

Thermoelastic Properties of Cadmium Fluoride†

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The second-order elastic moduli, as well as their temperature and pressure derivatives, and the thermal expansion of single-crystal CdF_2 were determined at room temperature. The values of the elastic moduli (in units of 10^{11} dyn/cm²) are $c_{11}=18.270$, $c_{12}=6.674$, and $c_{44}=2.175$. The measured values of the temperature derivatives (in units of 10^{-4} deg⁻¹) are $d \ln c_{11}/dT = -3.71$, $d \ln c_{12}/dT = -5.08$, and $d \ln c_{44}/dT = -5.33$; the pressure derivatives are $dc_{11}/dP = 7.11$, $dc_{12}/dP = 5.52$, and $dc_{44}/dP = 1.35$; the thermal expansion is 2.2×10^{-5} deg⁻¹. From the elastic data, a Debye temperature of 328°K was deduced. The experimentally measured values of c_{44} and the pressure derivatives were compared with theoretically calculated ones. Good agreement was found for the pressure derivatives, while a large discrepancy for c_{44} was noted. The possible reasons for these correlations and the conclusions pertaining to the lattice interactions in CdF_2 are discussed.

I. INTRODUCTION

THE thermoelastic properties of CdF_2 are of interest on several counts. Very few data about the lattice properties of the material are available. Also, CdF_2 is closely related to CaF_2 , both having the same structure, the same anion, and nearly the same unit-cell size (5.388 Å versus 5.453 Å). In addition, the ionic radii for the cations are nearly the same. Thus, any differences between the elastic properties of CaF_2 and CdF_2 should be mainly dependent on the difference in the inner electronic structures of Cd^{++} and Ca^{++} , as the elastic properties are independent of the nuclear mass.^{1,2} The elastic properties of CaF_2 have been extensively investigated³⁻⁷; thus it may be possible to deduce the effect of the electronic structure on the elastic properties by studying the latter in CdF_2 . With this in mind, a study of the thermoelastic properties of single-crystal CdF_2 was undertaken. The room-temperature second-order elastic moduli (SOEM), as well as their temperature and pressure derivatives, were measured. The experimentally determined quantities were compared with theoretically calculated ones, and some conclusions pertaining to the lattice forces in CdF_2 are drawn.

II. EXPERIMENTAL

The sample used in the present study was cut from a single-crystal boule of CdF_2 , grown by the Koch-Light Laboratories. The boule was oriented, and a right

parallelepiped with faces corresponding to (110), ($\bar{1}\bar{1}0$) and (001) crystalline planes cut, by the RCA Laboratories. The cut sample was handlapped until opposite faces were parallel to within a few parts in 10^5 , and then the orientation was checked by x-ray Laue backreflection. The faces were found to correspond to the crystalline planes to within $\frac{1}{2}^\circ$. The final size of the sample was $11 \times 19 \times 19$ mm.

Cadmium fluoride, being cubic, has three independent SOEM: c_{11} , c_{12} , and c_{44} . The latter were determined from the absolute value of the sound velocity, while from the changes in this velocity with hydrostatic pressure and with temperature, the derivatives were determined. With the available sample, five different sound propagation modes could be utilized, and the three SOEM and their derivatives were computed by a least-squares fit.

The sound waves were generated by means of X- and Y-cut crystalline quartz transducers, operating at their fundamental frequency of 15 MHz. The transducers were bonded to the samples with phenylsalicylate (salol).

The absolute value of the sound velocity was measured by the McSkimin pulse-superposition method,^{8,9} while the changes in the sound velocity with temperature and pressure were determined by the frequency-modulated pulse-superposition method.^{10,11} The temperature of the sample was monitored carefully at all times, and all the results with the changes in pressure were normalized to 295°K.

The absolute value of the sound velocity was determined in a manner described previously.¹² The accuracy in each single measurement was one part in 10^4 ; however, the over-all error in the SOEM is larger, owing to possible deviation of the directions of the sound propagation from the crystalline axis, and to errors in the

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¹ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., New York, 1954).

² R. A. Cowley, *Proc. Roy. Soc. (London)* **A268**, 121 (1962).

³ D. R. Huffman and M. H. Norwood, *Phys. Rev.* **117**, 709 (1960).

⁴ C. Wong and D. E. Schuele, *J. Phys. Chem. Solids* **28**, 1225 (1967).

⁵ C. Wong and D. E. Schuele, *J. Phys. Chem. Solids* **29**, 1309 (1968).

⁶ P. S. Ho and A. L. Ruoff, *Phys. Rev.* **161**, 864 (1967).

⁷ S. Alterovitz and D. Gerlich, *Phys. Rev.* **184**, 999 (1969).

⁸ H. J. McSkimin, *J. Acoust. Soc. Am.* **33**, 12 (1961).

⁹ H. J. McSkimin and P. Andreatch, Jr., *J. Acoust. Soc. Am.* **34**, 609 (1962).

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¹¹ H. J. McSkimin and P. Andreatch, Jr., *J. Acoust. Soc. Am.* **41**, 1052 (1967).

¹² S. Alterovitz and D. Gerlich *Phys. Rev. B* **1**, 2718 (1970).

TABLE I. Sound transit times for the different modes of propagation.

Mode No.	Propagation direction	Polarization direction	Length (cm)	Transit time (μsec)	ρv^2 (10^{11} dyn/cm^2)
1	[110]	[001]	1.1279 ± 0.00005	12.2474 ± 0.0015	2.1740 ± 0.0005
2	[110]	[110]	1.1297 ± 0.00005	4.716 ± 0.002	14.657 ± 0.014
3	[110]	[110]	1.1297 ± 0.00005	7.4966 ± 0.0007	5.8006 ± 0.0015
4	[001]	[001]	1.9230 ± 0.00005	7.1907 ± 0.0005	18.268 ± 0.0035
5	[001]	(001) plane	1.9230 ± 0.00005	20.8442 ± 0.0018	2.1733 ± 0.0007

TABLE II. SOEM of CdF_2 at 295°K . (Units are 10^{11} dyn/cm^2 .)

c_{11}	c_{12}	c_{44}	B^S	B^T
18.270 ± 0.0026	6.6744 ± 0.0059	2.175 ± 0.0022	10.5396 ± 0.0048	10.06 ± 0.12

temperature normalization, polarization direction, and transducer resonant frequency. The thermal expansion was measured directly, using a Johansson Mikrokator dial gauge. The sample was sandwiched between two fused silica blocks, and heated with a stream of hot air. The setup was calibrated with crystals of CaF_2 and SrF_2 , and agreement within 10% of another independent measurement¹³ was found.

III. RESULTS

The linear thermal expansion at room temperature was determined as $(22 \pm 2) \times 10^{-6} \text{ deg}^{-1}$. The room-temperature density was measured by the weight-displacement method and found to be $6.386 \pm 0.002 \text{ g/cm}^3$, which agrees very well with the x-ray value.¹⁴

Table I shows the values of the round trip travel time t for the five different modes of sound propagation. From the latter data, the three SOEM were calculated by a least-squares fit, and are shown in Table II. From the values of the SOEM, the magnitude of ρv^2 in any direction may be calculated; here, ρ is the density and v is the sound velocity. The values of ρv^2 for some directions of high symmetry are shown in Fig. 1. Here 3 refers to the longitudinal mode; 1 and 2 refer to the slow and fast shear modes, respectively. It is evident from Fig. 1 that CdF_2 is elastically highly anisotropic.

The changes in the sound velocity with temperature and pressure are summarized in Tables III and IV and Figs. 2-5. The dots in the figures represent the measured reciprocal resonant frequency for all of the five possible modes of propagation as a function of the temperature and applied hydrostatic pressure.

The straight lines are least-squares fits to the experimental data. As can be seen from the graphs, the changes in the sound velocity are linear over the whole of the measured range, within experimental error.

From the slopes of the lines in Figs. 2-5, the tem-

perature and pressure derivatives were determined from the following equations:

$$\frac{d \ln c_{ij}}{dT} = -\alpha - 2 \frac{d \ln t}{dT}, \quad (1)$$

$$\frac{dc_{ij}}{dP} = \frac{c_{ij}}{3B^T} + \left(\frac{d(\rho_0 W^2)}{dP} \right)_{P=0}. \quad (2)$$

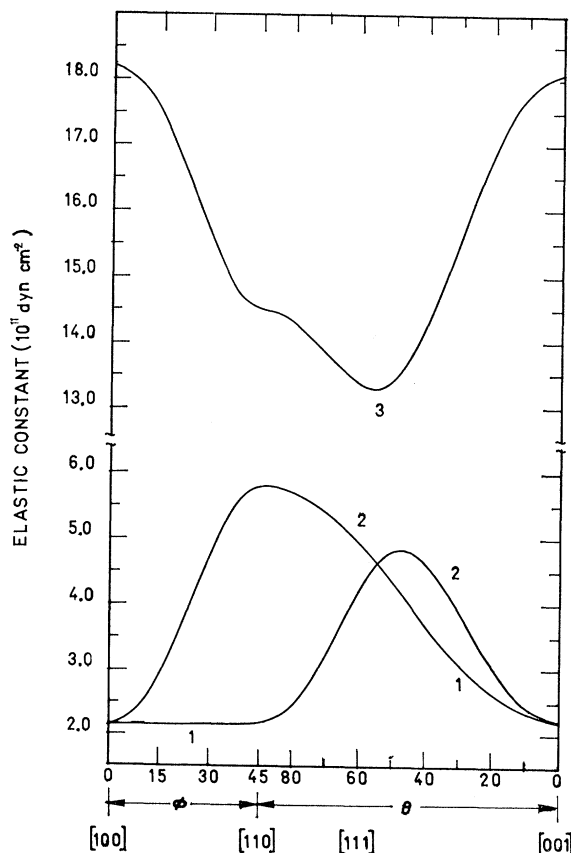


Fig. 1. Values of ρv^2 for some directions of high symmetry.

¹³ A. C. Bailey and B. Yates, Proc. Phys. Soc. (London) **91**, 390 (1967).

¹⁴ J. D. H. Donnay, A. C. A. Monograph 5 (Geological Society, New York, 1964).

TABLE III. Temperature dependence of the sound travel time for the five propagation modes.

Mode No.	Propagation direction	Polarization direction	ρv^2	$\frac{d \ln t}{dT} \times (10^{-6} \text{ deg}^{-1})$	$\left(\frac{d \ln c}{dT}\right)_P \times (10^{-4} \text{ deg}^{-1})$
1	[110]	[001]	c_{44}	255.4 ± 0.2	-5.328 ± 0.024
2	[110]	[110]	$\frac{1}{2}(c_{11} + c_{12} + 2c_{44})$	202.8 ± 0.6	-4.276 ± 0.033
3	[110]	[110]	$\frac{1}{2}(c_{11} - c_{12})$	137.8 ± 0.4	-2.976 ± 0.028
4	[001]	[001]	c_{11}	174.1 ± 0.1	-3.702 ± 0.013
5	[001]	(001) plane	c_{44}	252.3 ± 0.4	-5.266 ± 0.027

Here, c_{ij} is the effective elastic modulus, viz., ρv^2 , α is the linear thermal expansion, B^T is the isothermal bulk modulus, ρ_0 is the zero-pressure density, and W is the "natural" velocity¹⁵ ($W = L_0/t$, where L_0 is the zero-pressure length of the sound path). B^T was deduced from the following equations:

$$B^T = B^S(C_V/C_p), \quad (3)$$

$$C_p - C_V = (3\alpha)^2 B^S T V / C_p, \quad (4)$$

where C_p and C_V are the specific heat at constant pressure and volume, V is the volume, B^S is the adiabatic bulk modulus, and T is the absolute temperature.

As specific-heat data for CdF_2 are not available, the Debye model was utilized in calculating the specific

heat of CdF_2 . The Debye temperature was computed from the elastic data as described hereafter, and from it the room-temperature value of C_V for CdF_2 was determined as 70 J/mole deg.

The validity of the procedure was checked by computing in the same manner the room-temperature specific heats of CaF_2 , SrF_2 , and BaF_2 , and comparing the results with experimentally measured data. This comparison is presented in Table V, which shows an agreement of within 5% for the two sets of data.

From the five experimentally measured temperature and pressure derivatives, the derivatives of the SOEM were evaluated by a least-squares fit. The results are shown in Tables VI and VII. From the experimentally measured values of $[d(\rho_0 W^2)/dP]_{p=0}$, the three linear combinations of the third-order elastic moduli (TOEM) which are determined by hydrostatic pressure measurements only, viz., $C_{111} + 2C_{112}$, $C_{144} + 2C_{166}$, and $2C_{112} + C_{123}$, were evaluated, and are shown in Table VIII.

The errors in the quantities obtained by a least-squares fit are the standard deviations multiplied by 0.675. This was found to be the largest error as compared with all other procedures of error evaluation. It was also found that carrying out the least-squares fits with weights equal to the reciprocals of the standard deviations or with equal weights did not change the results significantly, its only effect being to reduce the computed errors by 10–20%.

The 0°K Debye temperature Θ_0 may be calculated to a good accuracy for cubic crystals with the aid of

TABLE IV. Pressure dependence of the sound travel time for the five propagation modes.

Mode No.	ρv^2	$(\rho_0 W^2)_{p=0}$	$(dc/dp)_T$
1	c_{44}	1.2250 ± 0.0041	1.297 ± 0.005
2	$\frac{1}{2}(c_{12} + c_{12} + 2c_{44})$	7.2209 ± 0.0489	7.705 ± 0.054
3	$\frac{1}{2}(c_{11} - c_{12})$	0.6393 ± 0.0037	0.8367 ± 0.0057
4	c_{11}	6.4669 ± 0.0555	7.067 ± 0.062
5	c_{44}	1.3038 ± 0.0089	1.372 ± 0.009

TABLE V. Specific heat C_V for some fluorites. (Units are J/mole deg.)

Material	Calculated value	Measured value
CaF_2	64.19	64.95 ^a
SrF_2	68.75	67.96 ^b
BaF_2	71.28	69.54 ^c
CdF_2	70.14	

^a H. H. Landholt and R. Bornstein, *Science and Technology* (Springer, Berlin, 1951), Vol. II, Part 4.

^b Reference 12.

^c S. S. Todd, *J. Am. Chem. Soc.* **11**, 4115 (1949).

TABLE VI. Temperature derivatives of the SOEM of CdF_2 at 295°K. (Units are 10^{-4} deg^{-1} .)

$\frac{d \ln c_{11}}{dT}$	$\frac{d \ln c_{12}}{dT}$	$\frac{d \ln c_{44}}{dT}$
-3.712 ± 0.010	-5.075 ± 0.056	-5.329 ± 0.058

¹⁵ R. N. Thurston and K. Brugger, *Phys. Rev.* **133**, A1604 (1964).

TABLE VII. Pressure derivatives of the SOEM of CdF_2 at 295°K.

$\frac{dc_{11}}{dP}$	$\frac{dc_{12}}{dP}$	$\frac{dc_{44}}{dP}$
7.107 ± 0.035	5.521 ± 0.066	1.353 ± 0.028

TABLE VIII. Three combinations of TOEM for CdF_2 . (Units are 10^{11} dyn/cm^2 .)

$C_{111} + 2C_{112}$	$C_{144} + 2C_{166}$	$2C_{112} + C_{123}$
263.0 ± 3.6	73.2 ± 1.6	143.1 ± 2.6

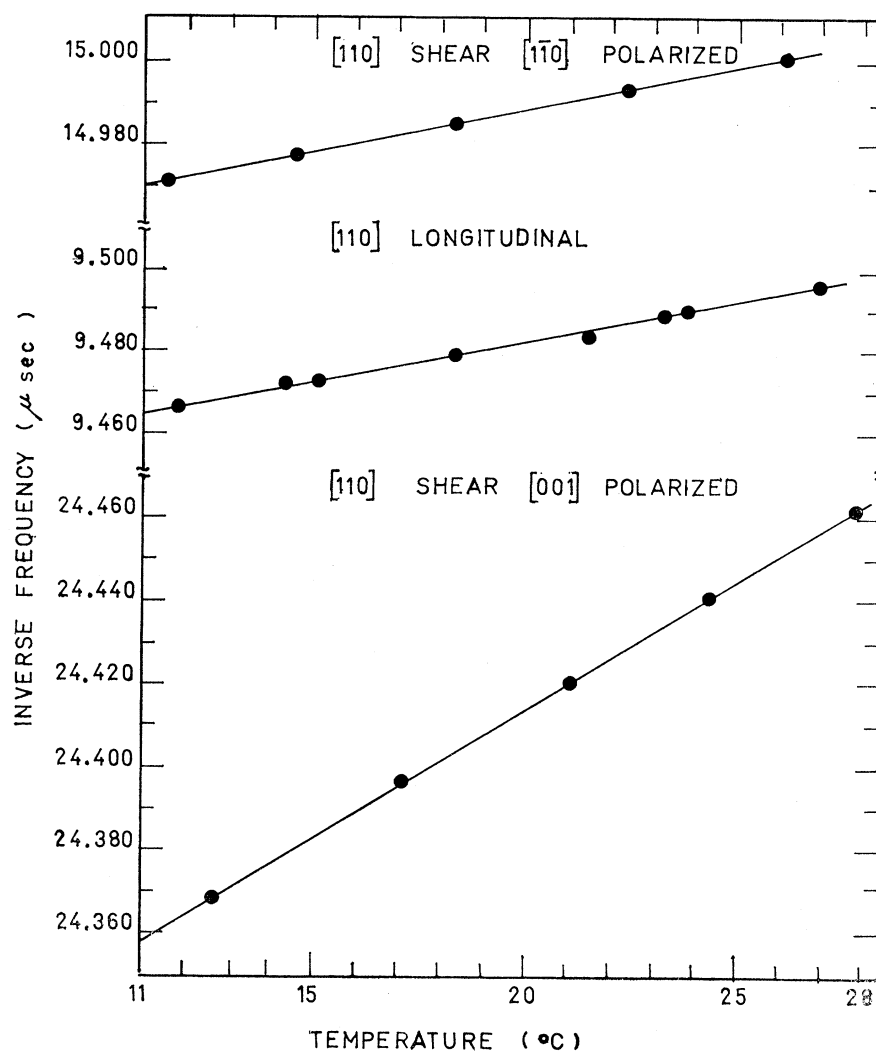


FIG. 2. Reciprocal resonant frequency as a function of temperature for sound propagating in the [110] direction.

De Launy's tables.¹⁶ The SOEM which enter the calculation are, however, 0°K values. In order to determine the latter, the quasiharmonic approximation¹⁷ was used to deduce the 0°K moduli from the room-temperature values and the temperature derivatives. The temperature dependence of the SOEM is given by

$$c_{ij}^S = \tilde{c}_{ij}^S (1 - D_{ij} \bar{\epsilon}), \quad (5)$$

where \tilde{c}_{ij}^S is the 0°K SOEM referred to the static lattice, D_{ij} is a constant, $\bar{\epsilon}$ is the average thermal energy given by

$$\bar{\epsilon} = \frac{3}{8} k \tilde{\Theta} + 3k \tilde{\Theta} \left(\frac{T}{\tilde{\Theta}} \right)^4 \int_0^{\tilde{\Theta}/T} \frac{\lambda^3}{\exp(\lambda) - 1} d\lambda. \quad (6)$$

¹⁶ J. De Launy, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 2.

Here, $\tilde{\Theta}$ is the harmonic Debye temperature¹⁷ derivable from \tilde{c}_{ij}^S . The 0°K SOEM were determined by a self-consistent calculation. Initially, from the room-temperature SOEM the starting value of $\tilde{\Theta}$ was computed. The latter was utilized in Eqs. (5) and (6) for the determination of the \tilde{c}_{ij}^S , the process being repeated three to four times until self-consistency in the values of the \tilde{c}_{ij}^S has been achieved.

The validity of the above method was tested using the room-temperature SOEM and their temperature derivatives for CaF_2 and SrF_2 in order to calculate their 0°K SOEM and their Debye temperatures $\tilde{\Theta}$ and Θ_0 . The results are shown in Table IX, together with the experimentally measured values. As is evident from the latter table, the agreement between the extrapolated and measured SOEM is within experimental error. The results obtained for CdF_2 are $\tilde{\Theta} = (337 \pm 3)^\circ\text{K}$, $\Theta_0 = (328 \pm 3)^\circ\text{K}$.

¹⁷ G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York 1961), Vol. 12

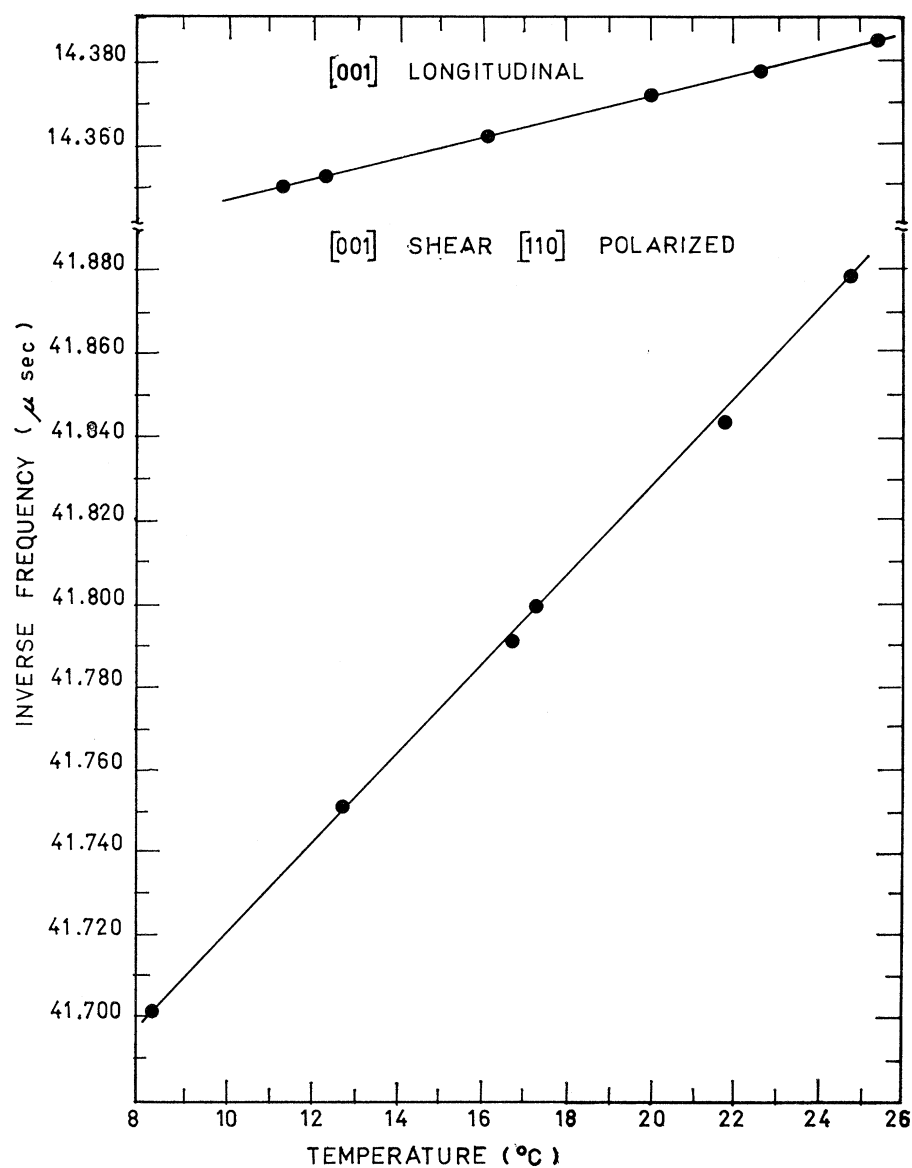


FIG. 3. Reciprocal resonant frequency as a function of temperature for sound propagating in the [001] direction.

TABLE IX. SOEM and Debye temperatures at 0°K for CaF_2 , SrF_2 , and CdF_2 . (Units of SOEM are 10^{11} dyn/cm^2 .)

Material		$c_{ij}(T=0^{\circ}\text{K})$ calc	Θ_0 calc	$c_{ij}(T=0^{\circ}\text{K})$ expt	Θ_0 expt	\bar{c}_{ij}	$\bar{\Theta}$
CaF_2	c_{11}	17.107		17.124 ^a		17.642	
CaF_2	c_{12}	4.708	517.4	4.675	519.4 ^a	4.907	528.3
CaF_2	c_{44}	3.601		3.624		3.782	
SrF_2	c_{11}	12.865		12.88 ^b		13.416	
SrF_2	c_{12}	4.678	379.6	4.748	380 ^b	4.965	389.2
SrF_2	c_{44}	3.344		3.308		3.556	
CdF_2	c_{11}	19.642		20.549	
CdF_2	c_{12}	7.357	328.5	7.808	336.9
CdF_2	c_{44}	2.410		2.565	

^a Reference 6.
^b Reference 18.

¹⁸ D. Gerlich, Phys. Rev. **136**, A1336 (1964).

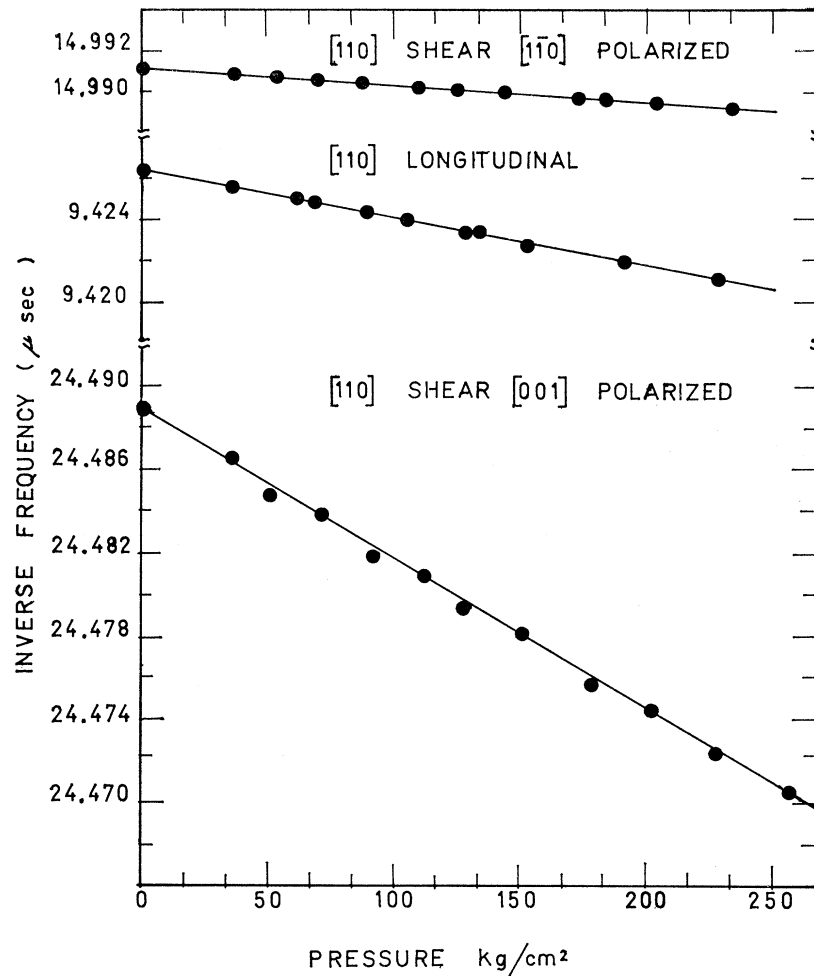


FIG. 4. Reciprocal resonant frequency as a function of pressure for sound propagating in the $[110]$ direction.

IV. DISCUSSION

A. Comparison with Theory

The values of c_{44} and the three linear combinations of the TOEM $C_{111}+2C_{112}$, $C_{144}+2C_{166}$, and $2C_{112}+C_{123}$ were calculated theoretically from a rigid-ion model and a shell model.^{1,2,19-21} In both models, a central-force interaction is assumed, consisting of a Coulombic interaction and exchange interactions to next-nearest neighbors. As it has been shown that the exchange interaction with third-nearest neighbors vanishes for the alkaline-earth fluorides,²² including only second-nearest-neighbor interactions is a justified approximation. The repulsive potential was assumed to be of the form A/r^n , where r is the distance between the interacting ions, A and n being constants. It was found that varying n from 6 to 12 changed the three computed

linear combinations of the TOEM and c_{44} by less than 5%. A value of $n=10$ was chosen for the computation. Being insensitive to n , the rigid-ion model has only two parameters c_{11} and c_{12} . Their values used in the computation were the harmonic values referred to in the static lattice, viz., \tilde{c}_{11} , and \tilde{c}_{12} .

In the shell-model calculation, two sets of parameters were used for the shell charge Y_2 and the shell-core spring constant K_2 of the cation F^- : (i) the average values used for the other alkaline-earth fluorides^{5,12} $Y_2 = -1.68$, $K_2 = 6.8 \times 10^5 \text{ dyn/cm}$; and (ii) Y_2 , as given by Dick,²³ and K_2 , as determined from the free-ion polarizability, i.e., $Y_2 = -2.40$, $K_2 = 1.27 \times 10^6 \text{ dyn/cm}$. The first set of shell-model parameters gave a better agreement with Axe and co-workers'²⁴ experimental effective charges of CdF_2 than the second one.

In Table X, the results of the theoretical calculation for c_{44} , $C_{111}+2C_{112}$, $C_{144}+2C_{166}$, and $2C_{112}+C_{123}$, together with the experimental data, are shown. As can

¹⁹ J. D. Axe, Phys. Rev. **139**, A1215 (1965).

²⁰ R. Srinivasan, Phys. Rev. **165**, 1041 (1968).

²¹ R. Srinivasan, Phys. Rev. **165**, 1054 (1968).

²² H. W. Verleur and A. S. Barker, Jr., Phys. Rev. **164**, 1169 (1967).

²³ B. G. Dick, Phys. Rev. **145**, 609 (1966).

²⁴ J. D. Axe, J. W. Caglianella, and J. E. Scardefuld, Phys. Rev. **139**, A1211 (1965).

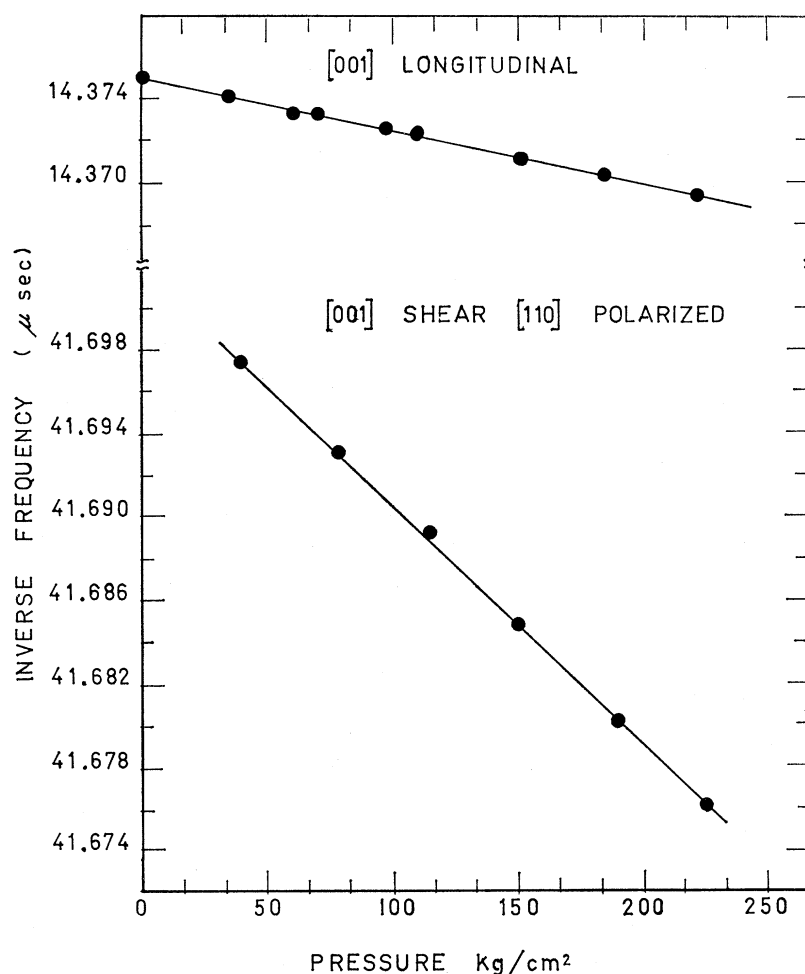


FIG. 5. Reciprocal resonant frequency as a function of pressure for sound propagating in the [001] direction.

be seen, there is good agreement between the measured room-temperature combinations of the TOEM and the 0°K measured ones, while the values of c_{44} disagree. Although the comparison for the TOEM is made between measured room-temperature data and calculated 0°K values, the TOEM are not expected to be strongly temperature dependent, as is indicated by measurements on CaF_2 and BaF_2 .^{5,6}

As can be seen from Table X, the model is quite successful in accounting for the measured values of the linear combinations of the TOEM in CdF_2 . It should also be pointed out that the calculated combinations of the TOEM are very insensitive to the choice of model,

TABLE X. Comparison of the experimental and theoretical elastic constants of CdF_2 . (Units are 10^{11} dyn/cm².)

	\tilde{c}_{44}	$C_{111}+2C_{112}$	$C_{123}+2C_{112}$	$C_{144}+2C_{166}$
Experimental	2.57	263.0	143.1	73.24
Rigid-ion model	6.39	255.4	168.3	89.4
Shell model a	5.48	255.4	168.3	81.7
Shell model b	4.33	255.4	168.3	72.1

as can be seen from the close agreement of the TOEM combinations computed from the rigid-ion and shell models. The reason for this is that the combinations of the TOEM are mainly determined by the core-core interaction. The discrepancy between the calculated and measured values of c_{44} is noteworthy, especially as in the case of the closely related material CaF_2 , there is good agreement with experiment, where the calculation is based on the same model as above.¹⁹ It should be pointed out that the electrostatic contribution to c_{44} is large and negative; thus the calculated value will depend strongly on the short-range interactions, and hence will be quite sensitive to the nature of the assumed model. It is possible that because of the different electronic structures of Ca^{++} and Cd^{++} , there is a stronger deviation from a two-body central-force interaction in the CdF_2 than in the CaF_2 lattice. Since no first-principle calculations of the short-range interaction in the fluorite lattice have been done up to now, this point cannot be further elaborated.

Utilizing the measured pressure derivatives, the explicit temperature dependence of the SOEM may be

TABLE XI. Constitution of the temperature derivatives of the SOEM at 295°K. (Units are 10^{-4} deg^{-1})

	$\left(\frac{d \ln c_{ij}}{dT}\right)_P$	$\left(\frac{d \ln c_{ij}}{dT}\right)_V$	$+3\alpha B^T \left(\frac{d \ln c_{ij}}{dP}\right)_T$
c_{11}	-3.71	1.12	2.59
c_{12}	-5.08	-0.44	5.52
c_{44}	-5.33	1.18	4.15

evaluated as follows:

$$\left(\frac{d \ln c_{ij}}{dT}\right)_P = \left(\frac{d \ln c_{ij}}{dT}\right)_V + 3\alpha B^T \left(\frac{d \ln c_{ij}}{dP}\right)_T. \quad (7)$$

Here, $(d \ln c_{ij}/dT)_P$ is the measured temperature derivative, and $(d \ln c_{ij}/dT)_V$ is the intrinsic change of the effective SOEM with temperature, which should be zero if the quasiharmonic approximation is strictly applicable. In Table XI, the values of the explicit and implicit temperature derivatives for CdF_2 are presented. As can be seen, the quasiharmonic approximation is a reasonable one for CdF_2 at room temperature.

The Debye temperature may also be evaluated by the Lindemann formula when the melting point of the material is known.²⁵ Table XII shows the value of the Debye temperature as derived from the elastic data and the Lindemann formula. As can be seen, for CdF_2 the agreement between the two Debye temperatures is of the same order as for the other alkaline-earth fluorides.

B. Gruneisen Gammas

Utilizing the room temperature and 0°K SOEM together with their pressure derivatives, the mode Gruneisen gammas γ_i ($i=1, 2, 3$), and the low- and high-temperature limits of their thermal average, γ_L and γ_H , may be evaluated.²⁶ The values thus obtained

TABLE XII. Debye temperature of some fluorides: comparison of Lindeman's formula (Θ_L) and elastic data (Θ_0).

	Θ_0	Θ_L
CdF_2	328	340
CaF_2	519	518
SrF_2	380	360
BaF_2	282	295

²⁵ N. F. Mott and H. Jones, *The Theory and Properties of Metals and Alloys* (Dover, New York, 1958).

²⁶ D. E. Schuele and C. S. Smith, *J. Phys. Chem. Solids* **25**, 801 (1964).

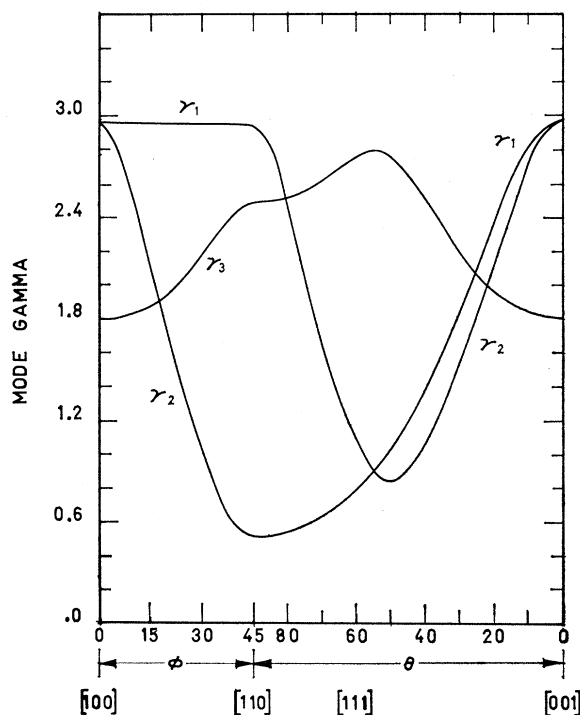


FIG. 6. Mode gammas as a function of crystalline direction.

are $\gamma_L = 2.05$ and $\gamma_H = 1.96$. The γ_i 's for some directions of high symmetry are shown in Fig. 6, where ϕ denotes the azimuthal angle and θ denotes the colatitude; 3 refers to the longitudinal mode, 1 and 2 refer to the slow and fast shear modes, respectively. The value of γ_H deduced from room-temperature thermal expansion is 2.23, which is in fair agreement with γ_H deduced from the elastic data. This is in contrast with the case of the other alkaline-earth fluorides,^{4-7,27} where a large discrepancy was found between two values of γ_H . This again may have some bearing on the difference in the electronic structure of Ca^{++} , Sr^{++} , and Ba^{++} on the one hand, and Cd^{++} on the other hand.

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²⁷ D. Gerlich, *Phys. Rev.* **168**, 947 (1968).