

THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: ALKALI HALIDES

BY DR. C. S. VENKATESWARAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1. Introduction

IN a recent paper published in these *Proceedings*, the author (1941) has applied the theory of groups to the analysis of the lattice spectrum of rock-salt. The unit cube was assumed to contain four sodium and four chlorine atoms, each group possessing tetrahedral symmetry. The character table for the crystal showed that the twenty-four degrees of freedom of the atoms in the unit cell are distributed among eight modes of triply degenerate vibrations. One of them corresponds to the translations of the cell as a whole. All of them being antisymmetric to the centre of symmetry, are forbidden in the Raman effect. Two of them appear under the symmetry class which is active in the infra-red, while the remaining five are inactive. In the present paper the author proposes to discuss these results in relation to the spectroscopic and specific heat data available for sodium and potassium chloride crystals.

2. Identification of the Lattice Frequencies of Rock-salt

The infra-red spectra.—Barnes and Czerny (1931) and Barnes (1932) have carried out detailed investigations of the infra-red absorption spectra of thin plates of several halides and shown that in every case there are at least two, if not three, absorption maxima. One of them is very pronounced and has been identified by them as the principal vibration frequency of the crystal. The others are relatively weak and in cases in which three are observed, one of them almost coincides with the rest-strahlen frequency reported by Schæfer and Matossi (1930). For rock-salt, Barnes and Czerny have given two absorption frequencies at $61.6 \pm .3 \mu$ (strong) and 40.5μ (weak). These frequencies have to be identified with the two triply degenerate infra-red active vibrations expected from the group-theoretical analysis of the spectrum.

The Raman Spectra.—The Raman spectra of alkali halides do not ordinarily yield any line as was pointed out by Schæfer (1929) and Krishnamurti (1930). Fermi and Rasetti (1931) have subsequently published a remarkable

photograph together with a microphotometric record, of the Raman spectrum of a single crystal of rock-salt taken with 2537 Å radiations of the mercury arc. They have firstly made the observation that the spectrum of rock-salt is very weak, an exposure time of eight hours being required with particularly intense irradiation whereas the strongest Raman line of calcite was recorded in one minute. This extreme feebleness of the spectrum as well as the inability of Schæfer and Krishnamurti to observe the same with 4046 A. U. radiations is in agreement with the conclusion arrived at theoretically by the present author. Secondly, these authors have indicated that the spectrum, in the main, consists of bands, one part lying in the close proximity of the exciting line between 0 and 50 cm.⁻¹ and the other part lying in the region 160 to 365 cm.⁻¹ The region between 50 and 160 cm.⁻¹ shows further, a weak continuum. From their reproduced spectrum, several measurable maxima may be easily identified. While many of them are broad, a few are comparatively sharp. The author has measured this spectrum and obtained the following frequency shifts for the middle points of the maxima.

TABLE I
The Raman Frequencies of Rock-salt

| No. | Centre of maxima in cm. ⁻¹ | Fundamental Frequency in cm. ⁻¹ | Intensity (Estimate) | Remarks | Assignments |
|-----|---------------------------------------|--|----------------------|--------------------------------------|------------------------------|
| 1 | 40 | 20 | Medium | Broad with Continuum up to 2537 A.U. | Lattice Spectrum—4th order |
| 2 | 85 | 42 | Very weak | Very broad | Lattice Spectrum—3rd order |
| 3 | 162 | 81 | Weak | do. | Lattice Spectrum—2nd order |
| 4 | 228 | 114 | Very strong | Fairly sharp | } Lattice Spectrum—1st order |
| 5 | 273 | 136 | Medium | do. | |
| 6 | 299 | 150 | Strong | Broad | |
| 7 | 345 | 173 | do. | do. | |
| 8 | 365 | 183 | do. | do. | |

It has been pointed out by Bhagavantam and Venkatarayudu (1939) that the first overtone of every normal mode is active in the Raman effect of especially the crystals, irrespective of whether the fundamental is permitted or forbidden. This would especially be the case for the five inactive frequencies coming under class F_{2u} in the character table for rock-salt. For, the vibrations of the class F_{2g} are Raman active and those of class F_{2u} are similar to the latter except for the fact that they are antisymmetric to the centre of inversion, while those of F_{2g} are symmetric. The sum of the squares of the

characters of these two classes is therefore identical and accordingly, the overtones of the two classes of vibrations are equally probable. As indicated in Table I, the five frequencies, *viz.*, 228, 273, 299, 345 and 365 may be assigned to the first overtones of the vibrations of class F_{2u} . Besides the above, three bands appear with peak frequencies of 40, 85 and 162 cm^{-1} which are broader than the former. These are explained in what follows.

3. Superlattice Frequencies for Rock-salt

In a paper appearing in the present issue of these *Proceedings*, Sir C. V. Raman has indicated that in addition to the lattice vibrations of the smallest unit cell, the crystal possesses superlattice oscillations of several orders, which in favourable cases could be recorded in the Raman spectra of crystals. As the group theoretical method is equally applicable to assemblages of particles as to atoms and molecules symmetrically distributed in space, we shall analyse the superlattice vibrations by considerations similar to those applied to the unit cell itself. It will be remembered that out of the twenty-four degrees of freedom for the sodium and chlorine atoms in the unit cell, three contribute to the translations of the cell as a whole. When we consider similar motions of equivalent atoms in two neighbouring cells, there are two alternatives, *viz.*, that they may move in the same direction (*i.e.*, in phase) or in opposite directions (*i.e.*, opposite in phase). The symmetry of the crystal suggests that eight neighbouring unit cells should be treated at one time, which together have all the elements of symmetry possessed by the unit cell itself. The larger cell thus chosen (or the superlattice cell) is eight-fold in size and contents of the unit cell, and forms a face-centred cubic lattice. The problem of analysing the twenty-four degrees of freedom of translation of this larger unit thus becomes identical with the case of rock-salt which we have already considered. In general, it will be seen that there will be eight triply degenerate vibrations of which one alone is to be attributed to the translations of the unit as a whole. The remaining seven frequencies may be said to form the lattice spectrum of the second order. Taking thirty-two atoms (of Na and Cl) in this greater cell, the group theoretical analysis may be carried out rigorously. Simple considerations, however, lead to the ultimate result that each of the seven normal modes of the primary cell, while retaining their nature and frequency nearly the same, become each eight-fold, with the phase of vibration in different cells being the same or opposite as the case may be. In addition, we will get seven discrete frequencies characteristic of the superlattice of the first order. We can now repeat the process to superlattices of higher orders, each successive step yielding seven triply degenerate discrete frequencies together with three degrees of translation as a whole.

The effect of the superlattice vibrations on the normal modes of the smaller unit cell is to multiply each of the latter several-fold. Each line in a crystal thus theoretically represents a group of nearly identical frequencies and should accordingly appear broadened. This is in accordance with the experimental fact observed in several cases that the lattice Raman lines are generally broader than the internal vibrations of molecules or radicals (Venkateswaran, 1938); the latter remain comparatively unaffected by the surroundings due to the much greater strength and stability of the chemical bond involved.

It is common knowledge that the possible frequencies of an atomic group are the closer together, the greater the atomic masses and the smaller the forces between them. We should accordingly expect each group of superlattice vibrations to consist of a fairly narrow band of frequencies. Three Raman bands with their centres at 162, 85 and 40 cm.^{-1} appearing in the spectrum of rock-salt (Table I) may therefore be taken as representative of the lattice spectra of the second, third and fourth orders. As in the case of the lattice vibrations of the first order and for the same reason, these frequencies should be taken as the octaves; the fundamentals being respectively 81, 42 and 20 cm.^{-1}

4. *The Specific Heat of Rock-salt*

It is obvious from the foregoing discussion that in calculating the thermal energy of the crystal, Einstein functions corresponding to the seven triply degenerate frequencies of each order of the lattice spectra should be taken into account, as these spectral lines are essentially discrete in character. As there are four NaCl groups in the unit cell, the contribution to the molar specific heat arising from the lattice vibrations of the first order is

$$\frac{1}{4} \Sigma_1^7 3 R E (\theta_1)$$

where the θ_1 s are given by the frequencies and the temperature of observation. The second order lattice spectrum will yield

$$\frac{1}{4 \times 8} \Sigma_1^7 3 R E (\theta_2),$$

the third,

$$\frac{1}{4 \times 8 \times 8} \Sigma_1^7 3 R E (\theta_3),$$

and so forth. Hence,

$$C_v (\text{molar}) = \frac{1}{4} \Sigma_1^7 3 R E (\theta_1) + \frac{1}{4 \times 8} \Sigma_1^7 3 R E (\theta_2) \\ + \frac{1}{4 \times 8 \times 8} \Sigma_1^7 3 R E (\theta_3) + \text{etc.}$$

TABLE II
Table of Specific Heats of Rock-salt

| Temp. in Degrees Absolute | θ_1 VALUES | | | | | | | | $\frac{1}{2} \sum \theta_1$ | θ_2 118 | θ_3 54 | θ_4 28 | θ_5 18 | Total C_p (molar) Calculated | C_p^* Experimental |
|---------------------------|-------------------|-------|-------|-------|-------|-------|-------|-------|-----------------------------|-------------------|------------------|------------------|------------------|--------------------------------|----------------------|
| | 229 | 354 | 164 | 196 | 214 | 247 | 262 | | | | | | | | |
| 10 | .008 | .. | .112 | .032 | .0151 | .004 | .0012 | .0431 | .0014 | .0216 | .0110 | .0020 | .036 | .04 | |
| 25 | .128 | .. | .369 | .149 | .085 | .028 | .018 | .1943 | .1248 | .0917 | .0173 | .0024 | .28 | .32 | |
| 30 | .166 | .0062 | .771 | .374 | .241 | .107 | .074 | .434 | .2786 | .1119 | .0184 | .0024 | .605 | .58 | |
| 40 | .637 | .0677 | 1.714 | 1.081 | .813 | .474 | .369 | 1.289 | .4100 | .1251 | .0189 | .0025 | .99 | .96 | |
| 50 | 1.300 | .257 | 2.610 | 1.900 | 1.544 | 1.054 | .856 | 2.383 | .6606 | .1403 | .0195 | .0025 | 2.10 | 2.04 | |
| 60 | 2.011 | .571 | 3.326 | 2.630 | 2.260 | 1.697 | 1.485 | 3.50 | .8356 | .1481 | .0198 | .0025 | 3.40 | 3.53 | |
| 70 | 2.609 | .986 | 3.850 | 3.218 | 2.89 | 2.262 | 2.077 | 4.48 | .9819 | .1523 | .0200 | .0025 | 4.70 | 5.2 | |
| 80 | 3.126 | 1.431 | 4.258 | 3.709 | 3.380 | 2.840 | 2.618 | 5.345 | 1.031 | .155 | .0201 | .0025 | 5.70 | 6.3 | |
| 100 | 3.902 | 2.30 | 4.782 | 4.366 | 4.121 | 3.673 | 3.469 | 6.65 | 1.109 | .1568 | .0202 | .0025 | 6.7 | 7.0 | |
| 120 | 4.434 | 3.019 | 5.116 | 4.794 | 4.591 | 4.230 | 4.066 | 7.588 | 1.160 | .1590 | .0202 | .0025 | 7.93 | 8.28 | |
| 140 | 4.782 | 3.587 | 5.316 | 5.071 | 4.924 | 4.591 | 4.479 | 8.191 | 1.224 | .1601 | .0202 | .0025 | 8.948 | 9.08 | |
| 160 | 5.035 | 4.03 | 5.467 | 5.26 | 5.139 | 4.899 | 4.788 | 8.66 | 1.228 | .1608 | .0203 | .0025 | 9.6 | 9.64 | |
| 180 | 5.208 | 4.40 | 5.560 | 5.410 | 5.290 | 5.043 | 5.012 | 8.98 | 1.254 | .1614 | .0203 | .0025 | 10.09 | 10.05 | |
| 200 | 5.340 | 4.61 | 5.632 | 5.500 | 5.426 | 5.241 | 5.173 | 9.335 | 1.257 | .1616 | .0203 | .0025 | 10.42 | 10.38 | |
| 235 | 5.504 | 4.954 | 5.718 | 5.622 | 5.67 | 5.442 | 5.400 | 9.58 | 1.266 | .1618 | .0203 | .0026 | 10.78 | 10.67 | |
| 300 | 5.815 | 5.30 | 5.885 | 5.856 | 5.833 | 5.793 | 5.774 | 10.17 | 1.276 | .1620 | .0204 | .0026 | 11.04 | 11.10 | |
| Maximum | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 10.5 | 1.286 | .1624 | .0204 | .0026 | 11.54 | 11.60 | |
| | | | | | | | | | 1.3125 | .1643 | .0205 | .0027 | 12 | .. | |

* These experimental values are those obtained by Nernst and given in *Landolt-Börnstein Tabellen*. They show small variations from those given in the *Handbüch der Experimental Physik* and in the *International Critical Tables* and have therefore to be considered as not of a high order of accuracy.

From the infra-red and Raman spectra we have identified the following seven frequencies for the first order lattice spectrum of rock-salt: 161, 247, 114, 136, 150, 173 and 183 cm^{-1} . These give the θ_{1s} . As there is at present no spectroscopic method of ascertaining all the seven frequencies belonging to higher orders, it will be assumed, as a first approximation, that they may each be represented by a single frequency for the purpose of the calculation of specific heat. The three Raman frequencies given in Table I, viz., 81, 38 (instead of 42) and 20 cm^{-1} are chosen for θ_2 , θ_3 and θ_4 . In addition, 13 cm^{-1} is chosen as the representative lattice frequency of the fifth order from a perusal of the specific heat data at 20° absolute.

5. Table of Specific Heats for Rock-salt

Assuming the above values of frequencies, Table II exhibiting the specific heats is prepared for rock-salt for the temperature range of 10° – 300° T. The experimental values of specific heat are taken from Landolt and Börnstein Tabellen, and corrected for the work done for the expansion of the crystal by making use of the relation $C_p - C_v = 2.7 \times C_p^2 \times T \times 10^{-5}$ per gram atom, given in the *Handbuch der Experimental Physik*.

6. The Specific Heat of Sylvine

Exhaustive data for the specific heat of potassium chloride are given by Keesom and Clark (1935) from 3° to 17° T. and by Southard and Nelson (1933) from 17° to 285° T. and are therefore, particularly suitable for the verification of the above expression for the specific heat of crystals. The two infra-red active frequencies recorded for this crystal by Barnes and Czerny are 141 and 212 cm^{-1} corresponding to the absorption maxima at 70.7 μ (strong) and, 47 μ (weak). Unfortunately the Raman spectrum of sylvine has not been recorded as in the case of rock-salt. However, the remaining frequencies could be deduced from those of the latter on the assumption that

$\nu \approx 2\pi \sqrt{\frac{f}{\mu}}$. Since the force between K^+ and Cl^- is Coulombian, it may be varies as the square of the distance between the atoms, i.e., half the edge of the unit cube. This gives the relation

$$\frac{\nu_{\text{KCl}}}{\nu_{\text{NaCl}}} = \sqrt{\frac{(2.814)^2 \times 13.95}{(3.14)^2 \times 18.61}} = 0.78$$

The corresponding ratio of the infra-red active frequencies being 0.86, it may without serious error be assumed that the average ratio of 0.78 may be used for the purpose of calculation. The frequencies of the lattice spectrum of the first order for KCl thus obtained are $\nu_1 = 141$, $\nu_2 = 212$, $\nu_3 = 89$, $\nu_4 = 107$, $\nu_5 = 116$, $\nu_6 = 135$ and $\nu_7 = 143 \text{ cm}^{-1}$. The representative frequencies chosen

TABLE
The Specific

| Temp.* in Degrees Absolute | θ_1 VALUES | | | | | | | $\frac{1}{4} \Sigma \theta_1$ |
|-------------------------------------|-------------------|-----|-------|-----|-----|-----|-----|-------------------------------|
| | 202 | 304 | 128 | 153 | 167 | 194 | 205 | |
| 2.99 | .. | .. | .. | .. | .. | .. | .. | .. |
| 3.52 | .. | .. | .. | .. | .. | .. | .. | .. |
| 4.01 | .. | .. | .. | .. | .. | .. | .. | .. |
| 4.6 | .. | .. | .. | .. | .. | .. | .. | .. |
| 5.14 | .. | .. | .. | .. | .. | .. | .. | .. |
| 5.72 | .. | .. | .. | .. | .. | .. | .. | .. |
| 6.52 | .. | .. | .. | .. | .. | .. | .. | .. |
| 7.65 | .. | .. | .. | .. | .. | .. | .. | .. |
| 8 | .. | .. | .. | .. | .. | .. | .. | .. |
| 9.23 | .. | .. | .. | .. | .. | .. | .. | .. |
| 10.06 | .. | .. | ·0027 | .. | .. | .. | .. | ·0007 |

* These temperatures were chosen out of the numerous

TABLE

| Temp. T° C. | 202 | 304 | 128 | 153 | 167 | 194 | 205 |
|-------------|-------|-------|-------|-------|-------|-------|-------|
| 13.55 | .. | .. | ·0435 | ·0093 | ·0041 | ·0035 | .. |
| 14.73 | ·0013 | .. | ·0776 | ·0196 | ·0093 | ·0079 | ·0011 |
| 16.67 | ·0048 | .. | ·166 | ·051 | ·027 | ·0237 | ·0043 |
| 21.21 | ·0392 | .. | ·521 | ·221 | ·138 | ·053 | ·034 |
| 32.41 | ·456 | ·044 | 1.88 | 1.277 | ·932 | ·546 | ·430 |
| 39.86 | ·974 | ·168 | 2.701 | 1.97 | 1.641 | 1.118 | ·932 |
| 49.27 | 1.715 | ·466 | 3.502 | 2.815 | 2.482 | 1.877 | 1.660 |
| 59.61 | 2.564 | ·956 | 4.120 | 3.531 | 3.218 | 2.616 | 2.414 |
| 69.92 | 3.086 | 1.493 | 4.552 | 3.916 | 3.772 | 3.308 | 2.946 |
| 79.11 | 3.557 | 1.970 | 4.819 | 4.396 | 4.176 | 3.626 | 3.517 |
| 89.28 | 3.957 | 2.458 | 5.041 | 4.686 | 4.490 | 4.096 | 3.902 |
| 101.31 | 4.312 | 2.954 | 5.222 | 4.942 | 4.770 | 4.433 | 4.285 |
| 121.41 | 4.751 | 3.626 | 5.442 | 5.237 | 5.104 | 4.845 | 4.719 |
| 141.17 | 5.036 | 4.108 | 5.568 | 5.405 | 5.303 | 5.104 | 5.011 |
| 163.45 | 5.244 | 4.536 | 5.662 | 5.534 | 5.467 | 5.303 | 5.232 |
| 179.76 | 5.370 | 4.718 | 5.717 | 5.608 | 5.533 | 5.425 | 5.353 |
| 201.32 | 5.483 | 4.942 | 5.750 | 5.676 | 5.624 | 5.602 | 5.476 |
| 240.7 | 5.645 | 5.219 | 5.816 | 5.756 | 5.724 | 5.648 | 5.608 |
| 284.7 | 5.711 | 5.279 | 5.826 | 5.813 | 5.788 | 5.732 | 5.704 |
| Maximum | 6 | 6 | 6 | 6 | 6 | 6 | 6 |

III

Heats of Sylvine

| θ_2 80 | θ_3 42 | θ_4 22 | θ_5 14 | $\theta_6 + \theta_7$ etc. | Total C_v (molar) Calculated | C_v Experi- mental |
|------------------|------------------|------------------|------------------|-------------------------------|--------------------------------------|----------------------------|
| .. | .. | ·00072 | ·00052 | ·00032 | ·0016 | ·00206 |
| .. | ·00024 | ·00156 | ·00078 | ·00032 | ·0029 | ·00338 |
| .. | ·00074 | ·00256 | ·00101 | ·00032 | ·0046 | ·00470 |
| .. | ·00206 | ·00397 | ·00124 | ·00032 | ·0076 | ·00724 |
| .. | ·00315 | ·00534 | ·00142 | ·00032 | ·0102 | ·0101 |
| · | ·0057 | ·0067 | ·0016 | ·00032 | ·0143 | ·0145 |
| ·0009 | ·0108 | ·0085 | ·0017 | ·00032 | ·0219 | ·0191 |
| ·0041 | ·0204 | ·0106 | ·0019 | ·0003 | ·0373 | ·0368 |
| ·0058 | ·0238 | ·0111 | ·0020 | ·0003 | ·0430 | ·0460 |
| ·0169 | ·0391 | ·0129 | ·0021 | ·0003 | ·0710 | ·0620 |
| ·0291 | ·0449 | ·0138 | ·0022 | ·0003 | ·0907 | ·0840 |

data available, at regular intervals.

III (Contd.)

| $\frac{1}{4} \Sigma \theta_1$ | θ_2 80 | θ_3 42 | θ_4 22 | θ_5 14 | C_v Calcu- lated | C_v Ob- served |
|-------------------------------|------------------|------------------|------------------|------------------|--------------------------|------------------------|
| ·0151 | ·1248 | ·0773 | ·0164 | ·0023 | ·236 | ·238 |
| ·0292 | ·1697 | ·0862 | ·0169 | ·0024 | ·304 | ·310 |
| ·0692 | ·2511 | ·0984 | ·0176 | ·0024 | ·439 | ·438 |
| ·252 | ·4477 | ·1186 | ·0186 | ·0025 | ·839 | ·842 |
| 1·391 | ·8024 | ·1417 | ·0196 | ·0025 | 2·357 | 2·358 |
| 2·376 | ·9410 | ·1488 | ·0199 | ·0025 | 3·488 | 3·52 |
| 3·629 | 1·051 | ·1533 | ·0200 | ·0025 | 4·856 | 4·91 |
| 4·855 | 1·122 | ·1563 | ·0201 | ·0025 | 6·156 | 6·30 |
| 5·768 | 1·168 | ·1581 | ·0202 | ·0025 | 7·117 | 7·33 |
| 6·515 | 1·198 | ·1591 | ·0203 | ·0026 | 7·895 | 8·12 |
| 7·205 | 1·222 | ·1599 | ·0203 | ·0026 | 8·610 | 8·77 |
| 7·729 | 1·237 | ·161 | ·0204 | ·0026 | 9·150 | 9·35 |
| 8·431 | 1·256 | ·161 | ·0204 | ·0026 | 9·871 | 10·04 |
| 8·884 | 1·268 | ·161 | ·0205 | ·0026 | 10·336 | 10·60 |
| 9·245 | 1·275 | ·162 | ·0205 | ·0026 | 10·705 | 10·96 |
| 9·431 | 1·280 | ·162 | ·0205 | ·0026 | 10·90 | 11·13 |
| 9·638 | 1·283 | ·162 | ·0205 | ·0026 | 11·106 | 11·32 |
| 9·854 | 1·290 | ·162 | ·0205 | ·0026 | 11·329 | 11·58 |
| 9·963 | 1·295 | ·162 | ·0205 | ·0026 | 11·443 | 11·72 |
| 10·5 | 1·3125 | ·1643 | ·0205 | ·0027 | 12 | .. |

for the second to the fifth orders are respectively 56, 29, 15, and 10 cm.^{-1} . It will be noticed that these latter frequencies for the two salts are nearly in the ratio 1 : 0.78. The lattice spectra of orders higher than five are assumed to make their maximum contribution of .00032 calories per gm. mol. per degree. $C_p - C_v$ for sylvine is given by $2 C_p^2 \times 10^{-5}$ calories per gram atom.

7. Significance of the Results

The failure of Debye's theory of specific heat in these two cases is well known. Following Born's theory, Blackman (1935), Kellermann (1941) and others have sought to explain this latter as due to a variation of the characteristic temperature of the crystals. Keesom and Clark (1935) have pointed out that this variation of characteristic temperature is anomalous in the case of sylvine at low temperatures. Important deviations from the Debye formulæ in the case of rock-salt have been reported by Clausius, Goldman and Perlick (1934). It will be seen from Tables II and III that the values of specific heats calculated on the basis of the spectroscopic facts agree reasonably well with the observed data for both the crystals throughout the whole range of temperature, which in the case of sylvine nearly approaches the absolute zero. The investigation thus clearly demonstrates that the present approach to the theory of specific heat should replace the earlier ones due to Debye, Born and others.

An examination of the contributions to the thermal energy of each of the orders of the lattice spectra reveals interesting features, giving an insight into the distribution of the thermal energy at various temperatures. The contributions by orders higher than five become significant only at extremely low temperatures (less than 5°T.), the contribution of the first two orders of spectra then vanishing. As the temperature is raised to 50° for rock-salt and 40° for sylvine, the fifth and the fourth orders attain their maximum value of .0026 and 0.205 respectively. The contributions of the second and the third orders increase less quickly, becoming the maximum at about 100°T. At room temperature, practically 6/7 of the total energy (*i.e.*, 10.5 out of 12) is due to the lattice vibrations of the first order. The whole of the thermal energy of the crystal can be represented by considering a superlattice cell of edge length $50 \times 10^{-8} \text{ cm.}$

In conclusion the author wishes to thank Sir C. V. Raman for his keen and abiding interest in the work.

Summary

The character table for rock-salt derived from the theory of groups applied to the unit cell containing four atoms of sodium and four atoms of chlorine,

gives eight triply degenerate normal modes of vibrations. One of them corresponds to the translations of the cell as a whole, two are infra-red active and Raman inactive, and five are inactive both in the Raman and the infra-red. The overtones of the latter five modes should however, appear in the Raman effect. This analysis of the vibration spectrum of the rock-salt structure gives a complete explanation of the infra-red absorption spectra of the alkali halides observed by Barnes and the Raman spectrum of rock-salt obtained by Fermi and Rasetti. The two infra-red absorption maxima at 161 and 247 cm^{-1} are taken as the two fundamental frequencies and the five frequencies at 228, 272, 298, 346 and 366 cm^{-1} identified from the Raman spectrum reproduced by Fermi and Rasetti, are assumed to be the first overtones of the remaining five frequencies of the lattice. The latter also shows three broad bands with peak frequencies of 81, 42 and 20 cm^{-1} . These are shown to be the octaves of the superlattice frequencies of the second, third and fourth orders.

A general expression is derived for the thermal energy of cubic crystals of the rock-salt type in terms of the lattice and superlattice frequencies. The expression is evaluated for rock-salt and sylvine for a wide range of temperatures which in the case of sylvine is 3° to 285° absolute. Two of the lattice frequencies for sylvine are given by the infra-red spectrum and the others are deduced from those of rock-salt. The calculated values in either case are in reasonable agreement with experimental data, showing that the thermal energy of crystalline solids is satisfactorily explained on the basis of the ideas indicated in the foregoing paper by Sir C. V. Raman and developed further in the present communication.

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