

tensor depends on the magnetic field through  $D(\mathbf{k},0)$  and  $D(\mathbf{k},\omega)$ . These dielectric functions are expressed by an infinite sum as can be seen from Eqs. (21), (22) and have to be evaluated numerically.

#### IV. CONCLUSION

In arriving at our final results, Eqs. (37), (38), and (39), we have assumed [Eq. (29)] that the phonons are

in thermal equilibrium. This implies that the electron density fluctuates so fast at a frequency  $\omega$  much higher than  $\omega_k$  and therefore the phonons cannot follow the fluctuations.

Our result for the longitudinal conductivity is therefore valid when  $\omega \gg \omega_k$ . For the transverse conductivity our results are valid for  $|\omega - \omega_c| \gg \omega_k$ , which includes the case of low applied frequency  $\omega$  but  $\omega_c \gg \omega_k$ .

## Elastic Constants of Barium Fluoride Between 4.2 and 300°K

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The elastic constants of single-crystal barium fluoride have been determined in the 4.2–300°K temperature range, by an ultrasonic pulse-echo technique. The values of the elastic constants, extrapolated to 0°K, in units of  $10^{11}$  dyn/cm<sup>2</sup>, are:  $c_{11}=9.810$ ,  $c_{12}=4.481$ , and  $c_{44}=2.544$ . The constants  $c_{11}$ , and  $c_{12}$  change by about 10%, while  $c_{44}$  hardly changes over the above temperature range. Barium fluoride is found to be mechanically isotropic, the value of the anisotropy factor  $2c_{44}(c_{11}-c_{12})^{-1}$  being close to unity between 4.2 and 300°K. A value of 282°K for the Debye temperature at 0°K is computed from the elastic constants. The values of the elastic constants are deduced theoretically from a rigid-ion model, and the results compared with the experimental data.

### I. INTRODUCTION

THE alkaline-earth fluorides have been extensively investigated over the last years, especially their optical properties<sup>1</sup> and the behavior of paramagnetic-ion impurities in their host lattices.<sup>2</sup> As they form ionic crystals, and thus their lattice forces might be derived theoretically from a simple rigid-ion model,<sup>3</sup> it is of interest to investigate their mechanical properties. The elastic constants of CaF<sub>2</sub> from 4.2 to 300°K have been determined recently,<sup>4</sup> and the present report describes measurements of the adiabatic elastic-stiffness constants of BaF<sub>2</sub> over the temperature range 4.2–300°K. Measurements of elastic constants, and their temperature dependence provide information about the mechanical and thermodynamic properties of the lattice. They can also be compared with the theoretically calculated values, and thus the validity of the assumptions underlying the theoretical model can be examined.

### II. EXPERIMENTAL TECHNIQUE

Barium fluoride is a cubic crystal, and thus it has three independent elastic constants:  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$ . The latter were determined by measuring the sound

velocity in different crystalline directions, by a pulse-echo technique, utilizing unrectified pulses at 15 Mc/sec.<sup>5</sup> Such a technique avoids the necessity for the "time-of-flight correction," and also increases the accuracy. A single crystal of BaF<sub>2</sub> was oriented by means of x-ray Laue back reflection, and two pairs of parallel surfaces were ground on it. One set of surfaces corresponded to a (111) crystalline plane, while the other set was a (110). X- and Y-cut quartz transducers of 5-Mc/sec fundamental frequency, operating at their third harmonic, were used in generating longitudinal and shear sound waves, respectively. For the room-temperature measurements, phenyl salicylate (salol) was used in bonding the transducer to the sample, glycerine, and "Nonaq" stopcock grease were used from below room temperature, to about 120°K. From there, down to 4.2°K, Dow-Corning No. 200 silicone fluid, 1000-cstoke viscosity, was used as a bonding agent. Where measurements with different bonding materials were made in overlapping temperature ranges, the agreement of the results was within the limit of error. After bonding the transducer, the crystal was placed inside a cryostat, under a dry helium atmosphere, where its temperature could be varied between 4.2 and 300°K.

The elastic constants were determined by measuring the sound velocity of five different propagation modes. These were a longitudinal and shear wave in the [111] direction, and a longitudinal and two shear

<sup>1</sup> W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howarth, *Phys. Rev.* **127**, 1950 (1962).

<sup>2</sup> W. Low, in *Advances in Quantum Electronics*, edited by J. Singer (Columbia University Press, New York, 1961).

<sup>3</sup> M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954).

<sup>4</sup> D. R. Huffman and M. H. Norwood, *Phys. Rev.* **117**, 709 (1960).

<sup>5</sup> S. Eros and J. R. Reitz, *J. Appl. Phys.* **29**, 683 (1958).

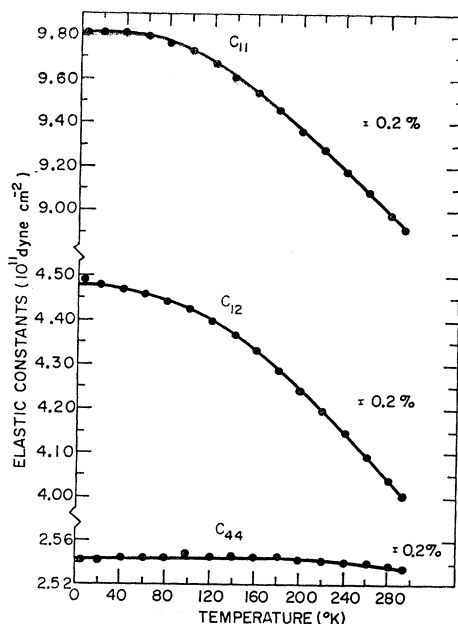


FIG. 1. The elastic constants of BaF<sub>2</sub> as a function of temperature.

waves in the [110] direction, the shear waves being polarized in the  $[1\bar{1}0]$  and [001] directions, respectively. The three elastic constants were then computed from the five measured values of the velocity, and the density by means of a least-square fit. A value of 4.886 g-cm<sup>-3</sup> was used for the room-temperature density of BaF<sub>2</sub>.

Based on an error of  $\pm 0.2\%$  in the sound velocity, and judging by the scatter of the data, the error in the elastic constants is estimated as  $\pm 0.2\%$ .

### III. RESULTS AND DISCUSSION

The three elastic constants,  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$  as a function of temperature, over the range 4.2–300°K, are shown in Fig. 1. The values of the thermal expansion coefficient over the same temperature range, which are required for correcting the changes in path length and density with temperature, are computed from its room-temperature value,<sup>6</sup> the specific heat of BaF<sub>2</sub> as a function of temperature,<sup>7</sup> and the Grüneisen relation.<sup>8</sup> Although this is a rough estimate only, it is amply sufficient for the present purpose since the correction due to thermal expansion is very small.

In Table I, the present room-temperature data are compared with the results of Bergmann,<sup>9</sup> which were determined by the elastogram method. As can be seen, there is good agreement between the two sets of measurements.

<sup>6</sup> R. J. Paff (private communication).

<sup>7</sup> K. S. Pitzer, W. V. Smith, and W. M. Latimer, *J. Am. Chem. Soc.* **60**, 1826 (1938).

<sup>8</sup> N. F. Mott and H. Jones, *Theory of Metals* (Clarendon Press, Oxford, 1936).

<sup>9</sup> L. Bergmann, *Z. Naturforsch.* **12a**, 229 (1957).

TABLE I. Comparison of the values of the elastic constants of BaF<sub>2</sub> at room temperature (in units of 10<sup>11</sup> dyn cm<sup>-2</sup>).

	$c_{11}$	$c_{12}$	$c_{44}$
Present results	8.915	4.002	2.535
Bergmann	9.01	4.03	2.49

The value of the anisotropy factor  $2c_{44}(c_{11}-c_{12})^{-1}$  for BaF<sub>2</sub> as a function of the temperature is plotted in Fig. 2. As can be seen, it is close to unity over the whole range 4.2–300°K. Barium fluoride thus has the interesting property of being a mechanically isotropic single crystal. It might thus be very useful for studies of ultrasonic mixing and harmonic generation.

The elastic constants of CaF<sub>2</sub>, which has the same crystal structure as BaF<sub>2</sub>, have been calculated theoretically,<sup>10</sup> assuming a rigid-ion model, and approximating the repulsive energy by a term proportional to  $r_0^{-10}$ , where  $r_0$  is the lattice constant. The agreement between the experimental and theoretical values was found to be reasonably good. The results of the elastic constants of BaF<sub>2</sub>, utilizing the values of the bulk modulus, and the principal Raman line,<sup>11</sup> together with the experimental room-temperature results are shown in Table II. The discrepancy between the theoretical

TABLE II. Theoretical and experimental values of the elastic constants of BaF<sub>2</sub> (in units of 10<sup>11</sup> dyn cm<sup>-2</sup>).

	$c_{11}$	$c_{12}$	$c_{44}$
Theoretical	9.57	3.85	2.84
Experimental	8.91	4.00	2.54

and experimental values is somewhat larger in the case of BaF<sub>2</sub> than for CaF<sub>2</sub>. It is possible that the rigid-ion model is less applicable to BaF<sub>2</sub> than CaF<sub>2</sub>, since due to the larger size of the cation in the case of the former, relative nucleus-shell polarization effects might be more important. The temperature variation

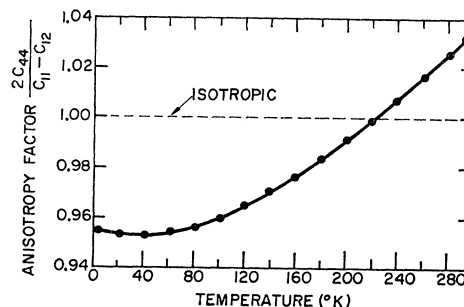


FIG. 2. The anisotropy factor of BaF<sub>2</sub> as a function of temperature.

<sup>10</sup> R. Srivinasan, *Proc. Phys. Soc. (London)* **72**, 566 (1958).

<sup>11</sup> R. S. Krishnan and P. S. Narayanan, *Indian J. Pure Appl. Phys.* (to be published); reported by A. V. R. Warriar and R. S. Krishnan in *Naturwiss.* **51**, 8 (1964).

of the elastic constants is larger for BaF<sub>2</sub> than in the case of CaF<sub>2</sub>, indicating that anharmonicity effects are more pronounced in the case of BaF<sub>2</sub>.

As can be seen,  $c_{11}$  and  $c_{12}$  vary by about 10% over the temperature range 4.2–300°K, while  $c_{44}$  hardly changes at all. A similar behavior is also observed for the alkali halides.<sup>12</sup> The reason for this being that the variation of  $c_{44}$  with temperature is caused only by the thermal expansion of the lattice. On the other hand, in the case of  $c_{11}$  and  $c_{12}$  the shift in the vibrational frequencies of the lattice with temperature also contributes to the temperature dependence<sup>13</sup> in addition to the contribution of the thermal expansion.

From the values of the elastic constants extrapolated to 0°K, the Debye temperature at 0°K can be com-

puted. Using the procedure of Marcus and Kennedy,<sup>14</sup> a value of 282°K for the Debye temperature at 0°K is determined. Since very-low-temperature specific-heat data for BaF<sub>2</sub> are not available, no direct comparison between the Debye temperatures determined from specific-heat and elastic data can be made. The Debye temperature determined from the lowest temperature (13.79°K) specific-heat data available<sup>6</sup> is 169°K. The discrepancy may be due to a rapid rise of the Debye temperature in the range 14–0°K.

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<sup>14</sup> P. M. Marcus and A. J. Kennedy, *Phys. Rev.* **114**, 459 (1959).

<sup>12</sup> G. Leibfried and H. Hahn, *Z. Physik* **150**, 497 (1958).  
<sup>13</sup> H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 213.

## Changes in Electrical Resistance Caused by Incoherent Electron-Phonon Scattering

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A small proportion of the events in which a conduction electron is scattered by an impurity atom involve the emission or absorption of a phonon. An investigation is made of the suggestion that such incoherent electron-phonon interactions may lead to appreciable deviations from Matthiessen's rule. The effect of such processes on the electrical resistivity is found to be too small to be observable.

### I. INTRODUCTION

ACCORDING to Matthiessen's rule, the electrical resistance of a dilute alloy is separable into a temperature-dependent part, which is characteristic of the pure metal, and a residual part due to impurities.<sup>1</sup> The deviations that have been observed<sup>2–4</sup> from this rule have not yet received a satisfactory explanation, for although a number of mechanisms that might cause such deviations have been suggested, none appears to give a numerical value that is sufficiently large.

One of the first such calculations was due to Sondheimer,<sup>5</sup> who took account of the fact that electron-phonon scattering is inelastic. His solution of the Boltzmann transport equation showed a deviation from Matthiessen's rule too small to agree with experi-

ment. The anisotropy of relaxation time of the conduction electrons in the noble metals has also been calculated,<sup>6</sup> but was found too small to explain the observed results.

An interesting suggestion was made by Koshino,<sup>7</sup> who proposed that the scattering of electrons by the thermal motion of the impurities could lead to a significant additional resistance. His result was later criticized on the grounds that in an expansion of the lattice displacements, he had omitted a set of terms which give a contribution almost exactly cancelling the rest of the series. A rigorous demonstration was given<sup>8</sup> that when the change in electron energy is neglected, the scattering of a single free electron by an impurity atom is quite independent of its thermal motion. No attempt was made to solve the Boltzmann equation using this revised expression for the scattering, and only an intuitive argument was given that the presence of other electrons

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<sup>3</sup> R. L. Powell, H. M. Roder, and W. J. Hall, *Phys. Rev.* **115**, 314 (1959).

<sup>4</sup> P. Alley and B. Serin, *Phys. Rev.* **116**, 334 (1959).

<sup>5</sup> E. H. Sondheimer, *Proc. Roy. Soc. (London)* **A203**, 75 (1950).

<sup>6</sup> P. L. Taylor, *Proc. Roy. Soc. (London)* **A275**, 209 (1963).

<sup>7</sup> S. Koshino, *Progr. Theoret. Phys. (Kyoto)* **24**, 484 and 1049 (1960).

<sup>8</sup> P. L. Taylor, *Proc. Phys. Soc. (London)* **80**, 755 (1962).