

per unit volume of bombarded material as long as the energy parameter of the incident ions is low enough so that energy loss by displacement production predominates. From calculations of the local temperatures produced by the ions and comparison between ions having different energies but similar penetrations, it appears that the effect of temperature spikes is unim-

portant for knock-on atoms in silica with energies near 45 kev.

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## Fundamental Lattice Dispersion Frequencies of NaCl and KCl at 82°K

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The infrared dispersion frequencies of NaCl and KCl at 82°K were measured by infrared absorption of thin films and were found to be  $170 \pm 2 \text{ cm}^{-1}$  and  $149 \pm 2 \text{ cm}^{-1}$ , respectively. These values can be compared with those predicted by formulas of Szigeti, Odelevski, Lundqvist, and others relating the dispersion frequency to the elastic and dielectric constants. Good agreement seems to be obtained using the Szigeti formula or a combination of the Lundqvist and Odelevski formulas at low temperatures where anharmonic effects are small.

### I. INTRODUCTION

IN this note experimental values of the fundamental infrared dispersion frequencies of NaCl and KCl at 82°K are reported. Measurements at these low temperatures enable anharmonic effects to be accounted for in a more satisfactory manner. This is important when comparing observed frequencies and those calculated using a formula derived independently by Szigeti<sup>1</sup> and Odelevski<sup>2</sup> which expresses the infrared dispersion frequency in terms of the elastic and dielectric constants. When room-temperature values of these constants are inserted, some deviations are found to occur. These may be attributed partly to anharmonic effects and partly to the simple model used in the derivation of the formula. By comparing observed frequencies at low temperatures with calculated frequencies using low-temperature dielectric and elastic constants, the nature of the deviations may be clarified. Attempts to explain part of the deviations in terms of a more complicated model of dielectric polarization have been made recently by Dick and Overhauser<sup>3</sup> and by Hanlon and Lawson<sup>4</sup> in connection with the related problem of the effective charge. A treatment assuming a more complicated potential involving three-body as well as two-body interactions

has been discussed by Lundqvist.<sup>5</sup> The frequencies calculated using these various proposed formulas will be given after the experimental data is presented.

### II. EXPERIMENTAL

These studies were carried out using a Perkin-Elmer Model 12 monochromator modified for grating operation as suggested by Lord and McCubbin.<sup>6</sup> A grating ruled at the University of Michigan with 320 lines per inch was employed. The resolution was about  $3 \text{ cm}^{-1}$ . The entire optical system was enclosed in a plastic film housing in which air was recirculated through a molecular sieve desiccant in order to reduce the intense water-vapor absorption.

The dispersion frequency was determined by measuring the frequency of maximum absorption of films of NaCl and KCl less than one micron thick which were vacuum evaporated onto quartz plates 0.58 mm thick. These quartz plates were cemented with General Electric 7031 varnish to the sample holder of a metal transmission Dewar having polythene windows. The sample holder was surrounded with a radiation shield. The temperature was measured in a separate experiment using a copper-constantan thermocouple soldered to a sheet of copper which was cemented to a piece of quartz in the sample position. The temperature measured in this manner was 82°K.

The data is shown in Table I along with Barnes and

<sup>1</sup> B. Szigeti, Proc. Roy. Soc. (London) **A204**, 51 (1950). See also M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), p. 111, for further discussion.

<sup>2</sup> V. I. Odelevski, Izvest. Akad. Nauk S.S.S.R. Ser. Fiz. **14**, 232 (1950).

<sup>3</sup> B. G. Dick, Jr., and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

<sup>4</sup> J. E. Hanlon and A. W. Lawson, Phys. Rev. **113**, 472 (1959).

<sup>5</sup> S. O. Lundqvist, Arkiv Fysik **9**, 435 (1955); Arkiv Fysik **12**, 263 (1957).

<sup>6</sup> R. C. Lord and T. K. McCubbin, Jr., J. Opt. Soc. Am. **47**, 689 (1957).

TABLE I. Comparison of calculated and observed frequencies.

	Temperature °K	Frequency in cm <sup>-1</sup> ( $\omega/2\pi c$ )	
		NaCl	KCl
Observed: Barnes and Czerny <sup>a</sup>	room	164	141
Observed: present results	room	164	142
Observed: present results	82	170	149
Calculated: Szigeti formula (1)	82	174 <sup>b,c</sup>	145 <sup>c,d</sup>
	82	176 <sup>b,e</sup>	147 <sup>d,e</sup>
Calculated: Odelevski formula (2)	82	160 <sup>b,c</sup>	140 <sup>c,d</sup>
Calculated: Lundqvist formula (4)	82	186 <sup>b,c</sup>	149 <sup>c,d</sup>
Calculated: Lundqvist-Dick- Overhauser formula (5)	82	185 <sup>b,c</sup>	148 <sup>c,d</sup>
Calculated: Lundqvist-Hanlon- Lawson formula (5)	82	177 <sup>b,c</sup>	142 <sup>c,d</sup>
Calculated: Lundqvist- Odelevski formula (6)	82	171 <sup>b,e</sup>	144 <sup>c,d</sup>

<sup>a</sup> See reference 7.<sup>b</sup> Elastic constants of NaCl from W. C. Overton, Jr., and R. T. Swim, Phys. Rev. **84**, 758 (1951). Index of refraction ( $n^2 = \epsilon_\infty$ ) at one micron from the *American Institute of Physics Handbook* (McGraw-Hill Book Company, New York, 1957), Chap. 6, p. 23. The temperature coefficient of the index of refraction and the lattice constant were sufficiently small and could be neglected. Temperature coefficient of dielectric constant from E. Bretscher, Trans. Faraday Soc. **30**, 684 (1934).<sup>c</sup> Dielectric constants from S. Haussühl, Z. Naturforsch. **12a**, 445 (1957).  
<sup>d</sup> Elastic constants of KCl from M. H. Norwood and C. V. Briscoe, Phys. Rev. **112**, 45 (1958). Index of refraction from the *American Institute of Physics Handbook*, reference b. Temperature coefficient of dielectric constant from A. Eucken and A. Büchner, Z. Physik **27**, 321 (1934).<sup>e</sup> Dielectric constants from A. Eucken and A. Büchner, reference d.

Czerny's measurements.<sup>7</sup> The frequencies calculated using the various proposed formulas are shown in the remaining rows of Table I. These will be discussed in the following section.

### III. DISCUSSION

A connection between the dispersion frequency and the compressibility has been realized for a long time.<sup>1</sup> A relation expressing the dependence and also taking the dielectric polarization into account in a satisfactory manner has been derived by Szigeti assuming central repulsive interactions between nearest neighbors and independently by Odelevski,<sup>2</sup> who also introduced a correction for the interaction between nearest-neighboring anions. The Szigeti formula for NaCl-type lattices is

$$\omega_0^2 = \left( \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right) \frac{6R_0}{\bar{M}\beta}, \quad (1)$$

where  $\omega_0$  is the infrared dispersion frequency,  $\beta$  the compressibility,  $\epsilon_\infty$  and  $\epsilon_0$  the high- and low-frequency dielectric constants,  $R_0$  the nearest-neighbor distance, and  $\bar{M}$  the reduced mass. The frequencies calculated using room-temperature values of the elastic and dielectric constants yield good agreement with experiment for most of the alkali halides. When the correction for nearest-neighboring anion interactions is included,

the Odelevski formula

$$\omega_0^2 = \left( \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right) \left( \frac{6R_0}{\bar{M}\beta} \right) \frac{1}{(1+s)} \quad (2)$$

is obtained, where  $1+s$  is related to the anion-anion repulsive potential. This may be expected to be a function of the anion-anion distance  $R_{aa}$  in the crystal divided by the ionic radius  $R_a$  and can be written as

$$1+s = F(R_{aa}/2R_a). \quad (2a)$$

The functional dependence of  $1+s$  on the dimensionless parameter  $R_{aa}/2R_a$  can be crudely estimated by inserting experimental values of the frequency, elastic constants, and dielectric constants in expression (2). Odelevski found that the  $1+s$  seemed to decrease as the value of  $R_{aa}/2R_a$  increased. Conversely, from a knowledge of  $R_{aa}/2R_a$ , it should be possible to estimate  $1+s$ . For NaCl and KCl, the values of  $R_{aa}/2R_a$  are 1.10 and 1.23, respectively.

Generalizations of the Szigeti formula (1) to take into account some additional aspects of dielectric polarization have been proposed independently by Dick and Overhauser<sup>3</sup> and by Hanlon and Lawson.<sup>4</sup> In their models the ions are considered to consist of cores and massless valence shells which are harmonically bound to each other by a force inversely proportional to the polarizability. Although these two treatments<sup>3,4</sup> differ in some other respects, both lead to an expression for NaCl-type lattices of the form

$$\omega_0^2 = \left( \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right) \left( \frac{6R_0}{\bar{M}\beta} \right) \left( \frac{1}{1+6R_0\lambda/\beta} \right), \quad (3)$$

in which  $\lambda$  is defined as

$$\lambda = \alpha_+/(n_+e)^2 + \alpha_-/(n_-e)^2, \quad (3a)$$

by Dick and Overhauser and as

$$\lambda = f(\alpha_+ + \alpha_-)/(ne)^2, \quad (3b)$$

by Hanlon and Lawson. Here  $\alpha_+$  and  $\alpha_-$  are the cationic and anionic polarizabilities in the crystal, respectively, and  $e$  is the electronic charge. The factors  $n_+$  and  $n_-$  represent the number of shell electrons of the anion and cation as estimated from the static dielectric constants and frequency dependences of the dielectric constant of rare gas atoms which are isoelectronic with the ions. For Na<sup>+</sup>, K<sup>+</sup>, and Cl<sup>-</sup>, the values are found to be 4.8, 8.7, and 8.7. The factor  $n$  is to be regarded as an average number of shell electrons contributing to the dielectric polarization. This is chosen as approximately four corresponding to two  $s$  electrons and two of the six  $p$  electrons. The factor  $f$  appearing in (3b) is evaluated by fitting experimental data to an expression involving the deviation of the ionic charge from an integral value and has been determined to be approximately two. As a result of these differences,

<sup>7</sup> R. B. Barnes and M. Czerny, Z. Physik **72**, 447 (1931).

the correction term  $6R_0\lambda/\beta$  for NaCl and KCl calculated using formula (3b) is about eight times larger than when calculated using formula (3a).<sup>8</sup>

A different approach to the problem was presented by Lundqvist<sup>5</sup> who treated vibrations of cubic ionic lattice in the Heitler-London approximation using a Hamiltonian containing three-body interactions in addition to the two-body central force interactions assumed in the derivation of the Szigeti formula (1). Such a Hamiltonian was employed by Löwdin<sup>9</sup> to treat the cohesive properties of solids. The inclusion of three-body interactions enabled Löwdin to account for the failure of the Cauchy relations for elastic constants  $c_{12}=c_{44}$ , which are satisfied for central forces in crystals in which the ions are located at centers of symmetry. Lundqvist succeeded in expressing the transverse and longitudinal frequencies of long polar vibrations as well as the effective charge in terms of the elastic constants. However, since he was not able to calculate all polarization terms, he also proposed the semi-empirical formula

$$\omega_0^2 = \left( \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right) \left( \frac{6R_0}{\bar{M}} \right) \left( \frac{1}{\beta} + c_{44} - c_{12} \right) \quad (4)$$

to take into account some aspects of this treatment. This formula indicates that in a crystal where the Cauchy relations are not fulfilled, the infrared dispersion frequency will be different from the Szigeti result. Of the few crystals whose elastic constants at low temperatures are known, the case of NaCl and KCl is particularly interesting in that  $c_{44}-c_{12}$  is relatively large for NaCl. In addition, since the anion polarizability is much larger than that of the cation, the dielectric polarization corrections given by the shell model may be expected to behave in the same way for both crystals. The results of the shell model contained in formula (3) may be combined with those of Lundqvist formula (4) giving

$$\omega_0^2 = \left( \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right) \left( \frac{6R_0}{\bar{M}} \right) \left( \frac{1/\beta + c_{44} - c_{12}}{1 + 6R_0\lambda(1/\beta + c_{44} - c_{12})} \right), \quad (5)$$

as suggested by Hanlon and Lawson. As can be seen in Table I, the shell corrections are negligible when

<sup>8</sup> Another estimate of this correction term has been given recently by W. Cochran, *Phil. Mag.* 4, 1082 (1959). This term is evaluated in a semiempirical manner involving the deviation of the ionic charge from an integral value. For NaCl and KCl the estimated correction for this treatment is about equal to that of Hanlon and Lawson (reference 4).

<sup>9</sup> P. O. Löwdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1.

calculated as indicated by Dick and Overhauser, but are significant when calculated as indicated by Hanlon and Lawson. Similarly, the Odelevski formula (2) and the Lundqvist formula (4) may be combined giving

$$\omega_0^2 = \left( \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \right) \left( \frac{6R_0}{\bar{M}} \right) \left( \frac{1/\beta + c_{44} - c_{12}}{1+s} \right). \quad (6)$$

This procedure is not rigorous, but may serve as a rough approximation.

It can be seen from Table I that the experimental data is in good agreement with frequencies calculated using the Szigeti formula (1) or the Lundqvist-Odelevski formula (6). On the other hand, the agreement is not as good using the Lundqvist formula (4) or the Odelevski formula (2) separately. This is because the term  $c_{44}-c_{12}$  in the Lundqvist leads to a positive frequency shift, while the term  $1/(1+s)$  in the Odelevski formula leads to a negative frequency shift of approximately the same magnitude. The value of these individual shifts is greater for NaCl than for KCl. The resulting agreement is quite good considering that many approximations have been made in the derivation of (6). It should be remembered that the evaluation of the anion-anion interaction parameter  $1+s$  is quite crude and was made using room-temperature data. In addition to this, there are other difficulties in accounting for anharmonic effects in the elastic<sup>10</sup> and dielectric<sup>11</sup> constants. Consequently, this agreement should not be regarded as final experimental proof of the Lundqvist-Odelevski formula until results from other materials become available.

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<sup>10</sup> It has been assumed here that use of parameters measured at 82°K would be adequate for evaluating the validity of the proposed formulas. The value of these parameters at this temperature are slightly different from the true harmonic values which are obtained by linearly extrapolating to 0°K in the manner indicated by G. Liebfried and H. Hahn, *Z. Physik* 150, 497 (1958) for the elastic constants.

<sup>11</sup> Higher order terms in both the potential and electric moments contribute to the dielectric constant and are believed to be responsible for the additional structure appearing in the infrared lattice vibration spectrum. Although such contributions decrease with temperature as evidenced by the positive temperature coefficient of the dielectric constant, there is still a residual contribution at low temperatures as indicated by the presence of structure in the infrared reflection spectrum at 80°K. The influence of higher order terms on the dielectric constant of ionic crystals is developed in a systematic way by B. Szigeti, *Proc. Roy. Soc. (London)* A252, 217 (1959).