On the Structure and Interpretation of the Infrared Absorption Spectra of Crystals

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An experimental and theoretical investigation of the absorption spectrum of MgO in the near infrared is reported. Part A is devoted to the experimental results, which were obtained by use of a rocksalt spectrometer. They show that the fundamental absorption is accompanied by a great deal of secondary structure. In Part B an interpretation of the results of A is undertaken on the basis of a quantum-mechanical treatment of anharmonic potential forces. On this basis, it is shown that a cubic crystal of the MgO type should not possess but a single near infrared absorption as previous calculations had indicated, but should possess an extremely complicated secondary structure. In Part C the possibilities of obtaining a quantitative correlation between experiment and theory are discussed and it is concluded that the former must be made the object of additional refinements.

INTRODUCTION*

IN the work to be described in the following paper, both experimental and theoretical investigations were carried on and are published here simultaneously. In order to keep them somewhat apart, we have decided to present the details of the first in Part A and those of the second in Part B, and to present a general account of their connection in the introduction and the conclusion.

As a result of conclusions drawn from the classical theory of crystal structure of Madelung, Born, von Kármán and other workers in the field,[1] it was generally believed until the past few years, that a cubic crystal possessed but one absorption frequency, corresponding to a motion in which like ions move together and unlike ions are 180° out of phase. For the alkali-halide crystals, this fundamental should be expected to vary inversely as the effective mass $m_1m_2/(m_1+m_2)$ of the two ions, and in fact, it was found that those corresponding to LiF, NaCl and KBr are at wave-lengths 32.6, 61.1 and 83.3μ, respectively. It is as a result of this fact that these crystals show a large transparency in the near infrared, KI being transparent as far out as 33μ.

Because of the supposed simplicity of their spectra, it was concluded that they should be ideal substances on which to test the classical theory of dispersion in the infrared, and in 1930 Czerny[2] presented the results of his attempt to use NaCl for this purpose. He reported the presence of a weak secondary maximum of absorption upon the short wave-length side of the fundamental. A similar result was obtained for KCl. In a second paper[3] it was shown that these crystals possessed not one but several secondary maxima, giving rise to absorption curves which differed considerably from those predicted on the basis of the previously mentioned theories, and only by using a layer of crystal 0.17μ thick were the authors able to obtain a curve of the theoretical type. Fig. 1, taken directly from the above paper shows the type of curve obtained for NaCl. Continuing this work, Barnes[4] showed that some fifteen crystals of this type possessed similar secondary maxima. At this time a good deal of structure was observed, but since the resolving power was very low, the work published was to be regarded as being essentially envelopes of possible additional structure.

Following this, Born and Blackman[5] sought an explanation of these results on the basis of anharmonic terms in the potential function of interaction of the lattice atoms, and handled the problem of a linear diatomic chain along classical mechanical lines. Their results showed that such terms would give rise to additional maxima, one on the short wave-length side of the fundamental

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[1] E. Madelung, Nachr. Gött. M. P. Klasse, March 1909 and Jan. 1910; Physik. Zeits. 11, 898 (1910); M. Born and Th. von Kármán, Physik. Zeits. 13, 297 (1912); M. Born and M. Goeppert-Mayer, *Geiger-Scheel Handbuch der Physik*, Vol. 24b.

[2] M. Czerny, Zeits. f. Physik 65, 600 (1930).

[3] R. Bowling Barnes and M. Czerny, Zeits. f. Physik 72, 447 (1931).

[4] R. Bowling Barnes, Zeits. f. Physik 75, 723 (1932).

[5] M. Born and M. Blackman, Zeits. f. Physik 82, 551 (1933); M. Blackman, Zeits. f. Physik 86, 421 (1933).
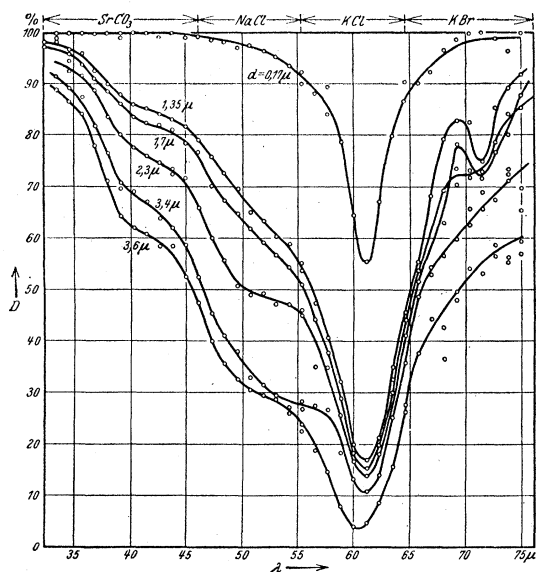
FIG. 1. Transmission of thin films of NaCl. (Barnes and Czerny.)

and one on the long wave-length side (the former agreeing reasonably well with the experimental values), so that a qualitative check of the validity of this assumption was obtained.

When good specimens of MgO became available, it was decided that a more thorough investigation of the structure of the absorption spectrum of a cubic crystal could be carried through than had been done previously.[6] This crystal is particularly suitable for near infrared investigation since its spectrum lies closer to the visible than does that of any other cubic crystal, and, moreover, it may be obtained in perfect crystalline as well as powdered form. Under these favorable circumstances an investigation was carried through and the principal experimental results may be tabulated as follows:

1. The absorption spectra of (a) powdered, (b) evaporated films and (c) cleavage plates of crystalline MgO are identical as far as maxima are concerned as long as the particle size of the powder is not such as to give rise to anomalous scattering or refracting effects.

2. The fine structure is reproducible on various thicknesses of material and indicates that there are more than forty absorption peaks on the near infrared side of the largest absorption peak when the crystal is at room temperature.

3. The fundamental absorption line does not lie at 14.2μ as has been previously supposed, but is further in the infrared.

[6] R. Bowling Barnes and R. Robert Brattain, Phys. Rev. 47, 416 (1935).

From this work, it was concluded that the results of Born and Blackman were not general enough to handle the case at hand and another approach to the theoretical side of the problem was undertaken. For this purpose it was assumed that the crystal could be handled as a three-dimensional quantum-mechanical system of interacting particles arranged at the mesh points of the NaCl type lattice and a general potential function of interaction was set up using only the group theoretical restrictions required by symmetry. This is to be contrasted with the type of potential function employed in the Born treatment of ionic crystals in which central forces are assumed between particles. The recent high precision work on the elastic coefficients by Quimby, Balamuth, Rose and Durand[7] indicates conclusively that the Cauchy-Poisson relations are not valid, the c_{12} of Voigt being only about half of the corresponding c_{44} for divalent ionic crystals of the type of MgO, while for monovalent crystals of the type of NaCl, c_{12} is ten percent larger than c_{44} in the neighborhood of absolute zero. Since equality of c_{12} and c_{44} was essential for the validity of the Born theory these facts point to a basic lack of generality in it and for this reason it is found necessary, for the time being, to employ a phenomenological description of potential fields in much the same way that is done in handling molecular potential functions.

By employing the anharmonic terms as perturbations, normal coordinates were introduced so as to afford a suitable system of quantum-mechanical variables and from these the first-order energy spectrum arising from the harmonic terms was determined. It is of course identical with the classical energy spectrum and for the diatomic face-centered lattice is included inside of two zones, in each of which there are three branches corresponding to the three directions of polarization of waves. The perturbing terms were then regarded as being such as to alter the selection rules for transitions without appreciably affecting the energy spectrum, and it was found that this effect can be regarded as important only for transitions in which two waves whose momentum vectors lie in the neighborhood of the sur-

[7] L. Balamuth, Phys. Rev. 45, 721 (1934); we are deeply indebted to these people for the use of results of their work that is as yet unpublished.
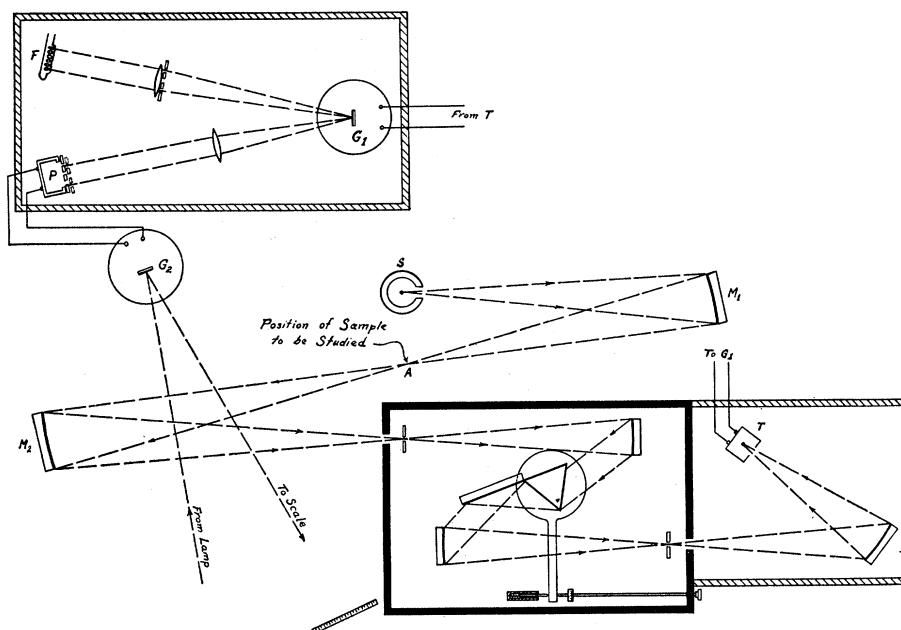
Fig. 2. Rocksalt spectrometer and amplifier.

faces of the zones and at regions near these surfaces where the energy gradient is zero, are simultaneously excited, since in this case the integrated effect of many insignificant absorption lines is appreciable in the vicinity of one wave-length. In this case both the sum and difference energies of the two waves will give rise to absorption peaks. The conclusions drawn were as follows:

1. The first-order anharmonic terms give rise to a large number of absorption lines of types to be described in a later section.

2. Any attempt at determining correlations between the experiment and theory at this stage of the development of the former is premature since the conditions under which the theory is presented are such that they will be realized best at low temperatures and it is only when such experiments are carried out that correlations may be sought for. There is no reason for expecting that such correlations do not exist, however.

PART A. EXPERIMENTAL SECTION. THE NEAR INFRARED SPECTRUM OF MgO

In order to be able to obtain better experimental results, a cubic crystal was sought whose fundamental corresponded to a wave-length in the near infrared where higher resolution could be employed. Consequently, the authors were

pleased to learn that The Norton Company, using an electric furnace which operated at a temperature above 2500°C were able to fuse MgO, and prepare large flawless single crystals from the molten material. The samples obtained possessed almost every property which would make them suited for this purpose. They were clear, hard, easy to cleave (down to 0.075 mm), were not affected by water, were obtainable in sizes up to $3 \times 4 \times 1$ cm, possessed almost perfect cleavage planes so that no polishing or grinding was necessary, were very tough and resistant to acids and heat, and the material had its fundamental in the near infrared. Both transmission and reflection measurements were made throughout the region from 1μ to 15.6μ. Previous x-ray investigations have shown that MgO crystals are cubic in their structure being of the NaCl or face-centered type.[8]

§1. Apparatus and procedure

For this investigation in which it was desired to be able to study the absorption of the samples throughout the near infrared, the experimental set-up shown in Fig. 2 proved very satisfactory. The radiation from a hot platinum strip (S),

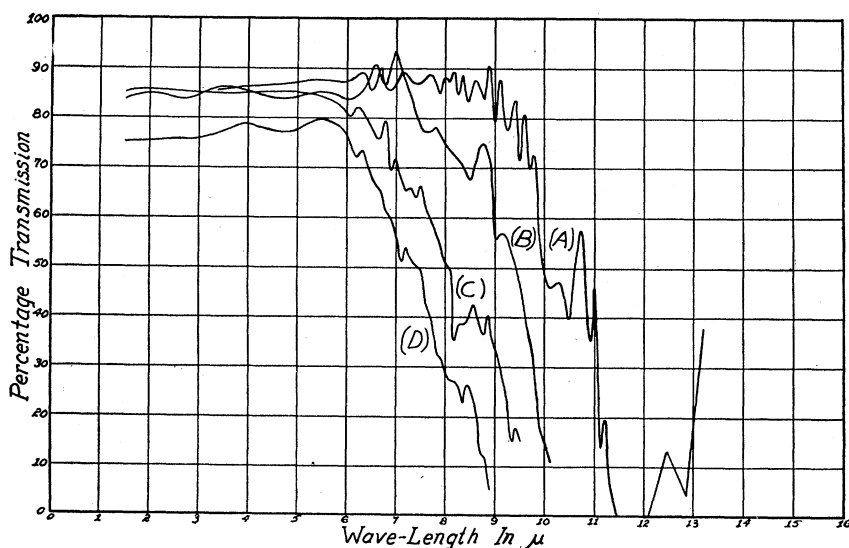[8] P. P. Ewald and C. Hermann, *Structurbericht* (Leipzig, 1931).

FIG. 3. Transmissions of cleaved plates of MgO. (a) 0.12 mm; (b) 0.47 mm; (c) 1.75 mm;
(d) 3.05 mm.

which was operated from a 22-volt transformer at a current of 20 amperes, was brought to a focus upon the sample by M_1, and after diverging was focused upon the slit of the spectrometer by the mirror M_2. After emerging from the spectrometer which contained a rocksalt prism and a Wadsworth mirror, this radiation was then concentrated upon a Moll linear thermopile. The latter was connected as shown to an original Moll galvanometer (55 ohms internal resistance), the deflections of which were then amplified by means of the photoelectric relay[9] system. The filament F (4 volts, 4 amperes) was focused by the two lenses over the galvanometer mirror to the photoelectric cell, P, which was a selenium cell of the blocking layer type and had an active surface 3×3 cm. The use of the grids as shown increased the sensitivity threefold. An H.S. Leeds and Northrup 16.4-ohm galvanometer was then used to read the currents produced by the photoelectric cell. After taking extreme precautions to avoid any unsteadiness due to fluctuations in the temperature and pressure of the room, the relay system was set and used at a magnification of about 150-fold. The thermocouple, although not of the vacuum type, was placed in an evacuated container in order to avoid the pressure effects

referred to just above. The scale distance was 2.5 meters.

The calibration of the instrument was determined empirically, by mapping the positions on the scale of many well-known sharp bands such as those of H_2O, the emission and absorption bands of CO_2, the reflection bands of quartz, the absorption bands of benzene, toluene and cyclohexane. Points were thus obtained at rather close intervals out to 15.2μ. The transmission curves obtained were accurately reproducible as far out as the measurements were made. The authors realize that the extreme wave-lengths may be uncertain, due to errors in the calibration curve, by as much as $\pm 0.05\mu$. The calibration curve was checked frequently, and aside from a shift back and forth from time to time of less than $\pm 0.01\mu$ due to changes in the temperature of the prism, was found to be constant.

At the position marked A in Fig. 2, a sliding tower was built which enabled the sample to be moved in and out of the light beam, several measurements being taken in each of these two positions. The curves plotted below are in every case the actual percentage transmissions as measured, no corrections having been made for the losses of energy at the two surfaces of the crystal. The accuracy of the curves with regard to the ordinates is about ± 2 percent.

[9] R. Bowling Barnes and F. Matossi, Zeits. f. Physik 76, 24 (1932); L. Bergmann, Physik. Zeits. 32, 688 (1931).
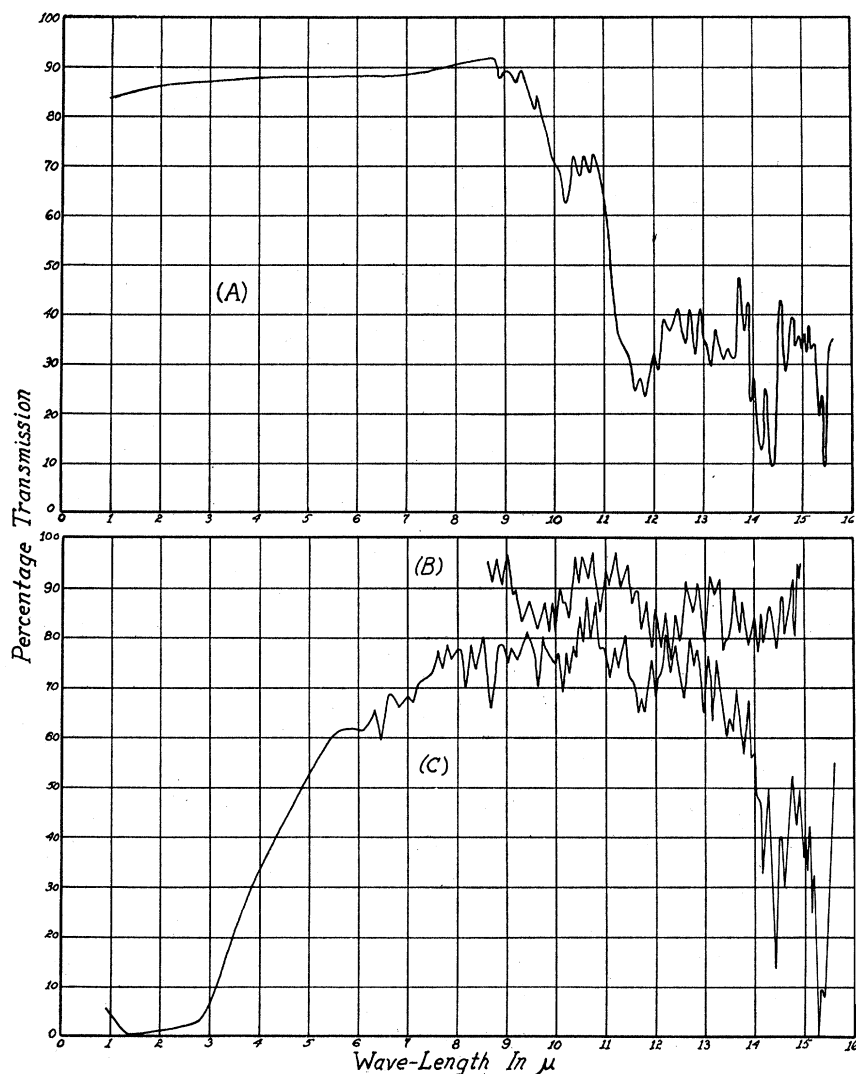
FIG. 4. (a) Transmission of a thin cleaved plate, $t=0.075$ mm. (b) Transmission of a 1μ layer of MgO evaporated onto a nitrocellulose film. (c) Transmission of a layer of MgO fumed onto a plate of NaCl.

§2. Results

(a) Fig. 3 shows the results plotted to a μ scale for different thicknesses of MgO prepared by cleaving plates from one of the large single crystals. The similarity between the curves will be noted. The agreement of the secondary structure in the various plates is good considering the resolving power of the instrument and the fact that as we proceed to greater thicknesses, the relative strengths and breadths of the absorption lines vary giving rise to absorption peaks of new shapes.

In Fig. 4 curve (a) the composite curve resulting from many separate runs on a cleaved plate 0.075 mm is given. No experimental points are indicated but each of the minima shown has been checked in at least two or three of the individual sets of measurements. The structure is quite complicated, yielding some 40 absorption lines between 6μ and 15.5μ.

(b) In the work of Czerny and Barnes[3] thin films of the alkali halides were prepared by heating the salts in a vacuum by means of a tungsten spiral and allowing them to condense onto a film
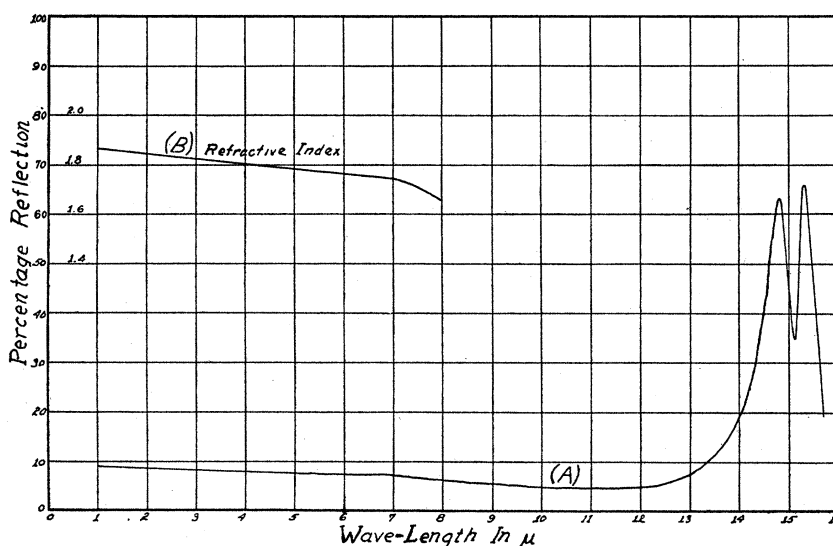
FIG. 5. (a) Reflection power of a crystal of MgO. (b) Dispersion curve of MgO calculated by use of the relation $R=(n-1)^2/(n+1)^2$.

of nitrocellulose. It was shown in their paper that the optical constants of a NaCl film prepared in this manner were identical with those of a massive plate of salt. Hilsch and Pohl[10] and their co-workers have also obtained results which showed that films prepared in this manner were really single crystals. Further proof that such films are really crystalline has been obtained by Kirchner,[11] using electron diffraction.

Curve (b) in Fig. 4 shows the result of a series of measurements upon such a thin film of approximately 1μ thickness. It is immediately obvious that the wave-lengths of the fine structure lines agree in almost every detail with those of the composite curve for the thin cleavage plate shown above in curve (a).

(c) In order to obtain still another check upon the existence of this secondary structure the transmissions of several thin films of finely powdered MgO were studied. The powders were prepared by two different methods, namely, by grinding up pieces of the large single crystals and by burning a piece of magnesium ribbon and allowing oxide to deposit upon a thin plate of NaCl. Curve (c) Fig. 4. shows the results of these measurements from which it is at once evident that the secondary structure is the same as that

found for the thin cleaved plate and the evaporated film.

(d) The positions of the source and M_1 were now changed and an extra plane reflection put in at the focus A in order to be able to study the reflection power of one of the large crystals. At each wave-length the crystal was interchanged with the plane silvered mirror and the ratios of the deflections from the two taken as the percent reflection power of MgO. These results are shown by curve (a) of Fig. 5. A double reflection maximum is seen at 14.8μ and 15.3μ. From the values of R for the region below say 8μ, the refractive indices of MgO may be obtained by using the simple equation $R=(n-1)^2/(n+1)^2$. The dispersion curve thus arrived at is shown by curve (b). The value of $n=1.86$ at 1μ is in fair agreement with the value $n_F=1.747$ reported by Brice and Strong.[12]

§3. Discussion of results

(a) MgO has been the subject of several investigations. Ångström in 1889 studied its absorption, while Coblentz in 1913 reported that with increasing wave-lengths its reflection power increased. In the latter investigation measurements were made at only 6 wave-lengths. In 1928, Fräulein S. Tolksdorf[13] made a study of

[10] R. Hilsch and R. W. Pohl, Zeits. f. Physik 57, 145 (1929). See later papers.
[11] F. Kirchner, Ann. d. Physik 11, 741 (1932); Zeits. f. Physik 76, 576 (1932).

[12] R. T. Brice and J. Strong, Phys. Rev. 47, 255 (1935).
[13] S. Tolksdorf, Zeits. f. physik. Chemie 132, 161 (1928).

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MgO from 2 to 15μ by means of a prism spectrom-
eter. Following a method suggested by herself and
Fräulein Laski,[14] she studied the transmission of
a thin film of finely powdered MgO held between
two plates of NaCl. A transmission curve was
obtained which ranged from about 40 percent at
2μ to 95 percent at 15μ and which showed three
distinct minima, located at 3.85, 7.65 and 14.2μ.
These she mistook for 4ν, 2ν and ν, respectively.
In view of the predictions of the classical theories
mentioned in the introduction, she called these
supposed overtones "anharmonic" vibrations.

Comparison of her results with those shown in
Fig. 4, shows that Fräulein Tolksdorf had mis-
taken the 14.2μ secondary maximum for the
fundamental, and had not measured any further
out in the infrared.

In 1931, Strong,[15] using reststrahlen, showed
that a layer of MgO fumed onto a NaCl plate
showed a very strong absorption in the neighbor-
hood of 23μ. A crystal of β-MgO showed 80 per-
cent reflection at this same wave-length. He
offered these results to show that the maximum
found by Tolksdorf at 14.2μ could not be the
fundamental of MgO.

In a short note, two of us reported the pre-
liminary results of this investigation.[16] At that
time we stated that we had found a strong ab-
sorption around 14μ which we identified with the
fundamental reported by Tolksdorf, the results of
Strong not being known to us. In view, however,
of the absorption band which we later observed
at 15.4μ and the work of Strong the identi-
fication of any one absorption band as the funda-
mental is quite uncertain. At present we are not
in a position to say, for example, whether the
reflection maxima of Fig. 5 are due to strong
secondary maxima or to the fundamental. This
question must be decided at a later date. From
our present results one can only say that the
fundamental absorption of MgO is accompanied
by many secondary maxima.

(b) The curves shown in Fig. 4 show very con-
clusively that the infrared spectrum of a solid
may be studied successfully in either of the three
forms, namely, cleavage plates, powder or

evaporated films. The last two methods require
great care and sometimes lead to spurious results.

Before using the powder method the investi-
gator should be familiar with the authors' paper
and those of Pfund on the infrared of powders.[17]
In the light of these papers, the increasing trans-
parency of the powdered MgO found by Tolks-
dorf as longer wave-lengths were reached, is
readily understood. In all cases where powders
are used the particle size of the powder must be
smaller than the wave-lengths of the regions being
studied in order to avoid spurious effects, and
shifts in the wave-lengths.

Hirsekorn[18] measured the transmission of films
of NaCl evaporated at atmospheric pressure, and
found spurious effects due to the particles. These
evaporated films must be prepared in the very
highest vacuum obtainable.

These last-named methods have been used to
advantage by many people, and it is therefore
very gratifying to see that all three methods when
applied to the same substance yield results
strictly comparable in every detail.

(c) In conclusion it must be mentioned that,
since these secondary maxima are probably due
to anharmonic terms in the force equation, they
should be sensitive to changes of temperature, as
will be discussed in Part B. Accordingly, prepara-
tions are under way to repeat these measurements
first at liquid air then at liquid hydrogen tem-
peratures. Then and only then could a complete
correlation with theory be expected.

§4. Experiments on other crystals

From time to time the complex structure of the
infrared absorption bands of various crystals,
as evidenced by reflection as well as transmission
measurements has surprised experimenters. As
increasingly higher resolving power has been em-
ployed, it has become more and more evident
that these bands possessed a real fine structure
the exact interpretation of which is unknown.

No attempt will be made at this point to give
a complete list of papers bearing upon the above
statements, however it is felt that several in-
vestigations should be cited.

[14] G. Laski and S. Tolksdorf, Naturwiss. 14, 21 (1926).
[15] J. Strong, Phys. Rev. 37, 1565 (1931).
[16] R. Bowling Barnes and R. Robert Brattain, Phys. Rev. 47, 416 (1935).

[17] R. Bowling Barnes, R. Robert Brattain and R. S. Firestone, Phys. Rev. 47, 792A (1935); A. H. Pfund, Phys. Rev. 36, 71 (1930); J. Opt. Soc. Am. 24, 143 (1934); J. Opt. Soc. Am. 23, 375 (1933).
[18] H. G. Hirsekorn, Ann. d. Physik 6, 985 (1930).

In addition to MgO Tolksdorf studied CaO, BeO, ZnO, CdO and HgO. For the first three she found the spectra to consist of several distinct maxima of absorption where only one or two were expected. For CdO and HgO, she was unable to locate the fundamentals because they were beyond 22μ, the limit of her spectrometer; however, she did find in the near infrared, several weak absorptions which are probably analogous to the secondary maxima reported above for MgO. A complete account of this work, and an attempt to identify these secondary maxima as harmonics and combinations will be found in the book of Schaefer and Matossi, *Das Ultrarote Spektrum*.

Silverman[19] measured, in the neighborhood of the 7μ band, the reflection and transmission of calcite, and found between 6.4μ and 7.4μ some 33 lines in each case. This unexpected fine structure he suggested was possibly due either to the disturbing effects of imperfections in the crystal, or to combinations with the far infrared bands of calcite.

Silverman and Hardy[20] showed that the 9μ quartz band also possessed an extremely complicated structure.

Recent papers from the laboratory of Schaefer and Matossi also point to the presence of complicated structure in the cases of many crystals.

Besides the original work discussed above, other investigators[21] have studied the alkali halides and verified the existence of the secondary maxima in every case.

Although the absorptions of all types of crystals seem to possess this fine structure, or secondary structure, the most important thing to be done right now is undoubtedly to obtain very accurate measurements on cubic crystals. Experiments performed at low temperatures, with polarized radiation, or with the radiation traversing the crystal in directions other than normal to the 100 plane, will yield results which will be of the greatest theoretical importance with regard to the study of the solid state.

PART B. THEORETICAL INTERPRETATION

§1. Previous developments: a criticism of the Born approximation

A sketch of the general scheme followed in an attempt to approach a theoretical interpretation of the previous results was presented in the introduction, and before proceeding with a detailed discussion of this, we shall pause to review some of the previous developments.

In the earliest period of observation of the reflection spectra of solids, it was found[22] that for cubic crystals the spectra could be accounted for by assuming that they possessed one fundamental absorption frequency and that the reflection properties were related to this by means of the well-known formulae of optics. In noncubic crystals, it was necessary to assume the presence of several absorption maxima. Following this, a number of dimensional equations relating this frequency for cubic crystals to other physical properties were suggested by Einstein, Lindemann, Braunbeck and others, and were found to give rough agreement with the established facts.

On the basis of some remarkably good assumptions concerning the arrangements of atoms in the alkali halides, Madelung[23] succeeded in relating the fundamental absorption frequency to the interaction forces and connected these with the elastic coefficients. This was followed by a paper of Born and von Kármán[24] in which the ideas behind Madelung's work were placed upon a firmer basis for analytical treatment. Although the conclusions which they drew from their development are not strictly correct when viewed in the light of modern knowledge, their treatment of vibrational waves has continued to be of service in many fields. In addition, this work gave an indication of the weaknesses of the Debye theory of specific heats in which the crystal was treated as a continuous solid—a question which has been the object of considerable qualitative and semiquantitative investigation in recent times.[25]

[19] S. Silverman, Phys. Rev. **39**, 72 (1932).
[20] J. D. Hardy and S. Silverman, Phys. Rev. **37**, 176 (1931); S. Silverman, Phys. Rev. **45**, 158 (1933).
[21] K. Korth, Nachr. d. Ges. d. Wiss. zu Gött. Math-Phys. Kl. 1932, p. 576; A. Mentzel, Zeits. f. Physik **88**, 178 (1934).

[22] A complete sketch of the work discussed in this paragraph is to be found in Schaeffer and Matossi, *Das Ultrarote Spektrum* (Berlin, 1930).
[23] E. Madelung, Nachr. d. Ges. d. Wiss. zu Gött. M. P. Klasse, March 1909, Jan. 1910; Physik. Zeits. **11**, 898 (1910).
[24] M. Born and Th. von Kármán, Physik. Zeits. **13**, 297 (1912).
[25] M. Blackman, Proc. Roy. Soc. **A148**, 365, 389 (1935); **A149**, 117, 126 (1935).

During a subsequent period, Born and co-workers succeeded in developing a theory of ionic crystals,[26] based upon the assumption of central force interaction of ions, by means of which a number of properties of such crystals such as dielectric constant and fundamental frequency could be correlated. Such correlations are to be regarded as first approximation connections which are valid when the assumptions made are correct to within factors that are essentially refinements. The principal assumption which is made is that of central force interaction of ions. For the purpose of many property-correlations, such as those mentioned previously, considerable inaccuracy in these assumptions may not lead to wide discrepancies in results, simply because the quantities correlated are not sensitive to alterations in the fundamental assumptions; that is, for example, neither the dielectric constant nor the fundamental frequency of a crystal will be greatly affected by small deviations of the interaction potential from one of the central type. This is not true of many other properties of crystals, however, particularly those which are the differences of relatively insensitive quantities. This question is of considerable importance when the problem of determining the positions of the secondary absorption maxima of crystals relative to the fundamental is raised, as will be shown in the following sections, and for this reason it is important that the extent to which the results of the assumptions of Born are valid be known. If they are found to be incorrect to a sufficient degree, it will be necessary to proceed from an entirely phenomenological standpoint, as will be shown to be the case.

One of the principal results of the assumption of central forces when dealing with arbitrary crystals is the so-called Cauchy-Poisson relations[27] between the components of the stress-strain tensor. For cubic crystals, with which we are principally concerned, these relations are such that equality is to be expected between the coefficients c_{12} and c_{44} of Voigt, the first of which connects the transverse stress to the strain along a given crystallographic axis, while the second

TABLE I.

°K	$c_{11}10^{-11}$ NaCl	$c_{11}10^{-11}$ MgO	$c_{12}10^{-11}$ NaCl	$c_{12}10^{-11}$ MgO	$c_{44}10^{-11}$ NaCl	$c_{44}10^{-11}$ MgO
273.1	5.035	28.841	1.277	15.350	1.279	8.705
210	5.284	29.128	1.298	15.421	1.253	8.585
150	5.508	29.396	1.315	15.472	1.127	8.535
80	5.754	—	1.332	—	1.159	—
77.4	—	29.547	—	15.501	—	8.462

relates the shearing stress in a plane orthogonal to one of the principal axes to a shearing strain in the same plane. A number of results concerning these relations for valence crystals and metals[28] revealed that they are not nearly satisfied. Previous[29] to some very recent work by Quimby, Balamuth, Rose and Durand[7] using oscillating circuit methods, the only measurements carried on for the determination of the constants for ionic crystals dealt with the monovalent alkali halides and were performed at ordinary temperatures. In these earlier cases the relationships were found to be valid to within an experimental error which we judge to be about 5 percent. The room temperature values are not particularly valuable for the present discussion, however, since the elastic coefficients are known to vary considerably with temperature and we are really interested in the absolute zero values. The work of reference 7, however, has furnished a good deal of information for both monovalent (NaCl) and divalent ionic crystals (MgO) over a temperature range extending down to 80 degrees Kelvin with an accuracy exceeding that previously obtained by about one power of 10. A sample set of values of the adiabatic coefficients of both of these crystals are given in Table I. The isothermal values may be determined from these by adequate small corrections which are always such as to lower c_{44} and leave c_{12} unchanged.

From these results it is clear that in the vicinity of absolute zero the c_{44} coefficient will be about 15 percent less than c_{12} for NaCl, while in the case of MgO the ratio is almost 2 to 1. This presents conclusive evidence that the Born approximation is a rather rough one for ionic crystals.

[26] A thorough review of this work is given by M. Born and M. Goeppert-Mayer in the Geiger-Scheel Handbuch der Physik, Vol. 24b.

[27] W. Voigt, Lehrbuch der Kristallphysik (Teubner, 1910), p. 607.

[28] A review of the work of Voigt on this subject may be found in M. Born's Atomtheorie des Festenzustands (Teubner, 1923), Chapter I.

[29] W. Voigt, reference 26, p. 741; P. W. Bridgman, Proc. Am. Acad. 64, 19 (1929). We are indebted to Professor Bridgman for correspondence concerning details of this work.

With the discovery of secondary maxima, Born and Blackman,[5] as we have stated in the introduction, sought an explanation of this phenomena on the basis of anharmonic potential terms and solved the problem of the diatomic linear chain, considering such terms to be small perturbations, as a classical mechanical one. As is well known, the frequency spectrum for this problem as a function of the variable $\sigma = 2\pi/\lambda$, λ being the wave-length, is represented by a curve of the type shown in Fig. 6 in which the discontinuity occurring for $\sigma = \pm \pi/Na$, where a is the distance between nearest like atoms, is a characteristic of the diatomic lattice that disappears when the masses of the particles are equal and $2N$ is the total number of atoms. The results of Born and Blackman show that on the basis of their classical reasoning one would expect frequencies $\nu_1 + \nu_2$ and $\nu_1 - \nu_2$ as well as the fundamental frequency ν to be absorbing. These results were then extended to the three-dimensional case again on a classical basis, but with neglect of a suitable analysis of the discontinuous zone structure that must exist by analogy with the results of the theory of metals. This last point represents a serious omission, even if the use of classical mechanics and the use of central forces were valid, and will be discussed more thoroughly in §3.

In view of these facts, the problem will be handled entirely anew in the following sections and with a view toward eventually obtaining correlations between experimental and theoretical results.
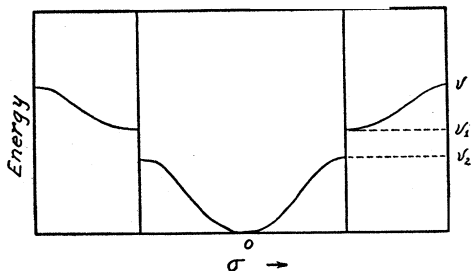

FIG. 6. A representative energy-wave number distribution for the linear chain. In the classical case the energy is proportional to the square of the frequency, while in the quantum case it is proportional to it. In the three-dimensional lattice, this is characteristic of the energy spectrum for one polarization and a line passing through the origin in σ-space. The discontinuities occur when this line intersects the zones.

§2. The symmetry restrictions induced on a general potential form

As a basis for a phenomenological discussion of the interaction potential of atoms, we shall assume that they are regularly arranged in a lattice at points

$$l\tau_1 + m\tau_2 + n\tau_3 + \rho_a \qquad (1)$$

where l, m and n are integers, τ_1, τ_2, τ_3 are the primitive translations of the lattice, and ρ_a is a vector independent of lmn which gives the position of the ath atom in a unit cell. For a diatomic face-centered lattice of the cubic type, τ_1, τ_2, τ_3 may be taken in the form

$$\begin{pmatrix} a \\ a \\ 0 \end{pmatrix}, \quad \begin{pmatrix} a \\ 0 \\ a \end{pmatrix}, \quad \begin{pmatrix} 0 \\ a \\ a \end{pmatrix}, \qquad (2)$$

respectively,[30] while ρ_a may be chosen to be zero for one atom (type a, say) and

$$\begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} \qquad (3)$$

for the other (type b), so that a is the closest distance between unlike atoms. Thus when the atoms are in their equilibrium positions, the lattice will be invariant under one of the 230 space groups and we must expect the equilibrium potential function to be likewise invariant (i.e., to belong to the unit representation of the space group). When the atoms are displaced from their equilibrium positions, so that the new position of an atom of type a, say, in the lmn-th cell relative to its old is given by the vector of component $x_a^i(lmn)(i = 1, 2, 3)$, the potential of the lattice will be altered, but we shall assume that it may be expressed as a power series expansion in these displacement variables in such a manner that all terms of a given degree are invariant under the group. As is well known, the constant term in this expansion need not be considered, while the linear terms will vanish as the condition of equilibrium. We shall regard the quadratic terms as being of principal importance and treat the cubic terms as small perturbations. For this purpose, we shall

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[30] For a presentation of the theory of crystal symmetry in terms of the notation to be presented here see F. Seitz, Zeits. f. Krist. 88, 433 (1934), et seq.

begin by neglecting the latter and choose a set of normal coordinates for which the quadratic is in normal form, which must be taken to be real since we will want to quantize the entire system. We shall consider the crystal to be fixed, so that the process of choosing normal coordinates is essentially one of resolving all of the x's into Fourier-like components and treating the amplitude-coefficients as a set of variables. Since one of these will correspond to pure translations, it is important that the potential be invariant under infinitesimal translations, and we must express it as a function of differences

$$x_a{}^i(l'm'n') - x_c{}^i(lmn) = \xi_{ac}{}^i(l'm'n',\, lmn) \quad (4)$$

of displacements, which will also allow us to express the potential change going with a homogeneous deformation of the lattice. It is implied that the coefficients in the power series expansion are so defined that the entire expression is invariant under infinitesimal rotations because we are dealing with a scalar form, so that we shall be concerned with all quadratic and cubic forms in the differences that belong to the unit representation of the space group. Of these a very large number may be neglected since they are considered to be physically unimportant, and we will actually consider but a very small fraction of the possible terms.

For simple crystals in which each atom is at a center of symmetry of the type for which the corresponding point group is that of the class to which the space group belongs, the problem of finding the desired form is comparatively easy. In this case the translational symmetry may be handled completely apart from the rotational, and we need only take the sum of the equivalent potentials of equivalent cells, these potentials being determined by mere rotation group considerations (i.e., screw operations and glide planes do not play a role).

In the lattice of the NaCl type (Fig. 7) with which we shall be entirely concerned, each atom possesses the symmetry O^h for which the ten irreducible representations have been given by Bethe.[31] The character system going with these is listed in Table II, in which Γ^+ and Γ^- are written together with the corresponding signs for the elements of determinant 1 and -1.

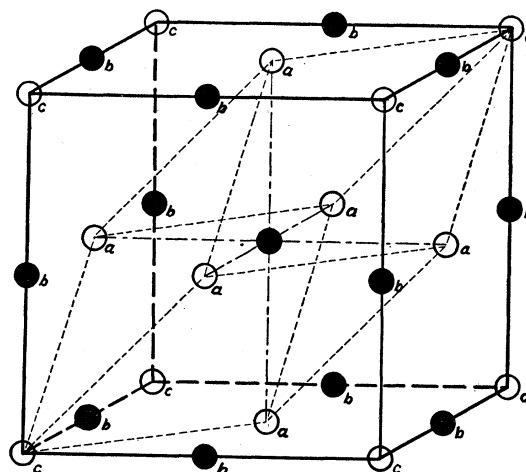[31] H. Bethe, Ann. d. Physik **3**, 133 (1929).

FIG. 7. Face-centered cubic lattice of the NaCl type.

Although the translation group is of the type $\Gamma_c{}'$, it is convenient to designate each atom by the integers lmn which specify its position vector of components la, ma, na, since these lie at all mesh points of a simple cubic lattice. Of the possible interaction terms of each atom with its neighbors, we shall consider only those between a given one and its twenty-six neighbors. Moreover, of these we shall be concerned only with quadratic terms of the type

$$\xi^i(l'm'n',\, lmn)\,\xi^j(l'm'n',\, lmn) \quad (5)$$

and with cubic terms of the type

$$\xi^i(l'm'n',\, lmn)\,\xi^j(l'm'n',\, lmn)\,\xi^k(l'm'n',\, lmn) \quad (5a)$$

and discard those in which the indices of the

TABLE II. *Character system for crystallographic group O^h.*

	E	$6C_2'$	$8C_3$	$3C_2$	$6C_4$	I	$6R_d$	$8S_6$	$3R_h$	$6S_4$
Γ_1	1	1	1	1	1	±1	±1	±1	±1	±1
Γ_2	1	1	-1	-1	1	±1	∓1	∓1	∓1	±1
Γ_3	2	2	0	0	-1	±2	±2	0	0	∓1
Γ_4	3	-1	1	-1	0	±3	∓1	±1	∓1	0
Γ_5	3	-1	-1	1	0	±3	∓1	∓1	±1	0

where: E is the unit element;
   $6C_2'$ is the class of 6 two-fold rotations about axes of the (110) type;
   $8C_3$ is the class of 8 three-fold rotations about axes of the (111) type;
   $3C_2$ is the class of 3 two-fold rotations about axes of the (100) type;
   $6C_4$ is the class of 6 four-fold rotations about axes of the (100) type;
   I is the inversion;
   $6R_d$ is the class of 6 reflection planes orthogonal to axes of (110) type;
   $8S_6$ is the class of 6 six-fold rotary reflections about axes of (111) type;
   $3R_h$ is the class of 3 planes orthogonal to axes of the (100) type;
   $6S_4$ is the class of 6 rotary reflections about axes of the (100) type.

type $l'm'n'$ in these differ among themselves. This simplification has the effect of reducing the total number of terms for the twenty-six neighbors to about a fourth. Of the terms considered, those which describe the interaction between unlike atoms are the same regardless of which type of atom is at the center of neighbors, and need to be counted but once for each cell, while those which describe the interaction of like particles appear with different coefficients depending upon the type of atom concerned.

The problem of analyzing the character system of the quadratic and cubic terms will not be gone into here, and it will suffice to tabulate the results. Regarding the former, it is found that there are ten forms to be considered as these may be classed as follows. In all cases the variables ξ, η, ζ will be considered in place of ξ^1, ξ^2, ξ^3, and because of the restriction (5) we may write $\xi\eta(l'm'n', lmn)$ in place of $\xi(l'm'n', lmn)$ $\cdot\eta(l'm'n', lmn)$, etc. The summation indicated will always imply that two terms in which a cyclic permutation of the variables that appear are to be added. The character system of the various cases is listed in Table III.

I Interaction of given atom with 6 unlike neighbors

    1. $\sum\{\xi^2(l+1mn)+\xi^2(l-1mn)\}$;

    2. $\sum\{\xi^2(lmn+1)+\xi^2(lmn-1)$
              $+\xi^2(lm+1n)+\xi^2(lm-1n)\}$.

II Interaction of given atom with 12 nearest like neighbors

    3. $\sum\{\xi^2(lm+1n+1)+\xi^2(lm+1n-1)$
             $+\xi^2(lm-1n-1)+\xi^2(lm-1n+1)\}$;

    4. $\sum\{\xi^2(l+1m+1n)+\xi^2(l+1m-1n)$
             $+\xi^2(l+1mn+1)+\xi^2(l+1mn-1)\}$;

    5. $\sum\{\xi\eta(l+1m+1n)+\xi\zeta(l+1mn+1)$
             $-\xi\eta(l+1m-1n)+\xi\zeta(l+1mn-1)\}$;

    6, 7 and 8 duplicate 3, 4, 5 for atoms of other type.

III Next nearest unlike neighbors

    9. $\sum\{\sum_{\pm 1}\xi^2(l\pm1, m\pm1, n\pm1)\}$;

    10. $\sum\{(\eta+\zeta)\xi(l+1m+1n+1)-(\eta-\zeta)\xi(l+1m-1n+1)$
           $-(\eta+\zeta)\xi(l+1m-1n-1)$
           $+(\eta+\zeta)\xi(l+1m+1n-1)$;
      $-(\eta+\zeta)\xi(l-1m+1m+1)+(\eta-\zeta)\xi(l-1m-1n-1)$
           $+(\eta+\zeta)\xi(l-1m-1n-1)$
           $-(\eta-\zeta)\xi(l-1m+1n+1)\}$.

In the following we shall designate the coefficient of each of the ten quadratic terms by $\alpha(1)$, $\cdots$, $\alpha(10)$, respectively.

Since we shall employ the cubic terms only

TABLE III. *Character system for quadratic terms considered.*

TYPE OF NEIGH-BOR	CONDI-TIONS (5)	E	$6C_2'$	$8C_3$	$3C_2$	$6C_4$	I	$6R_d$	$8S_6$	$3R_h$	$6S_4$	No.
I	$i=j$	18	0	0	6	2	0	2	0	12	0	2
I	$i\neq j$	18	0	0	-2	-2	0	2	0	-4	0	0
II	$i=j$	36	2	0	0	0	0	2	0	12	0	2
II	$i\neq j$	36	2	0	0	0	0	2	0	-4	0	1
III	$i=j$	24	0	0	0	0	0	4	0	0	0	1
III	$i\neq j$	24	0	0	0	0	0	4	0	0	0	1

insofar as they are able to break down the selection rules for optical transitions, and we shall assume that they do not affect the energy spectrum given by the quadratic terms, it will not be necessary to go farther than to write down the set of terms arising from (5a) when only the six nearest neighbors are considered for reasons that will become apparent in §5. The character system is given in Table IV.

The corresponding cubic forms are

1. $\sum\{\xi^3(l+1mn)-\xi^3(l-1mn)\}$

2. $\sum\{\xi^2\eta(lm+1n)-\xi^2\eta(lm-1n)$

          $+\xi^2\zeta(lmn+1)-\xi^2\zeta(lmn-1)\}$.

TABLE IV. *Character system for cubic terms considered.*

RELATIONS IN (5a)	E	$6C_2'$	$8C_3$	$3C_2$	$6C_4$	I	$6R_d$	$8S_6$	$3R_h$	$6S_4$
$i=j=k$	18	0	0	-2	2	0	2	0	4	0	1
$i\neq j=k$	36	0	0	-4	0	0	0	0	8	0	1
$i\neq j\neq k$	6	0	0	2	-2	0	2	0	4	0	0

§3. Normal coordinates: the energy spectrum

The process of reducing the quadratic expression, corresponding to the sum of the possible invariant terms introduced in §2, to normal form is essentially one of reducing a matrix to diagonal form, and since this matrix is invariant under an entire space group, we know that the normal coordinate system will be one in which the space group is reduced. When the Born-von Kármán boundary conditions are employed, it may be shown[32] that for all crystals these coordinates may be taken to be of the Fourier type

$$\chi_\sigma \exp(i\sigma\cdot\mathbf{r}) \qquad (6)$$

where χ_σ is invariant under the primitive translations of the lattice and σ is a vector such that

[32] F. Bloch, Zeits. f. Physik **52**, 555 (1929); F. Seitz, *On the Reduction of Space Groups* to appear in Annals of Mathematics, January (1936).

$$\sigma \cdot \mathbf{T}_i = 2\pi n_i. \qquad (7)$$

In this, $\mathbf{T}_i$ are the three vectors defining the polyhedron at the surface of which the boundary conditions are satisfied. For a simple cubic lattice of type Γ_c, for example, this polyhedron may be taken to be a cube so that these vectors lie along each of the three axes. In the case at hand in which we are dealing with lattice vibrations, χ_σ will be periodic in the primitive translations and will be a vector function which takes values only at the positions of the atoms. In other words, for a lattice of the type considered here, the functions (6) will represent waves in which the atom of type 1 at la, ma, na has the displacement

$$\chi_\sigma(1, lmn)\mathbf{f}_1(\sigma, lmn) \exp [i\sigma \cdot \mathbf{r}(lmn)] \qquad (8)$$

where χ_σ is the scalar amplitude of the wave, $\mathbf{f}_1$ is the unit vector in the direction of displacement and $\mathbf{r}(lmn)$ is the position vector of the atom, while atoms of type 2 at the other mesh points will have displacements of scalar amplitude $\chi(2)$ and direction $\mathbf{f}_2$, both of which will generally differ from $\chi(1)$ and $\mathbf{f}_1$. For an arbitrary, allowable σ, the three values of $\mathbf{f}_1$ and $\mathbf{f}_2$ which reduce the terms of type σ to normal form may be determined by solving an appropriate secular equation to be described later.

For a face-centered lattice in which the primitive translations are given by (2), the allowable form of σ is

$$\frac{2\pi}{2Na}\begin{pmatrix} n_1+n_2-n_3 \\ -n_1+n_2+n_3 \\ n_1-n_2+n_3 \end{pmatrix} \qquad (9)$$

corresponding to the boundary conditions being satisfied at the surface of the rhombic dodecahedron of height $2Na$ (Fig. 8), where n_1, n_2, n_3 and N are integers. The lattice defined by allowing n_1, n_2 and n_3 to take on all integer values is the inverse lattice to the face-centered one and is seen to be a body-centered one having a unit cell of volume $4\pi/N^3a^3$. Not all values of the n's correspond to independent modes of vibration, however, and it is readily seen that the only ones which need to be considered are those contained in a cube whose corners are at the eight points corresponding to n_1, n_2, n_3 equal to $\pm N/2$. Within this there are $2N^3$ unit cells so that when
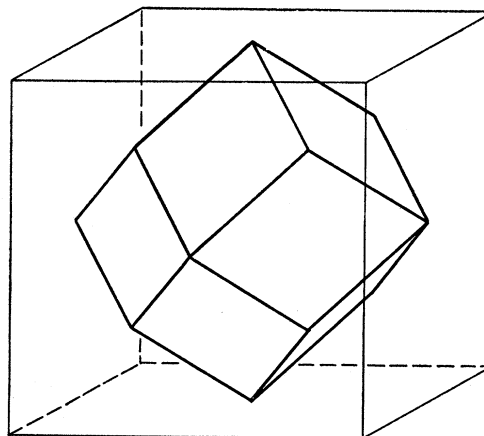

Fig. 8. The rhombic dodecahedron at the surface of which the boundary conditions are satisfied. It possesses one-fourth of the volume of the enclosing cube.

the three directions of polarization are taken into account, it corresponds to $6N^3$ degrees of freedom, which is in agreement with the fact that there are $2N^3$ atoms in the rhombic dedocahedron containing N^3 unit cells of the crystals, and each atom possesses three degrees of freedom.

From the standpoint of the energy spectrum, we may expect three energies going with each point in the cube described above corresponding to the generally different energies going with the three directions of polarization of a wave of given σ. It is to be expected that these energy functions $E^i(\sigma)$, where i ranges over the three polarization vectors, will generally vary smoothly from point to point except at the surfaces of definite polyhedra, or *zones*, where they will have discontinuities analogous to those met with[33] in describing electron waves in solids. The space between two zones will generally contain as many points of σ space as there are unit cells in the polyhedron at the surface of which the boundary conditions are to be satisfied—N^3 in this case, so that we may expect that there will be two zones in the problem at hand, and, in fact, for the lattice $\Gamma_c{}'$, these correspond to the cube and truncated octahedron shown in Fig. 9. Since we do not consider regions outside of this cube to be different from that inside, the energy surfaces will end at the

[33] L. Brillouin, *Quantenstatistik* (Berlin, 1931), Chap. VIII.

The basis for examining the connection between these zones and crystal symmetry is laid in the second of the references 32, and will be extended for presentation in this journal in the near future.
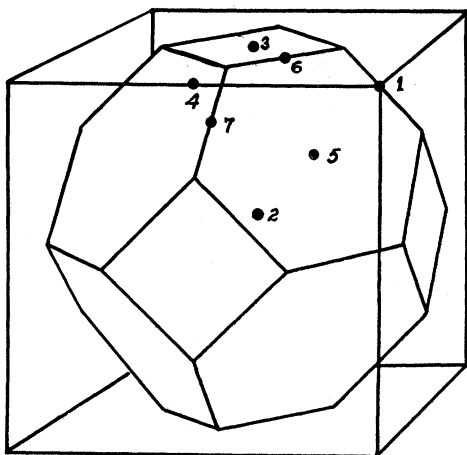
FIG. 9. First two zones for a face-centered diatomic crystal of the NaCl type (translation group Γ_c'). The inner zone is a truncated octahedron and the second is a cube. The difference in volume between the first and second is equal to that of the first. The numbers indicate particular points to be discussed in the text. (Note no. 2 is the center.)

cube, but may be expected to possess a vanishing gradient normal to the surface,[34] while at the surface of the truncated octahedron they will possess definite discontinuities, being continuous on each side of the surface, and will have a vanishing normal gradient there. Fig. 6 represents the characteristic behavior of $E(\sigma)$ for one direction of polarization as σ varies along a line passing through the origin. The discontinuity occurs when σ reaches the truncated octahedron, and the curve ends at the cube.

It is a general characteristic of this zone structure that each of the points in one zone may be viewed as being associated with a definite point in another zone in the sense that the waves going with the two have exactly the same symmetry properties (belong to the same irreducible representation), and in the present case these two points are connected by a vector of the same length as one of the vectors

$$\mathbf{s}^i = \frac{2\pi}{2a}\begin{pmatrix} \pm 1 \\ \pm 1 \\ \pm 1 \end{pmatrix} \qquad (10)$$

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[34] A proof of this may be derived from the work of H. Jones and C. Zener, Proc. Roy. Soc. **A144**, 101 (1934) by means of group-theoretical extensions that will be discussed in this journal in the near future.

joining the origin with a cube corner. These vectors are the only members of the $2N^3$ considered (aside from the origin), that possess the property that their scalar product with each of the primitive translations is 2π, or 0. It is readily seen that to each point between the cube and the truncated octahedron, the vector $\sigma+\mathbf{s}^i$ lies either outside of the cube (and is not to be considered) or inside of the truncated octahedron, the only ambiguous cases being those in which σ lies on the surface of the latter polyhedron, and this difficulty, which is never of physical importance, may be removed by assuming that one of any two such points that are connected by a vector $\mathbf{s}$ belongs to the inner zone and the other to the outer. Because of this fact and the fact that $\sigma\pm\mathbf{s}^i$ possesses the same properties as σ under the translation group, we need only consider points belonging to the truncated octahedron, and it will turn out that the correct multiplicity of solutions corresponding to the double-valuedness of each point inside will automatically follow. These two solutions are, in fact, the modes of vibrations in which neighboring atoms are out of phase by more or less than 90 degrees, respectively. Later on, we shall return to the characterization by use of all points in the cube, and consider the three energies going with the wave in which unlike neighboring atoms are most out of phase to be outside of the truncated octahedron.

Finally, it must be borne in mind that we want all waves to be real for the purposes of quantization, and for this reason, we shall replace $\exp(i\sigma\cdot\mathbf{r})$ in the preceding by both $\sin\sigma\cdot\mathbf{r}$ and $\cos\sigma\cdot\mathbf{r}$, and have for the Fourier resolution of the displacement vector $x^i(lmn)$ of atoms of type a and b:

(1) Atoms of type 1

$$x^i(lmn) = \sum_\sigma \sum_\alpha \left\{ \frac{\chi_\alpha(\sigma, c)}{\sqrt{m_1}} f_\alpha{}^i(\sigma, c) \cos \sigma\cdot r(lmn) \right.$$

$$\left. + \frac{\chi_\alpha(\sigma, s)}{\sqrt{m_1}} f_\alpha{}^i(\sigma, s) \sin \sigma\cdot r(lmn) \right\} \quad (11)$$

where $\chi_\alpha(\sigma, c)$ is the amplitude of the cosine wave polarized in the direction $f_\alpha{}^i$ $(\alpha = 1, 2, 3)$, etc. The allowed vectors $\mathbf{f}^i$ are to be determined by an appropriate set of equations.

(2) Atoms of other type

$$x^i(l'm'n') = \sum_\sigma \sum_\alpha \left\{ \frac{\psi_\alpha(\sigma, c)}{\sqrt{m_2}} g_\alpha{}^i(\sigma, c) \cos \sigma \cdot \mathbf{r}(l'm'n') \right.$$

$$\left. + \frac{\psi_\alpha(\sigma, s)}{\sqrt{m_2}} g^i(\sigma, s) \sin \sigma \cdot \mathbf{r}(l'm'n') \right\} \quad (11a)$$

where ψ and $\mathbf{g}$ have the same significance as χ and $\mathbf{f}$ in (1) and ψ_α accompanies χ_α.

The introduction of the factor $1/\sqrt{m_1}$ and $1/\sqrt{m_2}$ has the effect of reducing the kinetic energy form to one in which $\dot{\chi}^2$ and $\dot{\psi}^2$ have the same coefficient and it is only necessary to consider the potential form in determining the normal coordinates.

It may be readily shown that in all cases in which the atoms occupy points of inversional symmetry:

$$\begin{pmatrix} -1 & & \\ & -1 & \\ & & -1 \end{pmatrix},$$

the sine and cosine waves separate completely in all of the sums that will be taken so that we need only consider the latter and designate $\chi(\sigma, c)$ and $\psi(\sigma, c)$ by $\chi(\sigma)$ and $\psi(\sigma)$ for the present. In considering the cubic terms, it will be necessary to return to the previous notation. From this it is readily seen that for a given σ the six quantities $\chi_\alpha(\sigma)$, $\psi_\beta(\sigma)$ ($\alpha, \beta = 1, 2, 3$) will give rise to a secular equation of the sixth degree unless one or more of the polarization pairs is known beforehand, in which case the secular determinant may be reduced to a two- and a four-, or to three two-dimensional ones, depending upon whether one or two pairs is known. If they are not known, the solution of the secular equation will determine these directions in terms of the set of f_α and g_β that have been assumed at the start in (11) and (11a). It is clear from the symmetry of the quadratic form that the $\mathbf{f}$'s will be mutually orthogonal, as will be the $\mathbf{g}$.

§4. Wave quantization and selection rules

The process of quantizing the waves once the reduction to normal form has taken place is simply one of writing the Schrödinger equation corresponding to the Hamiltonian function

$$\sum_\sigma \sum_\alpha \tfrac{1}{2} \{ (\dot{q}^2(\sigma, c) + \kappa_\lambda{}^2(\sigma) q^2(\sigma, c))$$

$$+ (\dot{q}^2(\sigma, s) + \kappa_\lambda{}^2(\sigma) q^2(\sigma, s)) \} \quad (12)$$

where it assumed that the q_λ's are the amplitudes of the normal variables of given σ so that the total energy is the sum over σ and λ of terms of the type (12), the former taking on all values corresponding to the cube. The $\kappa_\lambda{}^2(\sigma)$ are the roots of the secular equation discussed in the last section. The Schrödinger equation for this problem is simply

$$\frac{h^2}{8\pi^2} \frac{\partial^2 \psi(q_\lambda(\sigma), n_\lambda(\sigma))}{\partial q_\lambda{}^2(\sigma)} + \frac{\kappa_\lambda{}^2(\sigma)}{2} q_\lambda{}^2(\sigma) \, \psi(q_\lambda(\sigma), n_\lambda(\sigma))$$

$$- E(n_\lambda(\sigma)) \psi(q_\lambda(\sigma), n_\lambda(\sigma)) = 0 \quad (13)$$

for which the energy of the stationary state $\psi(q_\lambda(\sigma), n_\lambda(\sigma)) (n_\lambda(\sigma) = 0, 1, 2, \cdots)$ is given by

$$\frac{h}{2\pi}(n + 1/2)\kappa_\lambda(\sigma), \quad (13a)$$

$\kappa_\lambda(\sigma)$ being the classical oscillator frequency.

The probability of optical transitions from a state ψ_n to $\psi_{n'}$ will be proportional to the square of the dipole moment matrix component connecting these two states, and this matrix will be zero for all σ except $\sigma = \mathbf{s}^i$ in which case the three waves of equal energy corresponding to a normal mode in which unlike neighbors are 180 degrees out of phase (i.e., the mode going with $\sigma = \mathbf{s}^i$ of the last section which we shall designate simply by $\mathbf{s}$ in the future) possess a nonvanishing matrix.[35] This matrix $\mathbf{p}_\tau(\mathbf{s})$ ($\tau = 1, 2, 3$) will be of the form

$$\mathbf{p}_\tau(\mathbf{s}) = e(s)\mathbf{q}_\tau(\mathbf{s})/\sqrt{M} \quad (14)$$

where $M = m_1 m_2/(m_1 + m_2)$ and $e(s^i)$ is the effective ionic charge to be determined from precise theoretical considerations. If the ions were rigid spherical structures, which the evidence of §1 indicates to be only roughly true, this would be the absolute value of the electronic charge for the alkali halides and twice this for MgO. In the present paper, however, we are interested only in the possibility of absorption and not in the intensity of the absorption lines so that this point

[35] C. J. Brester, *Kristallsymmetrie und Reststrahlen, Diss.* (Utrecht, 1923).

is not a critical one. Since $\mathbf{p}_\tau(\mathbf{s})$ is proportional to $\mathbf{q}_\tau(\mathbf{s})$ it will have nonvanishing matrix components only if $n' = n \pm 1$, so that only light quanta of frequency $\nu(\mathbf{s})$ may be emitted or absorbed in the quadratic approximation. This is of course just the classical result as was to be expected.

§5. Alterations induced by the presence of the cubic terms

As we have stated previously, we shall assume that the results of the presence of the cubic terms will be such as to leave the energy spectrum unaltered, but will affect the wave functions enough so that the selection rules of §4 are no longer strictly valid. These cubic terms will be of the form

$$\sum_l \{ \sum_{ijk} \sum_{l'l''l'''} \alpha_{ijk}^{l'l''l'''} \xi^i(l'l) \xi^j(l''l) \xi^k(l'''l) \}, \quad (15)$$

where l, l', l'', l''' designate triples lmn, etc. and the $\alpha^{l'l''l'''}$ are the coefficients upon which the proper symmetry restrictions have been placed. If the values of the x^i's are substituted, it is readily seen that this reduces to the form

$$\sum_{\alpha\beta\gamma} \beta_{\alpha\beta\gamma}(\sigma_1\sigma_2\sigma_3) q_\alpha(\sigma_1) q_\beta(\sigma_2) q_\gamma(\sigma_3), \quad (15a)$$

in which σ_1, σ_2, σ_3 in a given term are subject to the condition

$$\sigma_1 \pm \sigma_2 \pm \sigma_3 = \mathbf{s}', \quad (16)$$

where s' is any vector such that

$$\mathbf{s}' \cdot \tau^i = 2\pi n_i, \quad (16a)$$

τ_i being one of the primitive translations (2) and n_i an integer. There are rather important restrictions upon the β's as we shall see later, but we shall not be interested in these at the present time.

If we now add the sum of terms (15) to the Hamiltonian function, we may obtain the new stationary states by use of an appropriate perturbation scheme such as that of Schrödinger or Brillouin-Wigner.[36] The unperturbed eigenfunctions of the system will be of the form

$$\Psi_o = \Pi_\sigma, \, _\alpha\psi(q_\alpha(\sigma), n_\alpha(\sigma)) \quad (17)$$

corresponding to a state in which the coordinate $q_\alpha(\sigma)$ is in the $n_\alpha(\sigma)$th quantum state. The corresponding perturbed function will be of the form

$$\Psi(\cdots, q_i(\sigma), \cdots; \cdots n_i(\sigma)) = \Pi_{\alpha\sigma}\psi(q_\alpha(\sigma), n_\alpha(\sigma)) + \sum_{\sigma_1\sigma_2\sigma_3} \sum_{\alpha\beta\gamma} \gamma(n'_\alpha(\sigma_1), n'_\beta(\sigma_2) n'_\gamma(\sigma_3))$$

$$\times \psi(q_\alpha(\sigma_1), n_\alpha'(\sigma_1)) \psi(q_\beta(\sigma_2), n_\beta'(\sigma_2)) \psi(q_\gamma(\sigma_3), n_\gamma'(\sigma_3)) \cdot \Pi'_{\sigma\alpha}, \, _\alpha\psi(q_\alpha(\sigma); n_\alpha'(\sigma)), \quad (18)$$

in which σ_1, σ_2, σ_3 satisfy the rule (16), Π' does not include the wave functions of the variables $q_\alpha(\sigma_1)$, $q_\beta(\sigma_2)$, $q_\gamma(\sigma_3)$ and

$$n_\alpha'(\sigma_1) = n_\alpha(\sigma_1) \pm 1,$$

$$n_\beta'(\sigma_2) = n_\beta(\sigma_2) \pm 1, \quad (19)$$

$$n_\gamma'(\sigma_3) = n_\gamma(\sigma_3) \pm 1.$$

The coefficients γ are proportional to matrix components of the cubic perturbation term (15), which we need only assume to be small. The conditions (19) follow from the harmonic oscillator nature of the unperturbed problem and it is to be understood that n' cannot be negative. In order to find the transition probability two states of the type (18), it is necessary to examine the matrix components of $\mathbf{p}(\mathbf{s})$ given by (14) since, as was pointed out there, this represents the dipole moment for the entire crystal, and from

the remarks made in §4 it follows that $\nu(\mathbf{s})$ will still be the principal frequency because Ψ_0 is the prominent term in Ψ. Because of the presence of the higher order terms in (18), this may possess nonvanishing dipole moment components with other states Ψ' arising from nonvanishing components between the first-order term of Ψ and the second-order terms of Ψ' and vice versa.

There are several prominent cases that we shall handle separately:

Case I. Let us assume that in Ψ the various waves of $q_\alpha(\sigma)$ are in states given by the quantum numbers $n_\alpha(\sigma)$. Then among the higher order terms, which will be a linear combination of other states, there will be characteristic terms in which the states corresponding to $q_\alpha(\sigma_1)$, $q_\beta(\sigma_2)$,

[36] The Schrödinger perturbation scheme may be found in any textbook on quantum mechanics. L. Brillouin, J. de phys. et rad. (III) 1, 373 (1932); E. P. Wigner Bull., Hung. Acad. (to appear shortly).

$q_\gamma(\sigma_3)$, $q_\delta(\mathbf{s})$ are given by

$$n_\alpha(\sigma_1)\pm1, \quad n_\beta(\sigma_2)\pm1, \quad n_\gamma(\sigma_3)\pm1, \quad n_\delta(s), \quad (20)$$

where σ_1, σ_2, σ_3 must satisfy the condition (16). There will clearly be 2^3 such states, unless some of the n's are zero in which case only the positive sign may appear. These higher order terms will possess important nonvanishing components only with that state Ψ' in which the zero-order term has quantum numbers $n_\alpha(\sigma)$, excluding those going with $q_\alpha(\sigma_1)$, $q_\beta(\sigma_2)$, $q_\gamma(\sigma_3)$, $q_\delta(\mathbf{s})$ in which cases the quantum numbers must be

$$n_\alpha(\sigma_1)\pm1, \quad n_\alpha(\sigma_2)\pm1,$$

$$n_\alpha(\sigma_3)\pm1, \quad n_\gamma(\mathbf{s})\pm1, \quad (21)$$

in which the signs of the first three terms must agree with those of (20), so that the energy difference between Ψ and Ψ' is

$$h(\pm\nu_\alpha(\sigma_1)\pm\nu_\beta(\sigma_2)\pm\nu_\gamma(\sigma_3)\pm\nu_\delta(\mathbf{s})), \quad (22)$$

that is, all energies corresponding to the sum (22) may be absorbed or emitted, the first case being that in which the resultant quantity is positive and the second that in which it is negative. If the matrix components between the zero-order term of Ψ and the higher order terms of Ψ' are considered, it is readily seen that they introduce no new possibilities, while the terms arising from interconnection of the higher order term of both Ψ and Ψ' will be cast aside as negligible.

Case II. If σ_1 (or either of the other two σ's) is equal to s, the argument of case I is practically repeatable, the only difference being that but three waves $q_\beta(\sigma_2)$, $q_\gamma(\sigma_3)$, $q_\delta(\mathbf{s})$ need be considered. The energies that may be absorbed or emitted are now given by

$$\pm\nu_\beta(\sigma_2)\pm\nu_\gamma(\sigma_3) \quad (23)$$
or
$$\pm\nu_\beta(\sigma_2)\pm\nu_\gamma(\sigma_3)\pm2\nu(\mathbf{s}), \quad (23a)$$

which are just the results one would obtain from (22) by setting $\nu_\alpha(\sigma_1)=\nu(\mathbf{s})$.

Case III. If either of the σ's were equal to zero, difficulty would arise from the fact that the corresponding states belong to a continuous spectrum, and a special treatment would be required, but we may safely assume that the absorption involved in any single transition of this type is negligible and that the cases in which σ is prac-

tically, but not quite zero (see below) are the really important ones. For these, the discussion given above is valid, and the frequencies absorbed or emitted are practically

$$\pm\nu_\alpha(\sigma_2)\pm\nu_\beta(\sigma_3)\pm\nu(\mathbf{s}). \quad (23b)$$

The additional cases in which all of the σ's are equal to s or zero do not occur as will be seen later.

It is perhaps wise to repeat that the negative signs in (22), (23), (23a) are valid only if the corresponding states are excited in Ψ, since this fact will give rise to much of the temperature dependent effects; that is, at sufficiently low temperatures only the positive signs will be important.

The absorption (or emission) coefficient for any given frequency of the allowed type will necessarily be small if the assumptions made here are essentially correct, and in order to obtain a region of strong absorption, it is necessary that there be a large number of allowable combinations of σ in the equations of Case I and II for which the energy absorbed is practically constant and the relation (16) is maintained.[37] This implies that the energy spectrum in the neighborhood of each of the combining σ's must be such that its gradient is practically zero, which can only occur when the σ's are in the vicinity of those regions of the zone for which the gradient actually does vanish. This implies the need for precise knowledge of the zone structure of each lattice dealt with, and an examination of the zones described previously for the face-centered lattice shows that there are seven values of σ for which the gradient vanishes. (σ's which are sent into one another by symmetry operations are not counted as different). As may be expected, these points correspond to the interaction of the zones with symmetry axes, so that the polarization direction of the waves may be determined at once. Thus in the (100) direction, it is evident that there will be one wave polarized in this direction (longitudinal wave), and two waves of equal energy (differing from that of the longitudinal wave) for which the polarization directions are orthogonal to this. These points are listed below along with the number of different energies going with the three direction of

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[37] The importance of this was realized by Born and Blackman in their work.

polarization. The actual energies in terms of the parameters $\alpha(1)$, $\cdots$, $\alpha(10)$ of the potential energy expression will not be given at this time since correlations have not yet been obtained.

1. Intercept of the (111) axes with the cube; there are three equal energies.

2. The origin corresponds to three equal energies.

3. Intercept of (100) axis with cube. The two transverse waves have equal energies differing from that of the longitudinal wave.

4. Intercept of the (110) type of axis with the cube. There are two different energies corresponding to a wave polarized in the (100) direction and two polarized in the plane orthogonal to this, the latter two being degenerate.

5. The center of the hexagonal faces of the truncated octahedron. The longitudinal wave is polarized perpendicular to the face, and has a different energy from that of the two degenerate transverse waves.

6. The center of the edge of a square face of the truncated octahedron (say the (100) face). There are three waves of different energy, one of which is polarized in a direction orthogonal to the plane passing through the (100) axis and the point. The other two polarization directions lie in the (011) and the $(0\bar{1}1)$ directions.

7. The intercept of the (011) axis with the truncated octahedron, bisecting one of the edges of a hexagonal face; the three waves are of different energies and their polarization axes lie along this axis and in the two symmetry planes which intersect it, respectively.

The points corresponding to these cases are indicated by the appropriate number in Fig. 9.

Of these seven cases, it is to be noted that 1 and 2, 3 and 4, and 6 and 7, respectively, possess σ's which differ by a vector of the type $\mathbf{s}^i$, so that of these three pairs, one member may be assumed to have the three, possibly degenerate, energies going with the lower part of the discontinuity and the other the energies going with the upper part. In case 5, for which $2\sigma = s^i$, the discontinuity is such that both upper and lower branches have values at the same point; that is, the discontinuity arises from an actual double-valuedness of the energy surfaces at this point—a property that is intimately tied up with the symmetry properties.

Were the β's in (15) all nonvanishing, it would be safe to say that the spectrum would possess as its most prominent secondary lines, those transitions of the type (23), (23a) and (23b) in which σ_2 belongs to the lower side of the discontinuity and σ_3 to the upper, or *vice versa*, and in which the signs before both of these are positive. For in these cases $\nu(\sigma_1) + \nu(\sigma_2)$ would vary very slowly as

σ_2 and σ_3 take on values permitted by the relation $\sigma_2 \pm \sigma_3 = \mathbf{s}^i$ since one of these decreases as the other increases, and there would be a large accumulation of transitions of nearly constant energy. It is readily seen that there would be 17 possible combinations of this type, namely, those listed below:

3 and 4—four lines (two different polarization energies);
5 and 5—four lines (two different polarization energies);
6 and 7—nine lines (three different polarization energies).

Designating these 17 sums, $\nu_\beta(\sigma_2) + \nu_\gamma(\sigma_3)$, as multiplet A, the 17 lines corresponding to (23) would appear on the large frequency side of the fundamental, $\nu(\mathbf{s})$, since they are all found to be greater than it. Similarly, this same multiplet will appear at an equal interval on the large frequency side of $2\nu(\mathbf{s})$ and $3\nu(\mathbf{s})$ corresponding to (23b) and (23a), respectively.

The 17 difference frequencies $|\nu_\beta(\sigma_2) - \nu_\gamma(\sigma_3)|$ which we shall designate as multiplet B, would also be prominent at high temperatures and, corresponding to the cases (23), (23b) and (23a) we should have the cases

$$B, \quad \nu(\mathbf{s}) + B, \quad 2\nu(\mathbf{s}) + B.$$

Similarly, if we designate $-A$ by $\bar{A}$ and $-B$ by $\bar{B}$, the cases

$$-\nu(\mathbf{s}) + A, \quad \nu(\mathbf{s}) + \bar{B}, \quad 2\nu(\mathbf{s}) + \bar{B}, \quad 2\nu(\mathbf{s}) + \bar{A}$$

would be of importance, and indicate that the multiplet A would appear between 0 and $\nu(\mathbf{s})$, that the inverted multiplet $\bar{B}$ would appear be-
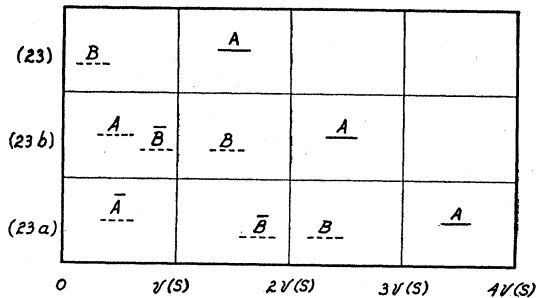

FIG. 10a. A schematic representation of the disposition of multiplets A, B and their inverses. The dotted lines represent lines that will disappear at very low temperatures. The three rows correspond to results arising from the three equations indicated.

tween 0 and $\nu(s)$ and $\nu(s)$ and $2\nu(s)$, respectively, and that the inverted multiplet $\bar{A}$ would appear between 0 and $\nu(s)$ (see Fig. 10a).

The restrictions on the β's, however, do not allow all of the 6×17 possible sums and differences of (23), (23a) and (23b) to appear, and in fact, the cases excluded are those corresponding to transitions in which states involving 1, 2, 3 and 4 are excited in any combination. This of

course, excludes the 4×3 transitions involving 3 and 4 mentioned above and also some others not yet discussed. This restriction may be brought out only by a detailed investigation of the type of trinomial expressions in the q's that may occur, the argument being essentially as follows.

In terms of the normal coordinates $q_\alpha(\sigma, c)$ and $q_\beta(\sigma, s)$ the displacement vector for the atom of type 1 or 2 situated at lmn is given by

$$x^i(lmn) = \sum_\alpha \sum_\sigma \{ q_\alpha(\sigma, c) f_\alpha{}^i(\sigma) p_\alpha(\sigma, lmn) \cos \sigma \cdot \mathbf{r}(lmn) + q_\alpha(\sigma, s) f_\alpha{}^i(\sigma) p_\alpha(\sigma, lmn) \sin \sigma \cdot \mathbf{r}(lmn) \}, \quad (24)$$

where $q_\alpha(\sigma)$ are the final normal coordinates, and σ extends throughout the entire cube in σ-space, $f_\alpha{}^i(\sigma)$, is the αth polarization vector going with the σth wave, which will be identical for like atoms, while $p_\alpha(\sigma, lmn)/p_\beta(\sigma, l'm'n')$ gives the relative amplitudes of the atoms at lmn and $l'm'n'$, assuming they have the same phase (this will be 1 if the atoms are identical). For the prominent values of σ in which we are interested, the polarization directions are identical for unlike atoms, so that we need not carry the indices lmn in these quantities.

Using (24), the quantity $\xi^1(l_i m_i n_i, lmn)$ is

$$\sum_\sigma \sum_\alpha \{ q_\alpha(\sigma, c) f_\alpha{}^i(\sigma) (p(\sigma, l_i m_i n_i) \cos \sigma \cdot \mathbf{r}(l_i m_i n_i) - p(\sigma, lmn) \cos \sigma \cdot \mathbf{r}(lmn))$$

$$+ q_\alpha(\sigma, s) f_\alpha{}^i(\sigma) (p(\sigma, l_i m_i n_i) \sin \sigma \cdot \mathbf{r}(l_i m_i m_i) - p(lmn) \sin \sigma \cdot \mathbf{r}(lmn)) \} \quad (25)$$

and if we set $\mathbf{r}(l_i m_i n_i) = \mathbf{r}(lmn) + \rho(l_i m_i n_i)$, this becomes

$$\xi^i = \sum_\sigma \sum_\alpha \{ [q_\alpha(\sigma, c) f_\alpha{}^i(\sigma) A(\sigma, l_i m_i n_i) - q_\alpha(\sigma, s) f_\alpha{}^i(\sigma) B(\sigma, l_i m_i n_i)] \cos \sigma \cdot \mathbf{r}(lmn)$$

$$+ [q_\alpha(\sigma, s) f_\alpha{}^i(\sigma) A(\sigma, l_i m_i n_i) + q_\alpha(\sigma, s) f_\alpha{}^i(\sigma) B(\sigma; l_i m_i n_i)] \sin \sigma \cdot \mathbf{r}(l_i m_i n_i) \} \quad (26)$$

where

$$A(\sigma, l_i m_i n_i) = -(p(\sigma, lmn) - p(\sigma, l_i m_i n_i) \cos \sigma \cdot \rho(l_i m_i n_i))$$

$$B(\sigma, l_i m_i n_i) = -p(\sigma, l_i m_i n_i) \sin \sigma \cdot \rho(l_i m_i n_i) \quad (27)$$

so that A is invariant under an inversion in lmn, while B goes into its negative. If terms of this type are substituted in one of the invariant forms of §2 and the result is summed over all values of lmn corresponding to like atoms, the result may be written in the form

$$\sum_{l_i m_i n_i} \gamma(l_i m_i n_i) \sum_{\sigma_1 \sigma_2 \sigma_3} \{ a(\sigma_1, l_i m_i n_i) a(\sigma_2, l_i m_i n_i) a(\sigma_3, l_i m_i n_i) - a(\sigma_1, l_i m_i n_i) b(\sigma_2, l_i m_i n_i) b(\sigma_3, l_i m_i n_i)$$

$$- b(\sigma_1, l_i m_i n_i) a(\sigma_2, l_i m_i n_i) b(\sigma_3, l_i m_i n_i) - b(\sigma_1, l_i m_i n_i) b(\sigma_2, l_i m_i n_i) a(\sigma_3, l_i m_i n_i) \} \quad (28)$$

where σ_1, σ_2, σ_3 must satisfy the relation (16), $l_i m_i n_i$ are summed over the values occurring in a given form with the proper coefficients γ, and

$$a(\sigma, l_i m_i n_i =) \sum_\alpha \{ q_\alpha(\sigma, c) f_\alpha{}^i A(\sigma, l_i m_i n_i) - q_\alpha(\sigma, s) f_\alpha{}^i B(\sigma, l_i m_i n_i) \},$$

$$b(\sigma, l_i m_i n_i) = \sum_\alpha \{ q_\alpha(\sigma, s) f_\alpha{}^i A(\sigma, l_i m_i n_i) + q_\alpha(\sigma, c) f_\alpha{}^i B(\sigma, l_i m_i n_i) \}. \quad (29)$$

Now since $\xi^i \xi^j \xi^k (l + \lambda_1 m + \mu, n + \nu)$ goes into $-\xi^i \xi^j \xi^k (l - \lambda, m - \mu, n - \nu)$ under inversion in the point lmn, the expression

$$\xi^i \xi^j \xi^k (l + \lambda, m + \mu, n + \nu) - \xi^i \xi^j \xi^k (l - \lambda, m - \mu, n - \nu) \quad (30)$$

must occur in each cubic invariant form if the first term does. As a result of this, it follows at once that in the result (28), when (29) is substituted, all terms not containing $B(\sigma, l_i m_i n_i)$ an odd number of times will vanish. Closer inspection shows quite readily that this fact does not depend upon the assumption that all three products in a given trinomial possess the same lmn and $l_i m_i n_i$.

Now in the cases 1, 2, 3 and 4 described previously, $\sin \sigma \cdot \rho(l_i m_i n_i) = 0$ for all values of ρ so that all intercombinations of these can give rise to no secondary maxima since the necessary combination of q's do not appear in (15).

For the combination of 5 and 1, and 6, 7, and 1, in the manner described above, this does not occur and all possible transitions are allowed, so that there are 13 frequencies $\nu_\beta(\sigma_2) + \nu_\gamma(\sigma_3)$ arising from these two cases, and the multiplets A and B as well as their inverses will contain this number of terms.

From the restriction discussed in the previous paragraph, it follows that the frequencies $2\nu(s)$, $3\nu(s)$ and $4\nu(s)$ may not occur as a combination of cases 1 and 2, as far as the cubic terms are concerned; moreover, it is easily seen that the case in which $\sigma_1 \neq s$ cannot lead to anything new if all restrictions are taken account of properly.

There is one additional possible source of secondary maxima, namely, those cases in which $\sigma_2 = -\sigma_3$ (and $\sigma_1 = s$), so that only transitions in which waves on the lower side or on the upper side play a role along with s are concerned. Such transitions undoubtedly have probabilities comparable with those considered above, but will probably not lead to maxima of the same intensity since the $\nu(\sigma_2) \pm \nu(\sigma_3)$ will not be constant for as large a range of σ_1 as in the preceding cases. It follows as before that only cases 5, 6 and 7 may occur along with 1.

At low temperatures, which means temperatures well below the characteristic temperature of the crystal, the peaks corresponding to cases in which negative signs occur in (23), (23a), (23b) (dotted lines in Figs. 10a and b) will disappear and only those in which all are positive will remain. The number of lines corresponding to these is 93 as compared with 260 in the high temperature case.

Part C. On the Correlation Between Experimental and Theoretical Results

If an attempt is made to find a satisfactory correlation between the preceding experimental and theoretical results, it is readily seen that the former is not complete enough either to confirm or deny the correctness of the latter. In the first place, it is essential that the fundamental frequency be unmistakably identified, and this is seen to be impossible at present because of the limitations on the long wave-length side of the spectrometer; that is, the absorption peak at 15.3μ would be the fundamental if it were definitely known that there were no additional high absorption regions beyond this, but that cannot be definitely stated. If the work of Strong can be accepted as correct, it would indicate that another region of absorption exists in the vicinity of 23μ. This difficulty may be removed by using another prism, such as one of KCl, or by using a grating spectrometer.

Second, the resolving power in the short wavelength region (5 to 10μ) of the present instrument is not sufficiently great to guarantee that the secondary structure has been determined to the same degree of accuracy as that in the region from 10 to 15μ; and, as a result, the position and number of peaks in the former region is not sufficient to test the symmetry about ν and 2ν, assuming the 15.3μ line is the fundamental.

Third, the broadening of all of the lines, because of the influence of high temperature on the coupling between waves, makes the precise position of the maxima very difficult to determine. This difficulty could be considerably reduced by

Fig. 10b. The plan is the same as that of Fig. 10a, the difference being that the multiplets arising from transitions involving waves on but one side of a discontinuity are shown.

cooling the observed sample to sufficiently low temperatures.

Concerning the precise position of the fundamental the following theoretical remarks may be made. If we make the very rough assumption that $\alpha(1)$ and $\alpha(2)$ are predominantly larger than any of the other 10 coefficients in B §2, and that these are related to the components of the stress-strain tensor, the fundamental frequency is found to be

$$\nu = (1/\sqrt{2}\pi)(A/M)^{\frac{1}{2}},$$

where

$$M = m_1 m_2/(m_1+m_2), \quad A = a(c_{11}+c_{44}),$$

a is the nearest distance between unlike atoms,

and c_{11} and c_{44} are the usual elastic coefficients. If the corresponding wave-lengths are determined using the results for the elastic coefficients discussed above, it is found that for NaCl and MgO the fundamental is at 49.5μ and 17.5μ respectively. Since the former is actually at 61.1μ, this suggests that the theoretical results are definitely low and indicates that the true value for MgO may be somewhat farther in the infrared.

In order to obtain experimental data that are capable of being compared with the preceding theoretical considerations, we are undertaking a thorough study of the absorption of the MgO crystal at low temperatures by means of an echelette grating spectrometer.

The Spectra of Strontium Hydride

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New SrH band systems photographed at high dispersion include: (1) an abbreviated $C\,^2\Sigma \rightarrow N\,^2\Sigma$ system with (0,0) band head at 3808A, (2) a many-lined $D\,^2\Sigma \rightarrow N\,^2\Sigma$ system between 5000A and 6700A, (3) an $E\,^2\Pi \rightarrow N\,^2\Sigma$ system consisting of a $\Delta v = 0$ sequence only with the (0,0) band at 5323A. The (0,0) and (0,1) C bands have three violent perturbations and a sharp cut-off due to predissociation at $K' = 19$. The form and magnitude of the perturbations are computed. Quantum analyses give $B_0 = 3.930$ and $D_0 = -9.31 \times 10^{-4}$ for the C state, $B_1 = 3.56$ for the normal state. Quantum assignments of the lines of the six principal branches of the (0,0) band of the E system are presented. For the E state $A = 117$, $B^*_{0, -\frac{1}{2}} = 3.6388$, $B^*_{0, +\frac{1}{2}} = 3.8687$ and perturbations at small J values distort the Λ-doubling curve for the $^2\Pi_{\frac{1}{2}}$ state.

Introduction

IT has previously been observed[1] that strontium hydride exhibits two band systems in the red region of the spectrum, a $^2\Sigma \rightarrow ^2\Sigma$ system with principal head at 7020A and a $^2\Pi \rightarrow ^2\Sigma$ system whose (0,0) band has heads at 7347A and 7508A. These bands lie slightly towards longer wave-lengths from the analogous systems of the CaH molecule. Since the lowest electronic levels of Sr and Ca are so very similar one would expect a fairly complete correspondence between the hydride spectra of these two elements.

In addition to the two CaH systems in the red there are three other systems[2] in the visible and

near ultraviolet. An interesting $^2\Sigma \rightarrow ^2\Sigma$ system consisting normally of but two bands, (0,0) at 3534A and (0,1) at 3696A, exhibits a sharp cut-off at $K = 9$ of the $v' = 0$ level due to predissociation. There is also in the range 4000A–5800A a weak $^2\Sigma \rightarrow ^2\Sigma$ system whose bands have no marked heads and whose upper vibrational levels all display violent perturbations. Finally, the existence of a $^2\Pi \rightarrow ^2\Sigma$ band at 4900A with Q branches having very closely spaced rotational lines has been noted. SrH band systems corresponding to all of these have been located by the writers. In each instance the system is displaced slightly towards the red from the position of the similar CaH system. We shall discuss in this paper the abbreviated $^2\Sigma \rightarrow ^2\Sigma$ bands in the near ultraviolet and the $^2\Pi \rightarrow ^2\Sigma$ system in the green region only.

[1] W. W. Watson and W. R. Fredrickson, Phys. Rev. **39**, 765 (1932).

[2] Cf. W. Jevons, *Report on Band Spectra of Diatomic Molecules* for references.