600 K in case of  $\text{PbF}_2$ , another due to the formation of interstitial defect concentrations<sup>3</sup> as high as 20% to 25% which is dominant over a narrow range of temperature around  $T_c$ , and the last one is due to a hopping motion of defects.<sup>6</sup> Dickens *et al.*<sup>6</sup> have generalized Zeyher's results<sup>25</sup> to the case of  $\text{PbF}_2$  and concluded that the hopping motion of the defects at  $T > T_c$  makes only a small contribution to the explanation of their data.

An explanation of the different behavior of  $C_{12}$  and  $C_{44}$  from that of  $C_{11}$  has been given by examining expressions for the elastic constants of a perfect fluorite lattice derived by Elcombe<sup>26</sup> and Kleppmann.<sup>27</sup> These expres-

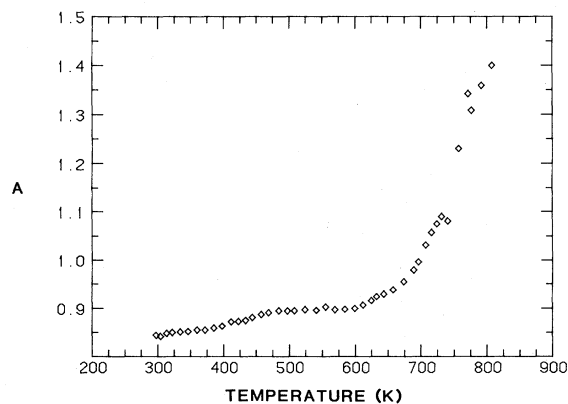


FIG. 3. Temperature dependence of the elastic anisotropy factor  $A = 2C_{44} / (C_{11} - C_{12})$ .

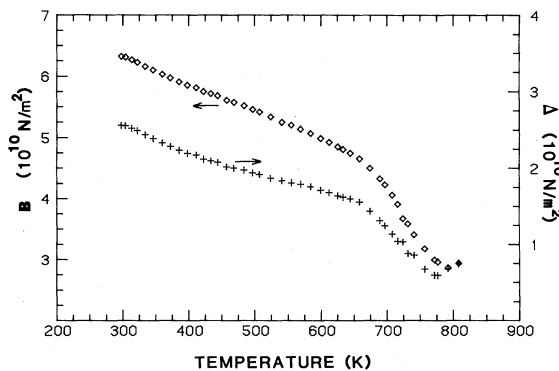


FIG. 4. Temperature dependence of the bulk modulus  $B = (C_{11} + 2C_{12})/3$  (diamonds) and the Cauchy relation failure  $\Delta = C_{12} - C_{44}$  (crosses).

sions show that for  $C_{11}$  the contributions due to Coulomb and short-range forces have the same sign, whereas for  $C_{12}$  and  $C_{44}$  they have opposite signs. Therefore the effect of interstitials on  $C_{12}$  and  $C_{44}$  is small because the changes in Coulomb and short-range terms tend to cancel each other. The present results show that  $C_{12}$  has a stronger temperature dependence near  $T_c$  than was observed in the Brillouin scattering measurements.<sup>3</sup>

Figures 3 and 4 show the results of bulk modulus  $B = (C_{11} + 2C_{12})/3$ , the anisotropy factor  $A = 2C_{44} / (C_{11} - C_{12})$ , and the Cauchy relation factor  $\Delta = (C_{12} - C_{44})$ , respectively. The bulk modulus decreases nearly linearly with temperature until a dramatic decrease occurs near  $T_c$ . The anisotropy factor  $A$ , which is unity for elastically isotropic materials, shows a small nearly linear increase with temperature, but in the vicinity of  $T_c$ , a rapid rise occurs. It is particularly interesting to note that  $\text{PbF}_2$  appears to be elastically isotropic very near  $T_c$ . The Cauchy relation failure (Fig. 4) decreases linearly with temperature from 297.5 to 800 K with a small anomalous decrease near the transition temperature.

Values of  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ,  $A$ ,  $B$ , and  $\Delta$  are calculated, assuming a linear relation between every two successive measurements, at six different temperatures and given in Table II. As seen in Fig. 3,  $\text{PbF}_2$  becomes elastically isotropic near the transition temperature  $T_c$ . This elastic isotropy near  $T_c$  is consistent with the idea of sublattice melting<sup>28,29</sup> though the level of disorder is not massive and the model perhaps not appropriate.<sup>30</sup> A larger deviation from the Cauchy condition occurs for  $\text{PbF}_2$  than for any alkaline-earth fluoride although it is smaller than that of  $\text{CdF}_2$ .<sup>13</sup> Since the Cauchy condition ( $C_{12} = C_{44}$ ) results from the assumption of point charges at inversion centers,<sup>31</sup> the Cauchy condition failure indicates that lead fluoride has the next to the largest amount of covalent bonding in the nominally ionic fluorides. This covalent bonding, however, decreases with increasing temperature up to  $T_c$ . The Cauchy condition is apparently satisfied near  $T_c$  as a result of the ion motion.

In conclusion, the present results of the temperature dependence of the elastic constants of cubic  $\text{PbF}_2$  are consistent with the change in elastic constants with temperature that have been measured in Brillouin and neutron

TABLE II. Cubic elastic constants, anisotropy factor  $A = 2C_{44}/(C_{11} - C_{12})$ , bulk modulus  $B = (C_{11} + 2C_{12})/3$ , and Cauchy relation failure  $\Delta = C_{12} - C_{44}$  are given. All units are  $10^{10}$  N/m<sup>2</sup> except for  $A$  which is unitless.

$T$ (K)	$C_{11}$	$C_{12}$	$C_{44}$	$A$	$B$	$\Delta$
300	9.637	4.663	2.104	0.843	6.292	2.553
400	9.034	4.255	2.065	0.864	5.845	2.187
500	8.441	3.942	2.013	0.895	5.371	1.929
600	7.764	3.587	1.881	0.901	4.975	1.705
700	6.545	3.003	1.783	1.007	4.173	1.210
800	4.384	2.186	1.511	1.380	2.903	0.712

scattering experiments,<sup>3,6</sup> and with the theoretical predictions of Elcombe<sup>26</sup> and of Kleppmann.<sup>27</sup> Measurements of ultrasonic attenuation in fluorites at high temperatures which are in progress should provide interesting tests of theories of ion motion in solid electrolytes without the complicating factor of crystallographic phase transitions.

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