

## Elastic Constants of Silver Chloride from 4.2 to 300°K\*

WALDO HIRSHAW, J. T. LEWIS,† AND C. V. BRISCOE‡  
*University of North Carolina, Chapel Hill, North Carolina*  
 (Received 6 June 1967)

The adiabatic elastic constants of single-crystal AgCl have been determined in the temperature range 4.2 to 300°K by an ultrasonic pulse-echo technique. The values of the elastic constants at 0°K, extrapolated from 4.2°K data, in units of  $10^{11}$  dyn/cm<sup>2</sup> are:  $c_{11}=7.590$ ,  $c_{12}=3.908$ , and  $c_{44}=0.6894$ . The values at room temperature are:  $c_{11}=5.965$ ,  $c_{12}=3.646$ , and  $c_{44}=0.618$ . The room-temperature elastic constants are all within 1% of those reported by Arenberg, but differ significantly from data given by Stepanov and Eidus. Of particular interest is the large degree of failure of the Cauchy relation,  $\Delta=c_{12}-c_{44}=+3.219\times 10^{11}$  dyn/cm<sup>2</sup> at 0°K, and the large discrepancy between the infrared lattice resonance frequency calculated from the elastic constants and that observed experimentally by other investigators. These two facts, coupled with the large temperature dependence observed for the elastic constants, indicate considerable anharmonicity in the lattice potential of AgCl. The Debye characteristic temperature derived from the 0°K elastic constants  $\Theta_D^{\text{el}}$  is 161°K according to Betts *et al.*, 165°K according to Anderson, and 164 and 139°K according to two approximations given by Fedorov.

## INTRODUCTION

THE elastic constants of a solid provide valuable insight into the nature of the atomic binding forces. Low-temperature ( $\sim 4.2^\circ\text{K}$ ) data are especially useful as a basis for semiempirical force models and as a final check of fundamental theories of lattice dynamics. The elastic constants may be theoretically related to many other properties of solids, such as specific heat, infrared lattice resonance frequencies, x-ray scattering, and various transport properties. In this paper particular attention will be given to theories which calculate at 0°K the temperature dependence of the lattice specific heat and the infrared lattice resonance frequency of ionic solids.

The simplest ionic crystals are the alkali halides in which the outermost electrons occupy closed shells. For these materials one expects the rigid-ion approximation used extensively by Born *et al.*<sup>1</sup> to yield reasonably good results. The Cauchy relations, which for cubic symmetry reduce to  $c_{12}=c_{44}$ , are expected to be obeyed if the ionic forces have only central, single-body character, the ions are centers of inversion symmetry, and the crystal is initially in an unstrained state. According to the above model the alkali halides satisfy this criterion. However, experimentally<sup>2</sup> it is observed that the Cauchy relation does not hold at 0°K for the alkali halides although the deviations in most cases are not large. Despite its inability to predict the failure of the Cauchy relation the Born-Mayer<sup>3</sup> model is quite

successful in predicting many of the elastic properties of the alkali halides; e.g., cohesive energy, compressibility, and the magnitudes of the elastic constants.

The most basic and successful attempt<sup>2</sup> to account for the observed failure of the Cauchy relation for the alkali halides has been the quantum-mechanical calculation of the cohesive energy and the elastic constants by Löwdin.<sup>4</sup> Certain three-center integrals appear in the theory, which, as originally pointed out by Löwdin,<sup>5</sup> cannot be replaced by equivalent two-body central forces. Thus, the criterion for the validity of the Cauchy relations is violated. Dick<sup>6</sup> has modified the Born-Mayer model by the inclusion of exchange-charge interactions due to the overlap of the ions in a real crystal. These exchange-charge interactions lead to forces which have a many-body character and their inclusion in the Born-Mayer model predicts the failure of the Cauchy relation. Mitskevich<sup>7</sup> has taken the dynamics of a Born-Mayer-type lattice into account by including terms in the potential energy due to the interaction of deformed (in the dipole approximation) electronic shells of ions and due to a charge-quadrupole interaction. This approach appears promising according to the one numerical calculation by Mitskevich for NaCl which is in good agreement with experiment.<sup>2</sup>

Although the noble-metal halides, such as AgCl, are of the same crystal structure (fcc) as the alkali halides, the outer electrons of the cations are not in closed shells as in the alkali halides. Thus one should not be surprised if differences in elastic behavior occur between the two types of materials. Burstein *et al.*<sup>8</sup> have pointed out, on

\* This work supported by the Air Force Office of Scientific Research under grant AF-AFOSR-645-64 and the Advanced Research Projects Agency under contract SD-100.

† Now at the University of Tennessee, Knoxville, Tennessee.

‡ Guest Professor for the 1966-67 academic year at the Technische Hochschule, Karlsruhe.

<sup>1</sup> For a thorough discussion of the rigid-ion model and what has been accomplished with it up until 1954 see the book by M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954).

<sup>2</sup> Low-temperature elastic constant data are given for 13 alkali halides in an article by J. T. Lewis, A. Lehoczy, and C. V. Briscoe *Phys. Rev.* **161**, 877 (1967).

<sup>3</sup> M. Born, *Atomtheories des Festen Zustandes* (B. G. Teubner,

Leipzig, 1923); M. Born and M. Goeppert-Mayer, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1933), Vol. 24, Part 2.

<sup>4</sup> Per Olov Löwdin, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1.

<sup>5</sup> P. O. Löwdin, *Arkiv Mat. Astron. Fysik* **35A**, 9, (1947); **35A**, 30 (1947).

<sup>6</sup> B. G. Dick, *Phys. Rev.* **129**, 1583 (1963).

<sup>7</sup> V. V. Mitskevich, *Fiz. Tverd. Tela* **3**, 3022 (1961) [English transl.: *Soviet Phys.-Solid State* **3**, 2202 (1962)].

<sup>8</sup> E. Burstein, P. L. Smith, and D. L. Arenberg, *Phys. Rev.* **82**, 314 (1951).

the basis of room-temperature data, that  $c_{44}$  is much less than  $c_{12}$  for AgCl. They speculate that this drastic failure of the Cauchy relation for AgCl is probably due to terms in the ionic potential which depend on exchange and correlation interactions and on the interactions of deformed ions.

### EXPERIMENT

The three independent elastic constants of AgCl (fcc crystal structure) can be determined from the measured velocity of sound in two different crystallographic directions. The equations used are:

$$\rho v_l^2 = c_{11}, \quad (1)$$

where  $v_l$  is the velocity of a longitudinal acoustic wave propagating in the [100] crystallographic direction and  $\rho$  is the density;

$$\rho v_t^2 = c_{44}, \quad (2)$$

where  $v_t$  is the velocity of a transverse wave propagating in the [100] crystallographic direction; and

$$\rho v_l^2 = (c_{11} + c_{12} + 2c_{44})/2, \quad (3)$$

where  $v_l$  is the velocity of a longitudinal wave propagating in the [110] crystallographic direction. The velocities were calculated from the length of the sample and the time intervals between the echos of a 10-MHz unrectified pulse of 1.5- $\mu$ sec duration. For descriptions of the ultrasonic pulse method of measuring elastic constants see Huntington<sup>9</sup> and Markham.<sup>10</sup>

The pulse-echo method requires that the quartz electromechanical transducer be physically bonded to the sample. At room temperature (R.T.) this was accomplished using salol. Measurements below 80°K were made using a mixture of approximately 64% propylene, 33% methane, and 3% nitrogen as the adhesive between the transducer and the sample. The mixture was applied at approximately 77°K in the form of a liquid. This procedure served to reduce considerably the differential thermal contraction between the sample, bonding agent, and the transducer and resulted in very clear echo patterns at 4.2°K. Measurements were made in the 90 to 180°K temperature range with xylene as the adhesive applied at about 250°K using the same equipment and procedures as with the gas mixture. A more complete description of the apparatus and procedures used has been published.<sup>11</sup>

The dimensions of the AgCl sample crystals were approximately 1.0 in.  $\times$  0.75 in.  $\times$  0.75 in. with the 0.75 in.  $\times$  0.75 in. faces oriented perpendicular (to within  $\pm 2^\circ$ ) to either the [100] or the [110] crystallographic direction by the supplier. The samples were polished until these smaller faces were parallel to within 0.6 mrad and flat to approximately 5 parts in  $10^4$ .

<sup>9</sup> H. B. Huntington, *Phys. Rev.* **72**, 321 (1947).

<sup>10</sup> M. F. Markham, *Brit. J. Appl. Phys. Suppl.* **6**, S56 (1957).

<sup>11</sup> A. Lehoczy, J. T. Lewis, and C. V. Briscoe, *Cryogenics* **6**, 154 (1966).

TABLE I. Elastic constants of AgCl.

Temperature (°K)	Density (g/cm <sup>3</sup> )	$c_{11}$ units of $10^{11}$	$c_{12}$ dyn/cm <sup>2</sup>	$c_{44}$ dyn/cm <sup>2</sup>	$\beta^{01}$ units of $10^{-12}$	$\beta^{obs}$ cm <sup>2</sup> /dyn
300	5.585	5.920	3.640	0.616		
293 (R.T.)	5.589	5.965	3.646	0.618	2.27	2.40*
290	5.591	5.985	3.655	0.619		
280	5.596	6.045	3.674	0.622		
270	5.601	6.110	3.690	0.624		
260	5.606	6.170	3.710	0.627		
250	5.611	6.230	3.730	0.629		
240	5.616	6.295	3.748	0.632		
230	5.620	6.355	3.765	0.635		
220	5.625	6.420				
210	5.630	6.480				
200	5.634	6.530				
190	5.639	6.590				
180	5.643	6.645		0.6512		
170	5.648	6.700	3.840	0.6536		
160	5.652	6.755	3.852	0.6564		
150	5.656	6.185	3.865	0.6588		
140	5.660	6.875		0.6612		
130	5.664	6.935		0.6638		
120	5.668			0.6660		
110	5.672			0.6686		
100	5.675			0.6710		
90	5.679			0.6734		
80	5.683	7.280	3.894	0.6758		
70	5.686	7.355	3.896	0.6782		
60	5.690	7.415	3.900	0.6808		
50	5.693	7.465	3.903	0.6830		
40	5.695	7.510	3.905	0.6854		
30	5.697	7.540	3.907	0.6870		
20	5.698	7.565	3.907	0.6884		
10	5.699	7.585	3.908	0.6892		
0	5.699	7.590	3.908	0.6894	1.95	
0 <sup>b</sup>	5.690	7.391	3.907	0.694		

<sup>a</sup> Reference 18.

<sup>b</sup> J. Vallin, *Arkiv. Fysik* **34**, 367 (1967).

### RESULTS AND DISCUSSION

The AgCl crystals were of optical quality obtained from the Harshaw Chemical Company, Cleveland, Ohio. To compute the velocity from the measured time intervals between echos it is necessary to know the length of the sample as a function of temperature. The room-temperature measured length was corrected down to 120°K using the thermal expansion data of Nicklow and Young.<sup>12</sup> Below 120°K the thermal expansion coefficient was approximated by assuming it proportional to the specific heat; see Grüneisen.<sup>13</sup> Clusius and Harteck<sup>14</sup> have reported specific-heat data for AgCl down to 10.5°K. Any error in the further extrapolation of the thermal expansion coefficient to 4.2°K should be negligible. Following Arenberg<sup>15</sup> the value 5.589 g/cm<sup>3</sup> determined by Bridgman<sup>16</sup> from x-ray data was used for the room-temperature density rather than the handbook value of 5.56 g/cm<sup>3</sup>. The density as a function of temperature was determined from the room-temperature value by use of the above thermal expansion corrections.

<sup>12</sup> R. M. Nicklow and R. A. Young, *Phys. Rev.* **129**, 1936 (1963).

<sup>13</sup> E. Grüneisen, *Ann. Physik* **26**, 211 (1908).

<sup>14</sup> K. Clusius and P. Harteck, *Z. Phys. Chem. (Leipzig)* **A134**, 243 (1928).

<sup>15</sup> D. L. Arenberg, *J. Appl. Phys.* **21**, 941 (1950).

<sup>16</sup> P. W. Bridgman, *Proc. Am. Acad. Arts. Sci.* **74**, 21 (1940).

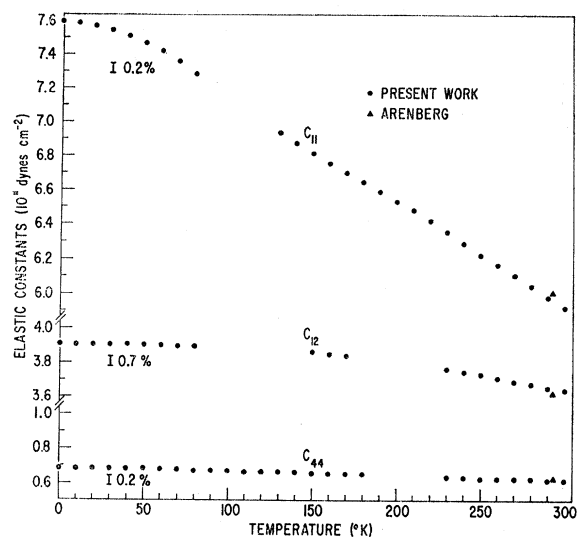


FIG. 1. Elastic constants of AgCl as a function of temperature. The error bars in percent were estimated from the scatter of the original velocity data at 4.2°K.

The elastic constants from 0 to 300°K are given in Table I with the densities used in the calculations. The values quoted in Table I were taken from smoothed plots of the experimental data. The elastic constants are given only for the temperature regions in which data was actually taken. From the scatter of the velocity data and the inaccuracies of the measuring equipment the error in  $c_{11}$  and  $c_{44}$  at 4.2°K is estimated to be  $\pm 0.2\%$ . The error in  $c_{12}$  is in general much larger because it is determined from the small difference in two relatively larger numbers [ $c_{12} = 2\rho v_l^2 - (c_{11} + 2c_{44})$ , from Eq. (3)]. For AgCl, however,  $c_{12} = 12.877 - 8.969 = 3.908$  in units of  $10^{11}$  dyn/cm<sup>2</sup> at 0°K, and a simple propagation of errors shows  $c_{12}$  to be accurate to within  $\pm 0.7\%$ . In Table II a comparison with the room-temperature data of Arenberg<sup>15</sup> (ultrasonic pulse-echo technique) and Stepanov and Eidus<sup>17</sup> (composite oscillator technique) is made. The agreement with the measurements of Arenberg is quite good (1% or less for all three constants) but the data of Stepanov and Eidus differ from the present results by as much as 29%.

TABLE II. Comparison of elastic constants of AgCl with room-temperature measurements of other investigators. The values in parentheses are the percentage differences between the present results and other work.

Source	$c_{11}$	$c_{12}$	$c_{44}$
	units of $10^{11}$ dyn/cm <sup>2</sup>		
Present Work	5.965	3.646	0.618
Arenberg <sup>a</sup>	6.01(+0.8)	3.62(-0.8)	0.625(+1.1)
Stepanov and Eidus <sup>b</sup>	4.94(-17.5)	2.58(-29)	0.615(-0.5)
Vallin <sup>c</sup>	5.860(-1.75)	3.582(-1.75)	0.622(+0.65)

<sup>a</sup> Reference 15.

<sup>b</sup> Reference 17.

<sup>c</sup> J. Vallin, Arkiv. Fysik 34, 367 (1967).

<sup>17</sup> A. V. Stepanov and I. M. Eidus, Zh. Eksperim. i Teor. Fiz. 29, 669 (1955) [English transl.; Soviet Phys.—JETP 2, 377 (1956)].

TABLE III. Elastic properties of AgCl.

	300°K	0°K
$c_{44}/c_{11}$	0.104	0.091
$\beta = 3/(c_{11} + 2c_{12})$ in units of $10^{-12}$ cm <sup>2</sup> /dyn	2.27	1.95
$A = 2c_{44}/(c_{11} - c_{12})$	0.541	0.374
$\Delta = c_{12} - c_{44}$ in units of $10^{11}$ dyn/cm <sup>2</sup>	3.024	3.219

In Fig. 1 the temperature dependence of the elastic constants of AgCl is shown. All three constants decrease with increasing temperature; the percentage changes from 300 to 0°K are  $c_{11}$ (28),  $c_{12}$ (7.5), and  $c_{44}$ (12). The relative change with temperature of the elastic constants,  $-(1/c_{ij})(dc_{ij}/dT)$ , is useful for comparison with other materials. Values at 300°K for  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$  are 1048, 495, and 421, respectively, in units of  $10^{-6}$  per °K. This large temperature dependence is only 5 to 10% more than for the heavier halides (Br and I) of K and Rb<sup>2</sup> and is indicative of considerable anharmonicity in these materials. In Table III several quantities which express the elastic behavior of AgCl are given at 300 and 0°K.

The compressibility of AgCl calculated from the elastic constants and listed in Table III is smaller than that of most of the alkali halides, being about equal to the compressibility of NaF and slightly larger than that of LiF.<sup>2</sup> Experimental measurements at room temperature by Richards and Jones<sup>18</sup> resulted in a compressibility of  $2.40 \times 10^{-12}$  cm<sup>2</sup>/dyn. This is to be compared with the value of  $2.27 \times 10^{-12}$  cm<sup>2</sup>/dyn listed in Table III for 300°K.

The elastic stiffness ratio  $c_{44}/c_{11} = 0.091$  at 0°K listed in Table III is about equal to that of the heavier halides of K and Rb. This means that AgCl has much more resistance to compressional than to shearing forces. The anisotropy factor  $A = 2c_{44}/(c_{11} - c_{12}) = 0.374$  at 0°K is not much different from that of KCl, KBr, or KI. Thus for three quantities describing elastic behavior—temperature dependence of  $c_{11}$ , elastic stiffness, and anisotropy—AgCl resembles the heavier halides of K and Rb. The relatively small value of compressibility  $\beta = 3/(c_{11} + 2c_{12})$  is due to the fact that  $c_{12}$  for AgCl is much larger relative to  $c_{11}$  [ $c_{11}/c_{12} = 1.94$  for AgCl at 0°K] than it is for any of the alkali halides.

Another and more significant result of this relatively large value of  $c_{12}$  is the degree of failure of the Cauchy relation,  $\Delta = c_{12} - c_{44}$  also listed in Table III. The value of  $3.219 \times 10^{11}$  dyn/cm<sup>2</sup> for the  $\Delta$  of AgCl at 0°K is much larger than for any of the alkali halides. At 4.2°K LiF has a  $\Delta$  of  $-2.25 \times 10^{11}$  dyn/cm<sup>2</sup> but note the difference in sign. Such a large value of  $\Delta$  for LiF can be attributed to the small size of the Li<sup>+</sup> ion relative to the F<sup>-</sup> ion. This results in the Cl<sup>-</sup> ions being in contact and the Li<sup>+</sup> ion occupying a sort of hole in the lattice. Consequently there are relatively large next-nearest-

<sup>18</sup> T. W. Richards and G. Jones, J. Am. Chem. Soc. 31, 158 (1909).

neighbor repulsive terms in the ionic potential for LiF. These terms contribute more to  $c_{44}$  than to  $c_{12}$ . Löwdin<sup>4</sup> has stated this in a slightly different way as being due to the contribution from the many-body forces associated with the overlapping of the ions which is positive for  $c_{44}$  and negative for  $c_{12}$ .

The large positive value of  $\Delta$  for AgCl can not be explained then in terms of many-body forces of the type used by Löwdin or merely by including next-nearest-neighbor halide repulsive terms in the ionic potential. The answer is probably in contributions from exchange and correlation energies and ionic deformation interactions, all of which are departures from purely ionic bonding. It would be interesting to have results for AgCl calculated according to the scheme of Mitskevich<sup>7</sup> which includes some of these interactions.

#### Lattice Resonance Frequency

For an ionic crystal such as AgCl the infrared dispersion frequency  $\omega_0$  can be related to the compressibility  $\beta$  and the high- and low-frequency dielectric constants  $\epsilon_\infty$  and  $\epsilon_0$ . See Born and Huang<sup>1</sup> for a complete discussion. The following two relations were first derived by Szigeti<sup>19</sup>:

$$\omega_0^2 = \frac{4\pi e^2 (\epsilon_\infty + 2)^2}{9mv_a \epsilon_0 - \epsilon_\infty}, \quad (4)$$

$$\omega_0^2 = \frac{3v_a (\epsilon_\infty + 2)}{mr_0^2 (\epsilon_0 + 2) \beta}, \quad (5)$$

where  $m$  is the reduced mass,  $v_a$  is the cell volume, and  $r_0$  is the nearest-neighbor distance. In the model used by Szigeti  $e$  is the charge on each ion and  $\beta$  is the theoretical compressibility derived assuming the overlap repulsion forces to be central and to act only between nearest neighbors. Since Eqs. (4) and (5) do not agree with experiment, we will, following Jones *et al.*,<sup>20</sup> discuss them in terms of "effective" ionic charge  $e^*$  and compressibility  $\beta^*$ . Jones *et al.* give the ratios  $e^*/e$  and  $\beta^*/\beta$  for AgCl derived from their 4.2°K and room-temperature values of  $\omega_0$ , the measured compressibility, and the room-temperature dielectric constants. The deviations of these ratios from unity is a measure of the inadequacy of Eqs. (4) and (5) in the description of this high-frequency polarization phenomenon. We will discuss the attempt of Lundqvist<sup>21</sup> to account for the magnitude of  $e^*/e$  and  $\beta^*/\beta$  because he expresses his results in terms of the measured elastic constants in a simple way. As cited earlier, in Löwdin's<sup>4</sup> quantum-mechanical calculation of the cohesive energy and the degree of failure of the Cauchy relations there

TABLE IV Comparison of  $e^*/e$  and  $\beta^*/\beta$ , calculated from Lundqvist's (Ref. 21) modification of the Szigeti (Ref. 19) relations using the elastic constants of AgCl, with the data of Jones *et al.* on the infrared lattice resonance frequency.

$T^\circ\text{K}$	$e^*/e^a$	$e^*/e^b$	$\beta^*/\beta^a$	$\beta^*/\beta^b$
300	1.34	0.71	2.89	1.70
4.2	1.37	0.83	2.68	

<sup>a</sup> Present work.

<sup>b</sup> Jones *et al.*, Ref. 20.

appear terms in the lattice potential due to forces of a many-body character. Lundqvist has considered the effect of these many-body forces on  $e^*/e$  and  $\beta^*/\beta$ . His results are

$$e^*/e = (r_0^2/e)(1.16c_{44} + 1.72c_{12})^{1/2}, \quad (6)$$

$$\beta^*/\beta = [1 + \beta(c_{44} - c_{12})]^{-1}, \quad (7)$$

where  $c_{44}$  and  $c_{12}$  are the elastic constants and  $\beta$  can be computed from the relation  $\beta = 3/(c_{11} + 2c_{12})$ .

In Table IV we have listed the values of  $e^*/e$  and  $\beta^*/\beta$  computed from the measured elastic constants of AgCl at 4.2 and 300°K using Eqs. (6) and (7). Also listed for comparison in Table IV are the data of Jones *et al.*<sup>20</sup> cited above. The data in columns 3 and 5 from the  $\omega_0$  measurements by Jones *et al.* show that the Szigeti relations, especially Eq. (5), are not very satisfactory in the case of AgCl. Furthermore, the modifications of Eqs. (4) and (5) by Lundqvist, taking into account many-body forces, is not very successful in explaining the  $e^*/e$  and  $\beta^*/\beta$  values derived from the  $\omega_0$  measurements. See columns 2 and 4 of Table IV. This is quite interesting because the magnitude of  $e^*/e$  for AgCl shown in column 3 of Table IV is not very different from that of the Na halides for which Lundqvist's theory is much more satisfactory. On the other hand  $\beta^*/\beta$  for AgCl is about 50% larger than is observed for any of the alkali halides. In AgCl the outermost electrons of the  $\text{Ag}^+$  ion are in  $d$  states and not  $p$  states as in the alkali metal ions. Thus it probably cannot be described very well by the above models which are based primarily on potentials arising from repulsive forces due to the overlap of closed shells.

#### Debye Temperature

The 0°K values (extrapolated from the 4.2°K data—negligible error involved in the extrapolation) of the elastic constants can be used to compute the limiting value, as the temperature approaches absolute zero, of the Debye characteristic temperature  $\Theta_0^{\text{el}}$ . Blackman<sup>22</sup> in 1935 first pointed out that, according to the simple theories of heat capacity,  $\Theta_0^{\text{el}}$  should be equal to the 0°K value of the Debye characteristic temperature  $\Theta_0^{\text{c}}$  derived from low-temperature specific-heat data. The large amount of work done since then on the theory of lattice dynamics in the harmonic approximation has not

<sup>19</sup> B. Szigeti, Trans. Faraday Soc. 45, 155 (1949); Proc. Roy. Soc. (London) A204, 51 (1950).

<sup>20</sup> G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London) A261, 10 (1961).

<sup>21</sup> S. O. Lundqvist, Arkiv Fysik 9, 435 (1955); 12, 263 (1957).

<sup>22</sup> M. Blackman, Proc. Roy. Soc. (London) A149, 117 (1935).

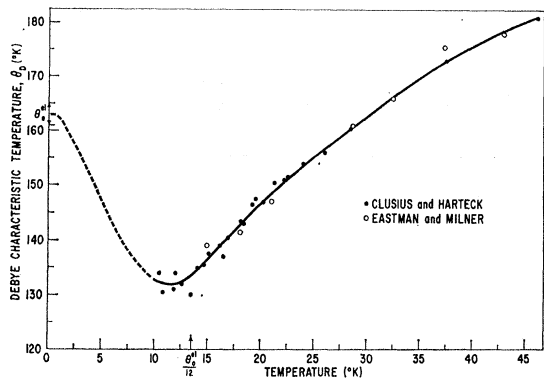


FIG. 2. Debye characteristic temperature of AgCl from the specific-heat data of Clusius and Harteck (Ref. 14) and of Eastman and Milner (Ref. 33). The  $\Theta_0^{\text{el}}$  was calculated from the 0°K elastic constants. The solid line is a smooth curve drawn to best-fit the data above 10°K and the dashed line is a speculation as to the behavior of the characteristic temperature below 10°K. Many materials have a minimum in the Debye characteristic temperature at about  $\Theta_0^{\text{el}}/12$ .

altered the validity of this relationship. For a comprehensive review of the use of the harmonic approximation in the theories of lattice dynamics see Maradudin *et al.*<sup>23</sup>

If one assumes the equivalence of low-energy thermal modes of vibration and long-wavelength acoustical modes of vibration,  $\Theta_0^{\text{el}}$  is given by<sup>24</sup>

$$\Theta_0^{\text{el}} = (\hbar/k)(9N/4\pi VI)^{1/3}, \quad (8)$$

where

$$I = \int_0^{4\pi} \sum_i (1/v_i^3) (d\Omega/4\pi), \quad (9)$$

and  $\hbar$  is Planck's constant,  $k$  is Boltzman's constant,  $N$  is the number of atoms,  $V$  is the volume of the specimen, and the  $v_i$  are the velocities of propagation for low-frequency vibrations and as such are functions of direction. Since the  $v_i$  are simple functions of the elastic constants for only a few directions in a cubic crystal it is necessary to use some approximate method of integrating over the solid angle in Eq. (9). The procedures most often referred to are those due to Quimby and Sutton<sup>25</sup> and Houston.<sup>26</sup> Betts *et al.*<sup>27</sup> have extended the work of Houston in a form which is accurate and easy to use. de Launay<sup>28</sup> using an electronic computer

<sup>23</sup> A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. No. 3.

<sup>24</sup> The review article by H. B. Huntington, [in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, pp. 213-351] has a good account of the methods of calculating  $\Theta_0^{\text{el}}$  from the elastic constants.

<sup>25</sup> S. L. Quimby and P. M. Sutton, *Phys. Rev.* **91**, 1122 (1953); P. M. Sutton, *ibid.* **99**, 1826 (1955).

<sup>26</sup> W. V. Houston, *Rev. Mod. Phys.* **20**, 164 (1948).

<sup>27</sup> D. D. Betts, A. B. Bhatia, and M. Wyman, *Phys. Rev.* **104**, 37 (1956).

<sup>28</sup> J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 220; *J. Chem. Phys.* **30**, 91 (1959).

has prepared extensive tables from which  $\Theta_0^{\text{el}}$  for a wide class of materials may be calculated. Alers and Neighbours<sup>29</sup> have shown by the use of an extensive numerical integration program for Eq. (9) that the above methods of determining  $\Theta_0^{\text{el}}$  differ by less than 1% for a large number of materials. Due to their accuracy and ease of use, de Launay's tables are often used to calculate  $\Theta_0^{\text{el}}$ ; however, for AgCl these tables are not applicable because of the large value of  $c_{12}/c_{44}=5.67$ . Consequently we have used the procedure given by Betts *et al.* and two simple methods of calculation recently suggested by Anderson<sup>30</sup> and by Fedorov<sup>31</sup> to determine  $\Theta_0^{\text{el}}$ . According to Betts *et al.*, if  $0.25 \leq 2c_{44}/(c_{11}-c_{12}) \leq 4.0$  then  $\Theta_0^{\text{el}}$  should be accurate to within 1%. This statement is verified by the work of Alers and Neighbours. Anderson states that his method of calculating  $\Theta_0^{\text{el}}$  should be accurate to about 1% if

$$\delta = 3[2c_{44} - (c_{11} - c_{12})]^2 / [12c_{44}^2 + 38c_{44}(c_{11} - c_{12}) + 3(c_{11} - c_{12})^2]$$

is less than 10%. At 0°K  $2c_{44}/(c_{11}-c_{12})=0.374$  (see Table III) and  $\delta$  is equal to 11.5%. Thus  $\Theta_0^{\text{el}}$  calculated using either method should be accurate to  $\pm 1\%$ . Fedorov gives no criterion for the accuracy of his method but he obtains excellent agreement between his calculations, the results of specific-heat experiments, and the calculations of other authors, e.g., Alers and Neighbours.<sup>29</sup>

Using the procedure of Betts *et al.* we obtain a  $\Theta_0^{\text{el}}$  of 161.04°K. Anderson's method results in a  $\Theta_0^{\text{el}}$  of 165.01°K. From Fedorov's "first and second approximations" we arrive at  $\Theta_0^{\text{el}}$ 's of 164.0 and 138.9°K, respectively. That the  $\Theta_0^{\text{el}}$ 's calculated according to Betts *et al.* and Anderson differ by 3% is a bit surprising. Alers and Neighbours<sup>29</sup> and Norwood and Briscoe<sup>32</sup> have demonstrated that  $\Theta_0^{\text{el}}$  is a more sensitive function of  $c_{44}$  than of  $c_{11}$  or  $c_{12}$ . The unusually small value of  $c_{44}$  relative to  $c_{11}$  and  $c_{12}$  ( $c_{44}=0.091c_{11}$  and  $c_{44}=0.176c_{12}$ ) may be responsible for the failure of the accuracy predictions for the case of AgCl. The result of Fedorov's "first approximation" ( $\Theta_0^{\text{el}}=164.0^\circ\text{K}$ ) is in reasonable agreement with Anderson and with Betts *et al.*, but the  $\Theta_0^{\text{el}}$  of 138.9°K obtained using his "second approximation" is difficult to understand. For LiF, NaCl, and KBr Fedorov reports better agreement between specific-heat results and  $\Theta_0^{\text{el}}$ 's calculated using his "second approximation" than those calculated from his "first approximation." Again the small value of  $c_{44}$  relative to  $c_{11}$  or  $c_{12}$  may be responsible for the apparent failure of Fedorov's "second approximation" in the case of AgCl.

The specific heat of AgCl has been measured from 10.5 to 125.6°K by Clusius and Harteck<sup>14</sup> and from 15°K

<sup>29</sup> G. A. Alers and J. R. Neighbours, *Rev. Mod. Phys.* **31**, 675 (1959).

<sup>30</sup> O. L. Anderson, *J. Phys. Chem. Solids* **24**, 909 (1963).

<sup>31</sup> F. I. Fedorov, *Dokl. Akad. Nauk SSSR* **164/4**, 804 (1965) [English transl.: *Soviet Phys.—Doklady* **10**, 896 (1966)].

<sup>32</sup> M. H. Norwood and C. V. Briscoe, *Phys. Rev.* **112**, 45 (1958).

to room temperature by Eastman and Milner.<sup>33</sup> Unfortunately this is not low enough in temperature to allow a reasonable determination of  $\Theta_0^\circ$  to be made. Barron *et al.*<sup>34</sup> and Martin<sup>35</sup> have shown that it is necessary to have specific-heat data at temperatures less than  $T = \Theta_0^\circ/50$  in order to derive  $\Theta_0^\circ$  to within an accuracy of about 1%. A plot of the Debye characteristic temperature  $\Theta_D$  versus  $T^\circ\text{K}$  using the above specific-heat data is shown in Fig. 2. As can be seen  $\Theta_D$  seems to have reached a minimum value in the 10 to 15°K temperature range and must increase quickly as  $T$  approaches 0°K if  $\Theta_0^\circ$  is to agree with  $\Theta_0^{\text{el}}$ . Such a minimum in  $\Theta_D$  at low temperatures is a common feature of many materials and is to be expected for AgCl. It is obvious that before a meaningful comparison of  $\Theta_0^{\text{el}}$  and  $\Theta_0^\circ$  can be made specific-heat data at much lower temperatures are necessary.

### SUMMARY AND CONCLUSIONS

Although AgCl is a fcc ionic type crystal as are the alkali halides, it has unusual elastic properties when compared to the alkali halides. The temperature dependence of  $c_{11}$ , the anisotropy, and the elastic stiffness ratio  $c_{44}/c_{11}$  of AgCl are quite similar to the heavier halides (Br and I) of K and Rb. However, the small compressibility is more like that of the lighter alkali halides LiF and NaF. This small compressibility is due to the relatively large value of  $c_{12}$  for AgCl. The ratio  $c_{11}/c_{12} = 1.94$  is much less than observed for any of the alkali halides. The most significant departure of the behavior of the elastic constants of AgCl from that of the alkali halides is in the degree of failure of the Cauchy relation  $c_{12} = c_{44}$ . At 0°K,  $\Delta = c_{12} - c_{44} = 3.219 \times 10^{11}$  dyn/cm<sup>2</sup> for AgCl. The largest value of  $\Delta$  observed in the alkali halides is  $-2.25 \times 10^{11}$  dyn/cm<sup>2</sup> for LiF. This large value of  $\Delta$  for LiF is due to contributions to the ionic potential of the repulsive forces resulting from the overlap of the halide ions. This overlap is caused by the small size of the Li<sup>+</sup> ion compared to the F<sup>-</sup> ion. Even if the Cl<sup>-</sup> ions in AgCl did overlap this explanation could not be applied because of the difference in the signs of  $\Delta$  for LiF and AgCl.

<sup>33</sup> E. D. Eastman and R. T. Milner, *J. Chem. Phys.* **1**, 444 (1933).

<sup>34</sup> T. H. K. Barron and J. A. Morrison, *Can. J. Phys.* **35**, 799 (1957); *Phys. Rev.* **115**, 1439 (1959); T. H. K. Barron, W. T. Berg, and J. A. Morrison, *Proc. Roy. Soc. (London)* **A242**, 478 (1957).

<sup>35</sup> D. L. Martin, *Proc. Phys. Soc. (London)* **83**, 99 (1964).

The failure of Lundqvist's<sup>21</sup> modification of the Szigeti<sup>19</sup> relations to account for the observations in AgCl has been pointed out previously by Jones *et al.*<sup>20</sup> The inclusion of low-temperature elastic-constant data in Eqs. (6) and (7) does not improve the situation. Martin<sup>36</sup> has interpreted this to a higher degree of anharmonicity in AgCl as compared to the alkali halides. The large temperature dependence of  $c_{11}$  and the drastic failure of the Cauchy relation certainly support this conclusion.

The Debye characteristic temperature  $\Theta_0^{\text{el}}$  calculated from the 0°K elastic constants of AgCl can not be compared to the Debye characteristic temperature  $\Theta_0^\circ$  derived from low-temperature specific-heat data due to the lack of data at sufficiently low temperatures. We have no explanation of the difference in the  $\Theta_0^{\text{el}}$ 's calculated using the procedure given by Betts *et al.*<sup>27</sup> (161.04°K) and that of Anderson<sup>30</sup> (165.01°K). Also quite puzzling is the difference in the  $\Theta_0^{\text{el}}$ 's obtained from Fedorov's<sup>31</sup> "first approximation" (164.0°K) and "second approximation" (138.9°K).

It is hoped that the large deviations observed in the behavior of the elastic constants and related quantities such as the infrared lattice resonance frequency of AgCl from that of the alkali halides will stimulate further theoretical investigations. Specific-heat data at temperatures below 4.2°K are needed for comparison to  $\Theta_0^{\text{el}}$ . In order to make such a comparison meaningful it will be necessary to have a more accurate determination of  $\Theta_0^{\text{el}}$  from the elastic constants, e.g., a computer calculation of the type performed by Alers and Neighbours.<sup>29</sup> *Note added in proof.* Professor Neighbours has communicated to us the result of his computer calculation of  $\Theta_0^{\text{el}}$  for AgCl using the data given in this paper. He obtains a value of 161.6°K which is in good agreement with our calculation using the procedure of Betts *et al.*

### ACKNOWLEDGMENTS

The authors are indebted to Professor W. A. Bowers and Professor L. M. Slifkin for critical readings of the manuscript. One of us (C. V. B.) would like to express his appreciation to Professor Buckel and the Technische Hochschule, Karlsruhe for hospitality during the final stages of preparing this work for publication.

<sup>36</sup> D. H. Martin, in *Advances in Physics*, edited by B. R. Coles (Taylor and Francis, Ltd., London, 1965), Vol. 14, p. 39.