Elastic constants of cadmium fluoride from 4.2 to 295 K*

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The adiabatic elastic constants of single-crystal cadmium fluoride have been measured over the temperature range of 4.2–295 K. The values of the elastic constants given in units of 10^{10} N/m² at 4.2 and 295 K, respectively, are $C_{11} = 19.79$ and 18.39, $C_{44} = 2.490$ and 2.196, and $C_{12} = 7.294$ and 6.619. The Debye temperature calculated from the elastic constants at 4.2 K is 331.6 ± 0.7 K. A phenomenological relationship between the Debye temperature and the reduced mass of the unit cell of the cubic-metal fluorides is reported.

INTRODUCTION

Cadmium fluoride is a cubic crystal with fluorite (calcium fluoride) structure. It is of interest as a potentially useful material for optical windows and as a semiconducting material when properly doped. As a characteristic property of a material, the elastic constants are sometimes useful in other solid-state experiments such as, for example, stress effects on nuclear-quadrupole splittings.¹ Cadmium fluoride also provides another fluoride on which sound-velocity measurements can be made, yielding information about the influence of the metal ion on the lattice properties of metal fluorides. Previous measurements of the elastic constants of cadmium fluoride at room temperature have been reported by Hart² and by Alterovitz and Gerlich.³ A Debye temperature for cadmium fluoride, which was calculated from room-temperature values of the elastic constants extrapolated to 4.2 K, has also been reported by Alterovitz and Gerlich.

THEORY

Owing to the symmetry of a cubic crystal, there are only three independent elements in the elasticconstant tensor. These elastic constants can be determined by the product of the density ρ and the square of the velocity V in certain directions. The relations⁴ used in this work were $\rho V_L^2 = C_{11}$, $\rho V_T^2 = C_{44}$, $\rho V_L'^2 = \frac{1}{2} (C_{11} + C_{12} + 2C_{44})$, and $\rho V_T'^2 = \frac{1}{2} (C_{11} - C_{12})$, where V_L and V_T are the ultrasonic velocities of waves propagated in the [100] direction for longitudinal waves and all polarizations of transverse waves, respectively, and where V_L' , V_T , and V_T' are the ultrasonic velocities of waves propagated in the [110] direction for longitudinal waves and transverse waves polarized in the [001] and [110] directions, respectively.

In order to calculate the elastic constants of cadmium fluoride as a function of temperature, it is

necessary to know the temperature dependence of the crystal specimen's length and density. Since no data are available, the temperature dependence is determined by utilizing the Grüneisen relation.⁵ In using the Grüneisen relation to obtain the thermal expansion, one assumes to first approximation that the compressibility and the Grüneisen parameter are constant. In the case of CdF_2 , the specific heat has not been measured, so that one must also approximate the specific heat. This is done by using the Debye temperature calculated from uncorrected elastic-constant data at 4.2 K and the specific heat expected from Debye theory. Since the elastic constants are proportional to the length squared divided by the volume, the correction due to thermal expansion appears reciprocally as a length correction to the first power. Error introduced into the elastic constants by this technique is less than experimental error. The density^{3,6} at 298 K is 6.386 g/cm^3 , the linear expansion coefficient³ at 295 K is 22×10^{-6} K⁻¹, and the Debye specific heat and internal energy are available in tabular form.⁷

EXPERIMENTAL

Two cylindrical, single-crystal specimens of cadmium fluoride approximately 2.0 cm in diameter and 2.5 cm in length were obtained from Optovac, Inc.⁸ Back-reflection Laue photography was used to orient one specimen with a faint yellow color to within 0.5° of the [100] direction and the other optically clear specimen to within 1° of the [110] direction. The difficulty in the orientation of 'the second crystal was due to what appeared as an "axis wobble," which resulted from the slight sagging of the crystal planes during the growing process.⁹ The end faces of both specimens were handlapped parallel to within two parts in 10^4 .

A block diagram of the electronic equipment that was used to measure the temperature dependence of the sound velocities is given in Fig. 1. The temperature dependence of the round-trip time of trav-

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FIG. 1. Block diagram of the electronic equipment used for the modified pulse-echo measurements.

el of the pulse is measured by aligning the peak rf oscillation in the initial pulse envelope along a reference mark on the oscilloscope, switching to any particular echo, and aligning the peak rf oscillation in its envelope to the same reference mark. This overlap is maintained during any particular run. The uncorrected time of pulse travel equals the amount of time delay necessary to align the echo pulse and is read directly from the digital delay generator with an accuracy of ± 1 ns. This method allows almost simultaneous viewing of the initial and echo pulses and reduces the errors due to oscilloscope jitter. Several errors are introduced by this technique unless noted and corrected for. The true round-trip time δ is related to the measured time t_p for p round trips by the expression¹⁰

$$t_{p} = p\delta - p\gamma/2\pi f + n/f + t_{c} , \qquad (1)$$

where f is the frequency of the ultrasound, γ is the phase shift introduced by the transducer and binder, n is an integer, and t_c is a constant time error introduced by the different electronic paths of the initial pulse and the pulse echoes. The McSkimin criterion for choosing n=0 involves measurements of t_p at two frequencies, typically resonance and 0.9 times the resonant frequency. The difference in measured round-trip times at these two frequencies is

$$\Delta t_{p} = (p/2\pi f_{R})(\gamma_{R} - 0.111\gamma_{0.9R}) + 0.111n/f_{R} . \qquad (2)$$

Since the phase shifts γ_R and $\gamma_{0.9R}$ can be calculated,^{10,11} measurement of Δt_p for different cyclefor-cycle overlaps allows one to unambiguously determine which cycle-for-cycle overlap corresponds to n = 0. It has been pointed out that matching leading edges of pulses is equivalent to choosing $\Delta t_p \simeq 0$ not $n = 0.^{12}$ If Eq. (1) is rewritten in terms of a single round-trip time τ uncorrected for the phase shift and a wrong cycle-for-cycle overlap, one finds

$$\tau_{p}/p = \tau + t_{c}/p , \qquad (3)$$

which indicates that a plot of τ_p/p vs 1/p should be linear and gives the uncorrected time τ at 1/p = 0. One finds that by measuring τ_p for several values of p at any temperature, one can eliminate errors of the form t_c and one can unambiguously eliminate uncertainties in the choice of the peak oscillation due to modulation effects resulting from diffraction and interference effects. Corrections for phase shift and incorrect cycle-for-cycle overlap must be made using the McSkimin criterion.

Measurements of the sound velocity using the McSkimin criterion for cycle-for-cycle overlap were made at room temperature on the [110]-oriented CdF₂. The temperature-dependent times t_p/p are adjusted so that they agree with the measurements obtained using the McSkimin criterion and so that the various runs overlap properly. The corrections for the difference between the true round-trip time δ and the measured round-trip time t_p/p are of the form

$$\delta - \frac{t_p}{p} = \frac{\gamma}{2\pi f} - \frac{n}{pf} - \frac{t_c}{p} , \qquad (4)$$

and amount to a maximum correction on the order of a few percent.

.The bond between the crystal and transducer was Nonaq stopcock grease for the temperature range 300-150 K. An organic mixture of five parts ethyl ether, six parts pentane, and two parts ethyl alcohol was used from 130 to 77 K, and solidified methane was used from 90 to 4.2 K.¹³

A type-T copper-constantan thermocouple with a 0 °C ice-bath reference was used to measure the temperature of the specimen, and was calibrated *in situ* with respect to the theoretical thermocouple curves¹⁴ at 4.2, 77.4, and 273.2 K. The emf measurements were taken with a Keithley model 171 digital multimeter, and the specimens were cooled at a maximum rate of approximately 15 K/h. The room-temperature measurements of sound velocity



FIG. 2. Temperature dependence of $C_{11} = \rho V_L^2$.

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FIG. 3. Temperature dependence of $C_{44} = \rho V_T^2$.

using the McSkimin criterion were made using a calibrated Si diode thermometer¹⁵ for the temperature measurement.

RESULTS

The temperature dependence of C_{11} , C_{44} , $\rho V_T'^2$, and C_{12} is given in Figs. 2, 3, 4, and 5, respectively, and the values of the above quantities and the density at 4.2, 77.4, and 296.7 K are given in Table I. All three elastic constants (C_{11} , C_{12} , and C_{44}) and $\rho V_T'^2$ have the same characteristic temperature-dependent curves as the alkali halides. The temperature dependence is approximately linear in the high-temperature region, and the slope of the temperature dependence goes to zero as the temperature approaches absolute zero.

The gap in all of the curves between 130 and 150 K is due to the limited temperature range of the binders, and the absence of data points above 275 K, for the data calculated from transverse waves, is due to the Nonaq binder not being rigid enough to couple transverse waves into the crystal. As stated previously, there are two independent methods of determining C_{44} , one of which is dependent upon the polarization of the transverse wave. The C_{44} data of Fig. 3, from 77.4 to 130 K, are taken



FIG. 4. Temperature dependence of $\rho V_T'^2 = \frac{1}{2}(C_{11} - C_{12})$.



FIG. 5. Temperature dependence of $C_{12} = C_{11} - 2\rho V_T^{\prime 2}$.

from a transverse wave propagated in the [100] direction, while the remaining data are taken from a transverse wave in the [110] direction with the proper polarization. The change in the method of determining C_{44} is due to the [100] CdF₂ crystal developing a crack during a low-temperature run. This reduced the signal quality below an acceptable level. There is good consistency of the C_{44} data from the two specimens which are of different orientations as well as different crystallographic and optical quality. The relatively small scatter of the data points of a particular run is an indication of the precision of the data. The resultant estimated accuracy for C_{11} , C_{44} , C_{12} , and $\rho V_T'^2$ is ±0.9, ±0.3, ± 0.9 , and $\pm 0.3\%$, respectively. It should be noted that the relatively high error in C_{11} is due to the measurements based on the McSkimin criterion being made on the [110]-oriented crystal where C_{11} is not measured directly. The elastic constants obtained using the McSkimin criterion are those given in Table I at 296.7 K.

A least-squares fit of the elastic-constant data above 150 K, using a polynomial of second order in temperature, is used to calculate C_{11} , C_{44} , C_{12} , and their slopes at 295 K. These values are used to calculate the compressibility,⁴ $\beta = 3/(C_{11} + 2C_{12})$; anisotropy,¹⁶ $A = 2C_{44}/(C_{11} - C_{12})$; and Cauchy relation failure,¹⁶ $\Delta = C_{12} - C_{44}$. The values of the above

TABLE I. Elastic constants, $\rho V_T^{\prime 2}$, and density ρ of CdF₂ at 4.2, 77.4, and 296.7 K.

Elastic constants	Temperature			
(10^{10} N/m^2)	4.2 K	77.4 K	296.7 K	
<i>C</i> ₁₁	19.79	19.66	18.37	
C_{44}	2.490	2.453	2.195	
C_{12}	7.294	7.233	6.615	
$\rho V_T^{\prime 2}$	6.246	6.215	5.881	
ρ (g/cm³)	6.471	6.466	6.387	

TABLE II. Characteristic parameters of ${\rm CdF}_2$ at 4.2 and 295 K.

	Temperature	
	4.2 K	295 K
Compressibility $(10^{-12} \text{ m}^2/\text{N})$	8.727	9.485
Anisotropy	0.3988	0.3731
Cauchy relation failure (10^{10} N/m^2)	4.804	4.423

TABLE IV. Comparison of the elastic constants and logarithmic slopes of CdF_2 at 295 K.

Elastic constants C_{ij} (10 ¹⁰ N/m ²)	<i>C</i> ₁₁	C ₄₄	<i>C</i> ₁₂
Present work Alterovitz and Gerlich Hart	18.39 18.27 18.6	$2.196 \\ 2.175 \\ 2.17$	$6.619 \\ 6.674 \\ 6.8$
$d \ln C_{ij}/dT$ (10 ⁻⁴ K ⁻¹) Present work Alterovitz and Gerlich	_3.655 _3.712	-5.896 -5.329	-4.447 -5.075

characteristic parameters at 4.2 and 295 K are tabulated in Table II, and the coefficients of the second-order least-squares fit for each of the elastic constants are given in Table III. Using the Madelung constant for the calcium fluoride structure¹⁷ and the lattice constant at 4.2 K, calculated from the lattice constant of cadmium fluoride⁶ at 295 K, the cohesive energy of the lattice¹⁸ is calculated to be $-2.151 \times 10^{6} \text{ J/mole}$ (-513.9 kcal/mole). The Debye temperature is calculated from 4.2-K data by the Betts-Bhatia-Wyman method¹⁹ to be 331.6 \pm 0.7, and by the De Launay method²⁰ to be 333.3 K. These values are in some disagreement with the value of 328 ± 3 K found by Alterovitz and Gerlich³ by De Launay's method²⁰ using extrapolated values of the elastic constants to low temperatures.

DISCUSSION

A comparison of the elastic constants and logarithmic slopes of CdF_2 at 295 K is given in Table IV. The values of the elastic constants agree well with the previous data, while the logarithmic slopes disagree in excess of experimental error. Of all cubic fluorides, cadmium fluoride has the smallest compressibility, the next to the smallest anisotropy, and the largest deviation from the Cauchy condition. Since the Cauchy condition (C_{12} $=C_{44}$) results from the assumption of point charges at inversion centers,²¹ the Cauchy condition failure indicates that cadmium fluoride has the largest amount of covalent bonding in the nominally ionic cubic fluorides.

Phenomenological relationships between the Debye temperature and various crystal parame-

TABLE III. Coefficients of the second-order leastsquares fit $C_{ij} = A + BT + CT^2$ of the elastic constants of CdF₂ above 150 K.

Elastic constants	C ₁₁	C ₄₄	<i>C</i> ₁₂
$\begin{array}{l} A \ (10^{10} \ {\rm N/m^2}) \\ B \ (10^7 \ {\rm N/m^2K}) \\ C \ (10^3 \ {\rm N/m^2 \ K^2}) \end{array}$	20.05	2.531	7.455
	-4.568	-0.9722	-2.725
	-36.47	-5.472	-3.705

ters have been suggested for cubic fluoride XF crystals, where X is a monovalent metal, as well as XY crystals, where Y is a halide.^{22,23} The phenomenological relationship between the Debye temperature and the standard reduced mass of the unit-cell constituents is extended here to the cubic alkaline earth and heavy metal fluorides, symbolized by XF_2 , where X is divalent. The reduced mass is defined for XF unit cells as $M_X M_F / (M_X)$ + $M_{\rm F}$) and for $X {\rm F}_2$ unit cells as $M_{\rm X} M_F / (M_{\rm X} + 2 M_{\rm F}).^{24}$ The Debye temperatures plotted in Fig. 6 are taken from Refs. 25-35 and in some cases are not from low-temperature elastic-constant or specific-heat data. Similar linear relations exist for other metal halides, but each halide has a different slope. Using this relationship, a Debye temperature of 205 K would be expected for cesium fluoride, whose reduced mass is 16.6 amu. Unfortunately no cubic XF_3 crystals exist to extend this relation and to test its validity.



FIG. 6. Illustration of the phenomenological relationship between the Debye temperature and the reduced mass of the unit cell of XF and XF_2 cubic fluorides.

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ACKNOWLEDGMENTS

The authors wish to thank S. M. Day for the loan of some of the electronic equipment, R. Konig for

- *This work was supported in part by a grant from the University of Arkansas Research Reserve Fund.
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making available crystal preparation facilities in the Department of Geology, and W. Hargreaves of Optovac, Inc. for loaning us the second crystal on which some of the measurements were made.

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