

Dispersion of Phonons in Silver Chloride

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(Received December 26, 1961)

The dispersion curves of silver chloride are computed on the basis of the shell model due to Woods, Cochran, and Brockhouse. Though the calculated curves agree better with the experimental results of Cole than the curves computed using the point ion model, there appears to exist a serious discrepancy between the theory and experiment. Plausible causes of this discrepancy are pointed out.

1. INTRODUCTION

THE lattice dynamics of ionic crystals have been discussed by many workers.¹⁻⁹ Kellermann³ investigated thoroughly the lattice dynamics of a system of point ions interacting with Coulomb forces and with central repulsive forces between nearest neighbors. Lyddane and Herzfeld¹ took into account the fact that the ions are polarized by the electric field accompanying the lattice vibrations, but they neglected the effect of the polarization of ions on the overlap forces. Woods, Cochran, and Brockhouse⁹ have used the shell model of Dick and Overhauser¹⁰ with certain extensions to investigate the lattice dynamics of ionic crystals with the NaCl structure. They specialized their model to the case of an alkali halide in which only one ion is polarizable and compared the computed dispersion curves with those obtained through neutron spectrometric experiments. So far, no such comparison has been made for a crystal in which both ions are polarizable. Cole¹¹ has experimentally determined the dispersion relations for acoustic waves in silver chloride by x-ray diffraction methods. It seems desirable to compute the theoretical dispersion curves on the basis of the shell model considering both ions in silver chloride polarizable.

2. CALCULATION OF DISPERSION CURVES

The secular equation determining the angular frequencies of the lattice waves in silver chloride is,

according to Woods, Cochran, and Brockhouse:

$$\begin{vmatrix} A(11) - m_1 \omega^2 & A(12) \\ A(12) & A(22) - m_2 \omega^2 \end{vmatrix} = 0. \quad (1)$$

where m_1 and m_2 are the masses of positive and negative ions and

$$\begin{aligned} A(11) &= R_0 - \frac{e^2}{f} \left(\frac{d_1^2}{\alpha_1} + \frac{S^2 d_2^2}{S_0^2 \alpha_2} \right) \\ &\quad + \frac{e^2}{fv} \left[C_1 \left(1 - d_1^2 \frac{\alpha_2}{\alpha_1} - \frac{S^2 d_2^2 \alpha_1}{S_0^2 \alpha_2} + 2d_1 \right) \right. \\ &\quad \left. + 2C_2 d_2 \frac{S}{S_0} (1 + d_1) + \frac{\alpha_2}{v} (1 + 2d_1) (C_1^2 - C_2^2) \right] \\ A(22) &= R_0 - \frac{e^2}{f} \left(\frac{d_2^2}{\alpha_2} + \frac{S^2 d_1^2}{S_0^2 \alpha_1} \right) \\ &\quad + \frac{e^2}{fv} \left[C_1 \left(1 - d_2^2 \frac{\alpha_1}{\alpha_2} - \frac{S^2 d_1^2 \alpha_2}{S_0^2 \alpha_1} - 2d_2 \right) \right. \\ &\quad \left. - 2C_2 d_1 \frac{S}{S_0} (1 - d_2) + \frac{\alpha_1}{v} (1 - 2d_2) (C_1^2 - C_2^2) \right] \\ A(12) &= R_0 - \frac{e^2}{f} \frac{S}{S_0} \left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right) \\ &\quad + \frac{e^2}{fv} \left\{ -C_2 \left[1 - \left(1 + \frac{S^2}{S_0^2} \right) d_1 d_2 \right] \right. \\ &\quad \left. - C_1 \frac{S}{S_0} \left(d_1^2 \frac{\alpha_2}{\alpha_1} + d_2^2 \frac{\alpha_1}{\alpha_2} \right) \right. \\ &\quad \left. + \left(C_1 \frac{S}{S_0} - C_2 \right) (d_1 - d_2) \right\}. \quad (2) \end{aligned}$$

Here, e is the electronic charge, v is the volume of the trigonal unit cell, d_1 is a measure of distortion polarizability and α_1 is the atomic polarizability of positive ions; d_2 and α_2 are the corresponding quantities for

¹ R. H. Lyddane and K. F. Herzfeld, Phys. Rev. **54**, 846 (1938).

² M. Iona, Phys. Rev. **60**, 822 (1941).

³ E. W. Kellermann, Phil. Trans. Roy. Soc. London **A238**, 513 (1940).

⁴ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

⁵ G. Leibfried, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin 1955), Vol. 7, Part 1, p. 104.

⁶ S. O. Lundqvist, V. Lundström, E. Tenerez, and I. Waller, Arkiv Fysik **15**, 193 (1959).

⁷ J. R. Hardy, Phil. Mag. **4**, 1278 (1959).

⁸ A. M. Karo, J. Chem. Phys. **31**, 1489 (1959); **33**, 7 (1960).

⁹ A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. **119**, 980 (1960).

¹⁰ B. G. Dick and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

¹¹ H. Cole, J. Appl. Phys. **24**, 482 (1953).

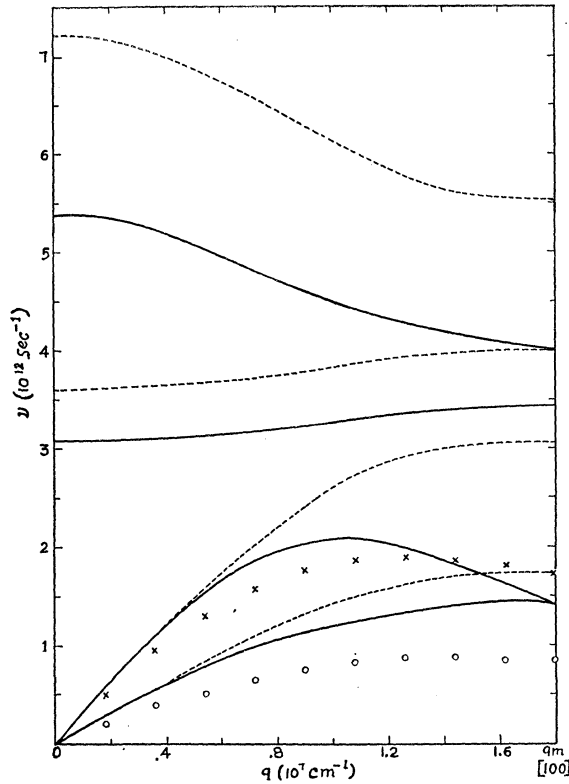


FIG. 1. Dispersion curves in [100] direction in AgCl. Theoretical curves: solid lines, shell model; dashed lines, point ion model. Experimental points: crosses, longitudinal acoustic branch; circles, transverse acoustic branch.

negative ions, S is the short-range force constant for interaction between the shells of ions, S_0 denoting its value when wave vector $q=0$; C_1 and C_2 are Coulomb coefficients, $R_0 - e^2(d_1^2/\alpha_1 + d_2^2/\alpha_2)$ characterizes the overlap force due to relative displacement of ions, and f stands for $1 + C_1/v(\alpha_1 + \alpha_2) + \alpha_1\alpha_2/v_2(C_1^2 - C_2^2)$.

Silver chloride strongly violates the Cauchy relation, and the values of R_0 derived from the compressibility β and the elastic constant c_{11} are very much different. The parameters R_0 , d_1 , and d_2 were fixed from the knowledge of the infrared absorption frequency $(\omega_T)_{q=0}$, the ratio of high and low frequency dielectric constants ϵ/ϵ_0 , the values of polarizabilities, and by estimating the ratio of d_1/d_2 on empirical grounds laid down by Cochran.¹² In cases of rubidium halide crystals where both the ions are polarizable, if the values of d_1 and d_2 given by Cochran and polarizability values due to Pauling¹³ are used, the empirical relation $d_1/d_2 = 2.3\alpha_1/\alpha_2$ roughly holds for each crystal. We can determine the disposable parameters on the basis of the assumption that this relation holds in AgCl, together with the following expressions for the frequencies of the transverse optic

and longitudinal optic modes of wave vector zero:

$$\mu(\omega_T)_{q=0}^2 = R_0 - \frac{e^2}{1 - \frac{4\pi}{3v}(\alpha_1 + \alpha_2)} \left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right) - \frac{4\pi e^2}{3 \left\{ 1 - \frac{4\pi}{3}(\alpha_1 + \alpha_2) \right\} v} \left[-1 + 2(d_2 - d_1) + 2d_1d_2 + \frac{d_1^2}{\alpha_1}\alpha_2 + \frac{d_2^2}{\alpha_2}\alpha_1 \right]. \quad (3a)$$

$$\mu(\omega_L)_{q=0}^2 = \mu(\epsilon_0/\epsilon)(\omega_T)_{q=0}^2 = R_0 - \frac{e^2}{1 + \frac{8\pi}{3v}(\alpha_1 + \alpha_2)} \left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right) + \frac{8\pi e^2}{3 \left\{ 1 + \frac{8\pi}{3}(\alpha_1 + \alpha_2) \right\} v} \left[-1 + 2(d_2 - d_1) + 2d_1d_2 + \frac{d_1^2}{\alpha_1}\alpha_2 + \frac{d_2^2}{\alpha_2}\alpha_1 \right]. \quad (3b)$$

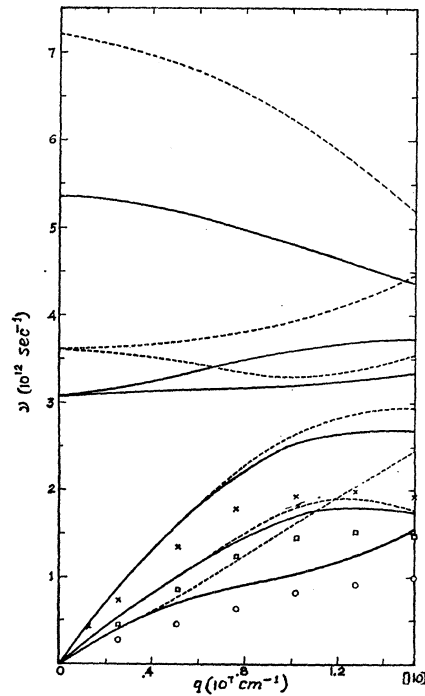


FIG. 2. Dispersion curves in [110] direction in AgCl. Theoretical curves: solid lines, shell model; dashed lines, point ion model. Experimental points: crosses, longitudinal acoustic branch; circles and squares, transverse acoustic branches.

¹² W. Cochran, Phil. Mag. 4, 1082 (1959).

¹³ L. Pauling, Proc. Roy. Soc. London A114, 181 (1927).

TABLE I. Values of the constants used in the calculation.

Values used to fix the disposable parameters were

$$\begin{aligned} r_0 &= 2.772 \text{ \AA} \\ v &= 42.6 \text{ \AA}^3 \\ \alpha_1 &= 0.783 \text{ \AA}^3 \text{ }^a \\ \alpha_2 &= 4.557 \text{ \AA}^3 \text{ }^a \\ (\omega_T)_{q=0} &= 1.94 \cdot 10^{13} / \text{sec} \text{ }^b \\ \epsilon &= 4.04 \text{ }^b \\ \epsilon_0 &= 11.3 \text{ }^b \end{aligned}$$

The disposable parameters are found to be

$$\begin{aligned} R_0 &= 4.55 \text{ d/cm} \\ d_1 &= 0.024 \\ d_2 &= 0.324 \end{aligned}$$

^a K. G. Bansgir and K. S. Iyengar, *Acta Cryst.* **14**, 727 (1961).

^b Reference 4, p. 85.

Here μ is the reduced mass. In Eq. (3b), we have assumed the validity of the Lyddane, Sachs, Teller relation¹⁴⁻¹⁶ that the ratio of the longitudinal and transverse optic frequencies at $q=0$ is equal to $(\epsilon_0/\epsilon)^{1/2}$. The values of the parameters together with the data from which they are evaluated are shown in Table I. The dispersion curves were calculated for the three symmetric directions [100], [110], and [111]. For comparison we have also calculated the dispersion curves on the basis of Kellermann's model with the same R_0 as determined above. The calculated curves are shown in Figs. 1, 2, and 3 together with the experimental data for the acoustic branches.

DISCUSSION

There is a marked discrepancy between the theoretical and experimental dispersion curves. The curves calculated on the basis of the shell model always lie nearer to the experimental points for acoustic branches as compared with the curves obtained using the point ion model. It is found that at long wavelengths the slope of the calculated dispersion curves does not agree with the velocities calculated from the elastic constants. In the case of sodium iodide, Woods, Cochran, and Brockhouse find a nice agreement between the calculations based on the shell model and reliable experimental results from neutron spectrometry. The serious discrepancy between the theory and the experiment found in the case of silver chloride may be attributed to:

(a) Departure from the ionic character and the predominance of the farther neighbor and noncentral

¹⁴ R. H. Lyddane, R. G. Sachs, and E. Teller, *Phys. Rev.* **59**, 673 (1941).

¹⁵ T. H. K. Barron, *Phys. Rev.* **123**, 995 (1961).

¹⁶ A. A. Maradudin and G. H. Weiss, *Phys. Rev.* **123**, 1968 (1961).

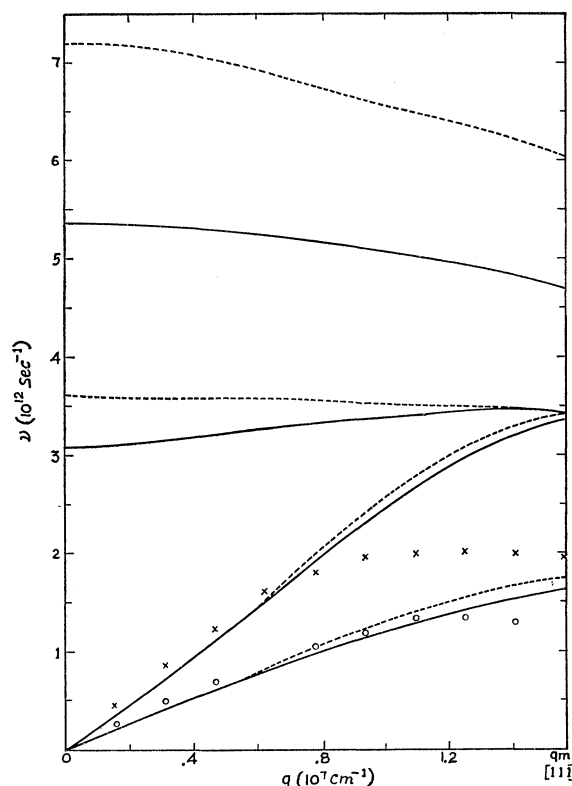


Fig. 3. Dispersion curves in [111] direction in AgCl. Theoretical curves: solid lines, shell model; dashed lines, point ion model. Experimental points: crosses, longitudinal acoustic branch; circles, transverse acoustic branch.

forces which is indicated by the large deviation from the Cauchy relation.

(b) Inaccuracies and approximations involved in the x-ray diffraction method of determining the dispersion curves.

It is therefore felt that a more sophisticated theory is needed to give an adequate theoretical treatment of the lattice dynamics of silver halides and more accurate experimental determinations of dispersion curves using neutron spectrometric techniques will be needed to test the validity of such a theory.

ACKNOWLEDGMENTS

The authors are grateful to Professor K. S. Singwi for helpful discussions and to Professor T. P. Das for correspondence. One of the authors (S.K.J.) is thankful to Council of Scientific and Industrial Research for a financial award.