THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT

Part II. Its Infra-Red Activity

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1. INTRODUCTION

THE basic questions in relation to the infra-red activity of crystals are, *firstly*, how does the activity arise and *secondly* how is it related to the structure of the crystal? Since these two questions are closely connected, it is evident that answers to them could most appropriately be sought for in relation to crystals of the simplest possible structure and composition and of the highest possible symmetry. For, the various complications such as those arising from the details of molecular structure, molecular anisotropy and molecular interactions would be avoided and the questions requiring answer would present themselves in the most definite and tractable form. It is also essential that the case considered is one which could be most completely explored by spectroscopic methods and experimental data obtained which could be compared with the consequences of theory. NaCl is a case in which these requirements are satisfied and hence is very suitable as a test-case.

Infra-red activity minifests itself in three different ways which are susceptible of experimental study. Firstly, we have the refractivity of the material which as we pass from the visible into the infra-red region clearly exhibits the effect of infra-red activity. Secondly, we have the reflecting power of crystal surfaces, and thirdly, the absorption of radiation in its passage through the material. The absorption is a mass-effect and where it is very powerful as in the case of rock-salt, we could scarcely expect studies of it to reveal its relationship to the spectroscopic behaviour in an obvious fashion. It is indeed necessary to obtain spectrographic records of the percentage transmission by plates whose thickness is varied step by step over the widest possible range and to make a comparative study of the records in order to obtain any useful indications.

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In the present memoir, we shall cover various aspects of the subject. Firstly, we shall consider it from a purely fundamental and general standpoint. Secondly, we shall discuss the relation between infra-red activity and the free vibrations of the structure as considered in the first part of the memoir. Thirdly, the results of experimental studies of the kind indicated in the foregoing paragraph will be presented. Lastly, these experimental results will be correlated with those of Czerny and collaborators mentioned in the first part of the memoir and then compared with the consequences of theory.

2. THE ORIGIN OF INFRA-RED ACTIVITY

Viewed from the point of view of classical mechanics, the absorption of infra-red waves in their passage through a crystal can be considered as a transfer of energy which is effected by the electric field of the waves acting on the charged particles in its structure and setting them in vibration. If the frequency of the field is sufficiently close to the frequency of a normal mode of vibration, the possibility of resonance arises. But whether such resonance would actually occur is a question that needs examination.

As there are two types of charged particles in the structure, *viz.*, the nuclei and the electrons, it is appropriate at first to consider the effects of the radiation field on them separately. The nuclei besides being positively charged possess masses enormously large compared with those of the electrons. It is a familiar consequence of classical mechanics that in a normal vibration the common centre of inertia of the particles of the system remains at rest. Likewise, in our present problem, the common centre of inertia of all the nuclei included in the vibrating structural unit would remain at rest in any free vibration. Hence, when all the nuclei have the same mass, as for example, in a crystal of diamond or silicon or germanium, the common centre of the positive charges carried by the nuclei would remain undisturbed during the vibration. It follows that when the crystal is traversed by infra-red radiation, the forces exerted by the field on the positive charges would in the sum total be unable to transfer energy to the crystal and hence they could not possibly excite such vibrations. The situation would be the same even when the nuclei in the crystal belong to different species, provided that the ratio of the masses to the charges is the same for the different nuclei, as is the case for example with rock-salt or quartz. It follows that the positive charges of the nuclei do not play any role in the infra-red activity of the crystals. *All the observed effects arise from the action of the field of incident radiation on the negatively charged electronic clouds.*

The question then arises why the infra-red absorption spectra of a crystal should be related in any way or bear any resemblance to the spectrum of free vibrations of the atomic nuclei considered in the first part of the present memoir. The answer to this is that there is a connecting link between the infra-red absorption and the vibration spectrum of the atomic nuclei. This is to be found in the fact that the electronic clouds are held in the crystal by their interactions with the positively charged nuclei; *vice versa*, the nuclei are held in their places by their interactions with the electronic clouds. Hence, a periodic disturbance of the electronic clouds produced by the field of the radiation *may* tend to disturb the nuclei from their positions and set them in synchronous vibration. *Vice versa*, vibrations of the nuclei *may* tend to disturb the electronic clouds and set them in synchronous vibration. A periodic movement of the electronic cloud is a *sine qua non* for the production of the effects described under the term of infra-red activity. Hence, unless a free vibration of the nuclei is associated with and gives rise to such a movement of the electronic clouds, it would not be set up under the action of the periodic external electric field.

The foregoing discussions, apart from emphasising the fundamental role played by the electrons in the absorption of infra-red radiation and other related effects, make it clear why the *asymmetry* of the nuclear vibrations plays such a highly important role in infra-red activity. For, in the absence of such asymmetry, there would be no periodic displacement of the electronic clouds and hence no excitation of the nuclear vibrations.

3. INFRA-RED ACTIVITY OF THE NORMAL MODES

From what has been stated in the preceding paragraph, it is clear that the four modes in which the Na nuclei alone or the Cl nuclei alone oscillate either normally or tangentially to the octahedral planes could not exhibit any infra-red activity. For, in these modes, two layers of Na nuclei approach or recede from an intermediate layer of Cl nuclei symmetrically on either side with equal amplitudes. Hence, the movements of electronic charges resulting therefrom when summed up over each of the structural elements of the crystal would vanish. This conclusion would be valid irrespective of the actual amplitude of the nuclear movements. Hence the four modes of the octahedral class can be disregarded in our consideration of the infra-red activity of the normal modes of vibration. We need only examine the behaviour of the five other normal modes in which the Na and Cl nuclei appearing in the cubic layers execute coupled oscillations.

The principal normal mode of highest frequency in which the Na and Cl lattices oscillate in a balanced movement stands in a class by itself

and will therefore be considered first. By reason of the difference in the masses of the Na and the Cl nuclei, the amplitude of movement of the Na nuclei would be proportionately greater than that of the Cl nuclei and hence the amplitudes of oscillation of the electronic clouds respectively held by them in close association would also be different. But by reason of the difference in the positive charges of the two nuclei, the negative charge of the electrons so held would be smaller for the Na nuclei than for the Cl nuclei. The resulting displacements of negative charge when totalled up would therefore cancel out more or less completely. What would be left over and needs special consideration is the part of the electronic cloud which comes under the influence of both sets of nuclei and its movements under the action of the field of incident radiation.

During one half-period of the oscillation, the Cl nucleus on one side of a Na nucleus approaches it and the Cl nucleus on the other side recedes from it. During the other half-period, these movements are reversed. It is clear, however, that the asymmetric displacements of electric charge with which we are here concerned would be in the same direction on both sides of the Na nucleus and that they would be reversed in successive half-periods of the oscillation. Hence, they would not cancel out but would add up to produce a periodic displacement of negative charge having the same frequency as the incident waves. Further, since the oscillation of the nuclei repeats itself from cell to cell, the effects of all the cells would add up and hence would result in a large effect. In other words, the normal mode of highest frequency would be powerfully infra-red-active, and it would need only a very small thickness of the material to make such activity manifest. The coherent phase relationship between the oscillations of electric charge in the adjacent cells of the structure would have a further consequence. The oscillating electric charges at and near the surface of the crystal would act as secondary sources of radiation and their conjoint action would result in a powerful reflection of the incident radiation at the surface of the crystal. This effect would be most powerful at and near the frequency of the normal mode under consideration. For, at such frequencies, the movements of the nuclei would be most vigorous and hence the displacements of negative electric charge associated therewith would be large.

The four other modes of coupled oscillation of the Na and Cl nuclei stand on an entirely different footing. In these modes, the oscillation reverses its phase as it passes from one cubic layer of the crystal to the next. Hence, the displacements of electric charge would be in opposite phases in the alternate layers and when summed up would cancel each other out. Hence, these four normal modes would not exhibit any infra-red activity.

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This statement is however subject to various qualifications, since it rests on two assumptions. The first assumption is the complete independence of the normal modes of vibration. The second assumption is that the amplitudes of vibration are extremely small. If these assumptions are not valid, the conclusion drawn that the four normal modes are inactive would also need reconsideration.

4. OVERTONES OF THE NORMAL FREQUENCIES

So far, we have proceeded on the basis of the theory of small vibrations of a connected system of particles in the classical mechanics. The curious feature of the case is that the forces which are effective in exciting the vibrations are not those acting on the masses, viz., the positively charged nuclei, but on the springs, viz., the negatively charged electrons which hold them together and effectively determine their frequencies of vibration.

We have now, of necessity, to introduce the fundamental notions of the quantum theory. The energy of the radiation appears in quanta proportional to its frequency and if such energy is to be completely taken up by the oscillators with which we are concerned, viz., the group of 8 Na and 8 Cl nuclei, the frequency of the mechanical oscillations should be the same as that of the incident radiation. In other words, we would have resonance. But we have also to consider the cases in which the frequency of the free vibration is not the same as that of the incident radiation. Of special interest are the cases in which the frequency of the incident radiation is a small multiple of the frequency of the oscillator, and hence the absorption of energy would involve the acceptance by the oscillator of two, three or larger number of quanta of the energy of radiation. It may be presumed that the probability of this happening would diminish rapidly with the increasing number of quanta thus taken up, in other words that the absorption would then become rapidly weaker and weaker in the series. But since we are dealing with a crystal, there should be no difficulty in observing such absorption. We have only to increase the thickness of the absorbing plate sufficiently to be able to record the absorption spectra of the higher orders.

The further question then arises, what is the factor which determines the diminishing strength of the absorption with the increasing number of quanta taken up by the oscillator? We may remark that an increase in the magnitude of the energy taken up involves an increase of the amplitude of the resulting vibration. The absolute dimensions of the oscillator being small, the amplitude of the movements corresponding only to one quantum of energy could by no means be considered as small, and the amplitude corresponding to two, three more quanta would far transcend any such

limits. The movements of the electronic clouds which are the operative cause of infra-red activity would become more and more nearly comparable with the dimensions of the electronic clouds more closely associated with the Na and the Cl nuclei. It would clearly, in these circumstances, cease to be justifiable to assume that the classical theory of small vibrations and its consequences would correspond with the facts of experiment. In other words, the appearance of overtones of the normal frequencies in absorption and the diminishing strength of such absorption with increasing frequency are both associated with the increasing amplitude of the resulting vibrations and the consequences arising therefrom.

We have already noticed that the normal mode of highest frequency would exhibit infra-red activity with great strength. It follows that this mode would also exhibit infra-red absorption of the higher orders in a conspicuous manner. It is also evident that the absence of infra-red activity of the four other modes of coupled oscillation which was remarked upon earlier would not extend to absorption of the higher orders corresponding to frequencies which are multiples of the frequencies of free vibration in those modes. For, their inactivity in the first order absorption was ascribed to the opposition of the phase of the oscillation in the alternate layers of the structure in those modes. When the amplitudes are large, the displacements of charge in one layer and in the next layer where the phase of the motion is opposite would not be numerically of equal magnitude and hence when they are summed up they would not cancel out completely. The residue would have twice the frequency of the oscillation. The octaves of these modes could therefore be expected to appear in absorption with considerable strength.

Another important consequence of the amplitudes of vibrations not being small is that the various normal modes would cease to be completely independent of each other. The sharpness of resonance which is a characteristic consequence of the theory of small vibrations would be notably departed from when, as in the present case, we have five normal modes which are spread over a wide range of frequencies and are not restricted to small amplitudes of vibration. In these circumstances, the energy of the incident radiation can be taken up for the excitation of vibrations which may be desc.ibed as a superposition of two or more normal modes approximating to each other in frequency. It is also possible for a vibration to be excited which may be described as a superposition of one normal mode as a fundamental with another normal mode as an overtone with a frequency which is not very different. More generally, the radiation may excite vibrations which may

be described as a summation of two or more normal modes differing from each other in frequency and either as fundamentals or as overtones.

Earlier, we discussed the reflection of infra-red radiation which occurs when the incident radiation has the same frequency as the normal mode of highest frequency. We have now to remark that reflections of notable strength may also arise at other frequencies in consequence of the incident radiation exciting superposed vibrations of the kind referred to above with sufficiently large amplitudes. We shall have occasion to consider such cases later in this memoir.

5. THE ABSORPTION SPECTRA OF ROCK-SALT

Some excellent specimens of transparent salt were available in the museum of the Institute and it appeared worthwhile to study their behaviour in absorption, making use of the Leitz infra-red recording spectrophotometer with KBr optics which covers the spectral range between $13\,\mu$ and $24\,\mu$. This, of course, is much outside the wavelength range within which powerful infra-red reflections are exhibited by rock-salt. The considerations set forth above however indicate that the absorption spectra of the higher orders could be recorded within the range of the instrument and evidence thus obtained both for the existence of such absorption and its relation to the specific modes and frequencies of vibration of the atomic nuclei in the crystal. Nine different thicknesses of the absorbing material ranging from $5 \cdot 2$ cm. down to $1 \cdot 5$ mm. were employed and their transmission percentages were recorded. A comparative study of the records reveals some very significant features. To illustrate them, the nine records are reproduced below in the text as Figs. 1 to 9, the absorption path being indicated below each figure.

Figure 1 recorded with a block $5 \cdot 2$ cm. thick exhibits nearly complete transparency at $13\,\mu$, followed by a progressive fall to opacity at $18 \cdot 5\,\mu$, beyond which there is a complete cut-off of all transmission. Very similar features are also exhibited in Figs. 2 and 3 which were recorded with blocks which were respectively $4 \cdot 3$ and $2 \cdot 8$ cm. thick. It will be noticed, however, that a rapid improvement in transparency in the wavelength range between $13\,\mu$ and $14 \cdot 5\,\mu$ appears as the absorption path is diminished. Whereas a difference of 18% in the transmissions at $13\,\mu$ and $14 \cdot 5\,\mu$ is noticed in Fig. 1 for the block $5 \cdot 2$ cm. thick, the difference is only 12% in Fig. 2 for a thickness of $4 \cdot 3$ cm. and only 5% in Fig. 3 for a thickness of $2 \cdot 8$ cm. On the other hand, in the region of longer wavelengths, as will be seen on a comparison of Figs. 1, 2, 3, 4 and 5, there is little or no change in transmission produced by the large change in the absorption path from $5 \cdot 2$ to $1 \cdot 5$ cm.
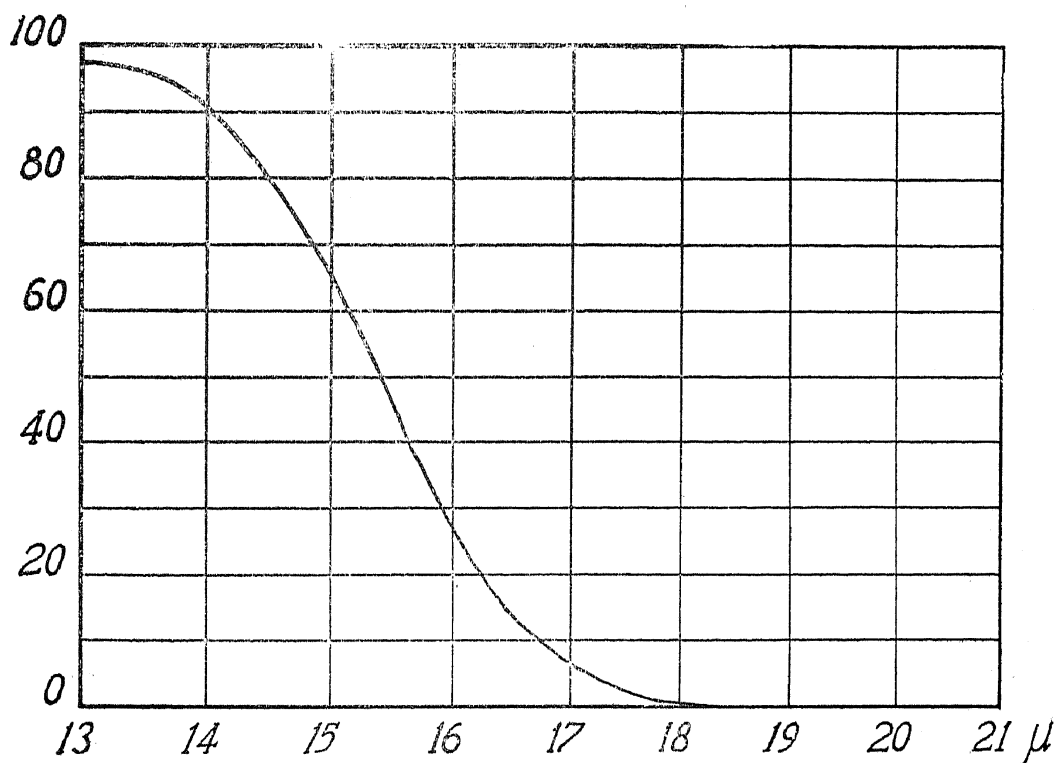
FIG. 1. Infra-Red Absorption by Rock-Salt : 5·2 cm.

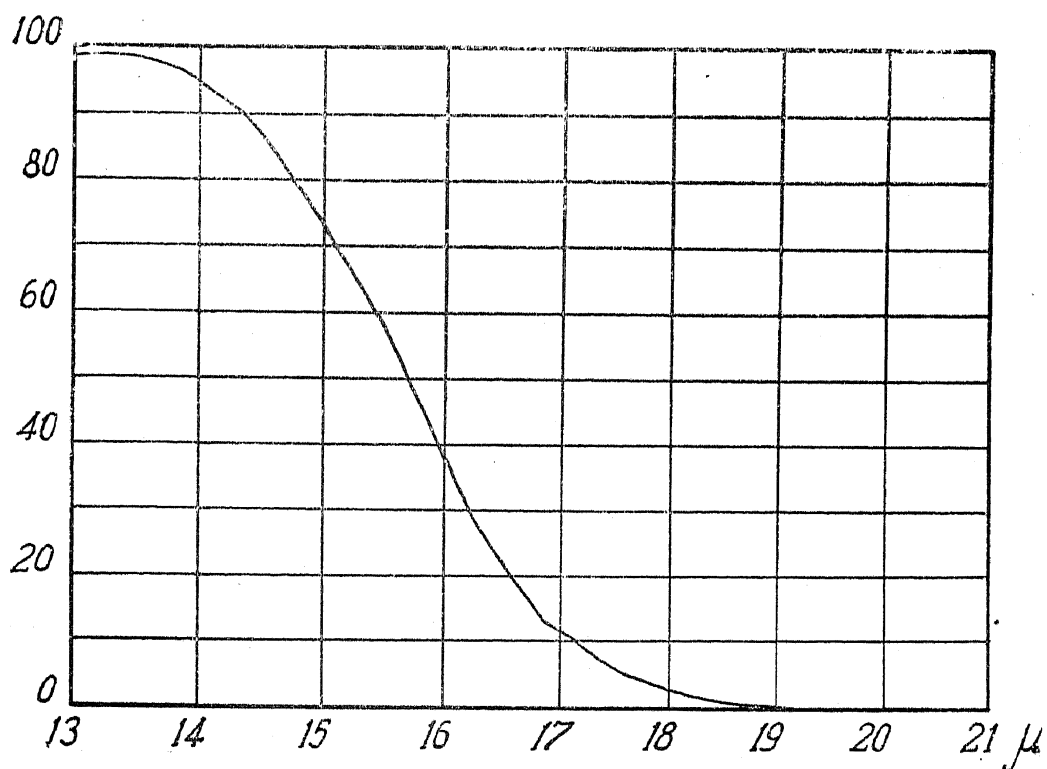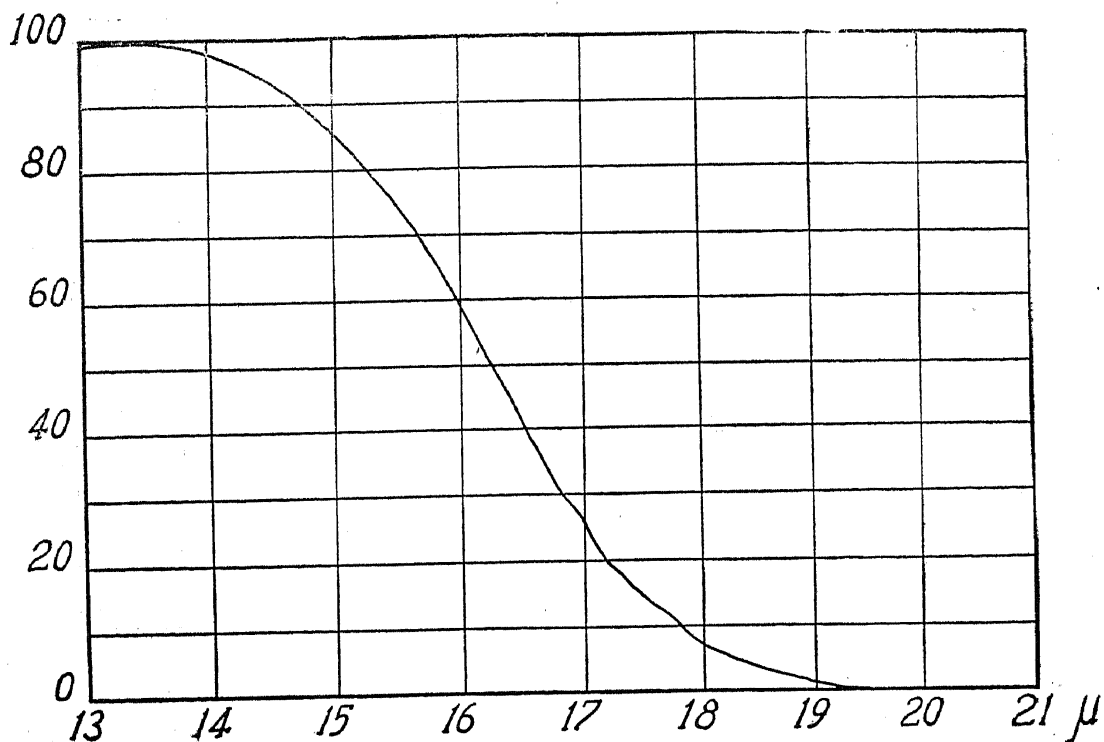
FIG. 2. Infra-Red Absorption by Rock-Salt : 4·3 cm.

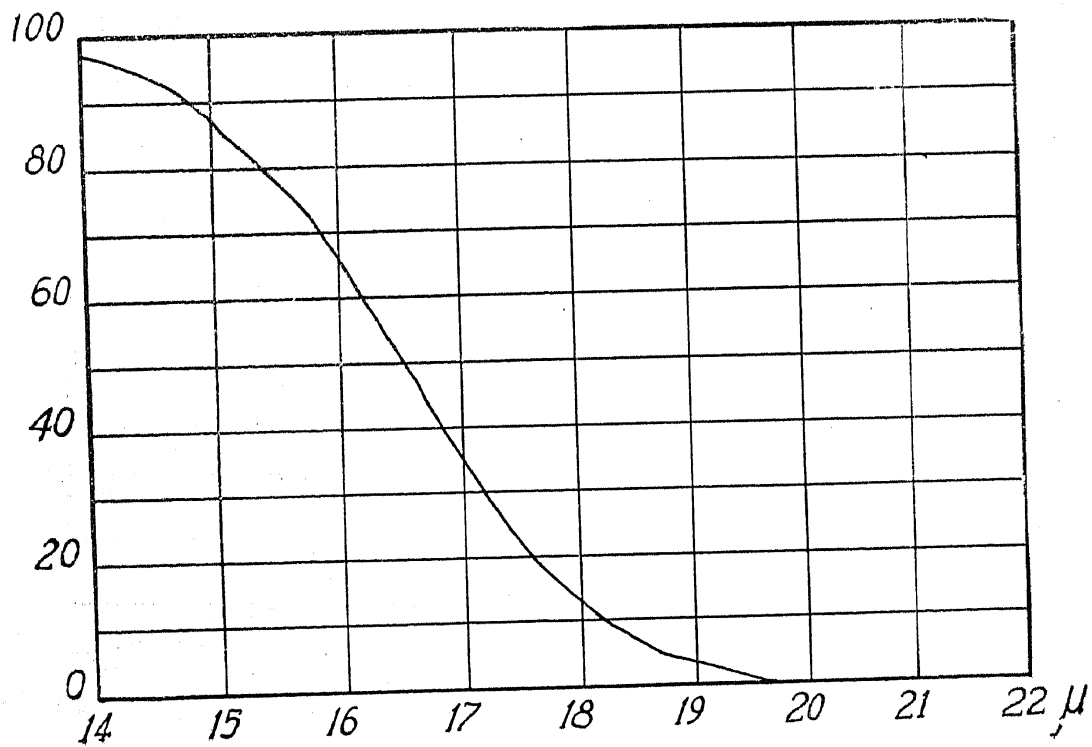FIG. 3. Infra-Red Absorption by Rock-Salt : 2·8 cm.

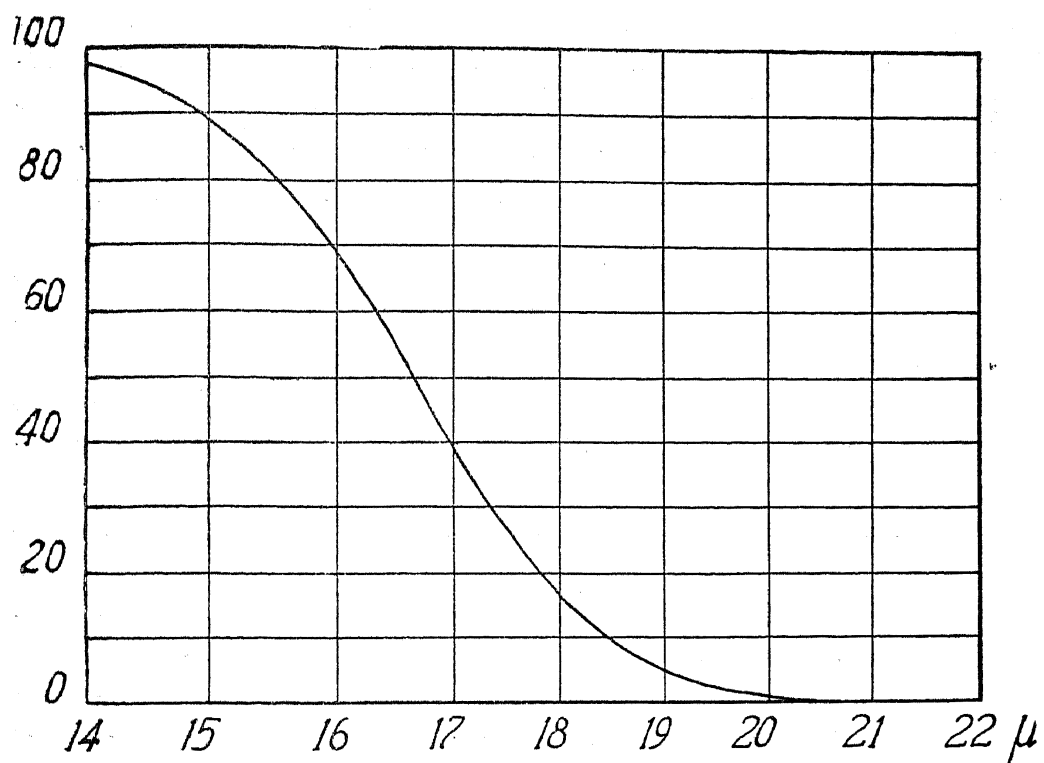FIG. 4. Infra-Red Absorption by Rock-Salt : 2·1 cm.

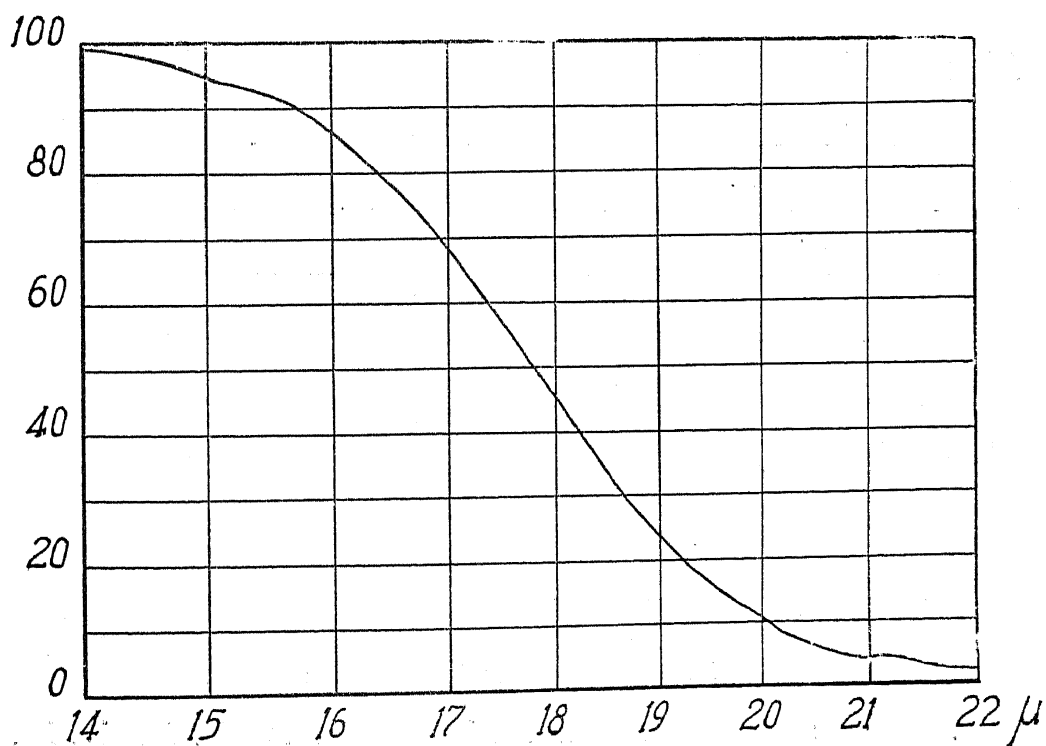Fɪɢ. 5. Infra-Red Absorption by Rock-Salt : 1·5 cm.

Fɪɢ. 6. Infra-Red Absorption by Rock-Salt : 0·8 cm.

The cut-off of the longer wavelengths persists and the transmission at $19\,\mu$ is either zero or very small in all five cases. It is clear from the spectro-graphic records that the absorptions in the spectral regions from $13\,\mu$ to $19\,\mu$ and from $19\,\mu$ to $24\,\mu$ are of totally different orders of magnitude.

As is to be expected in the circumstances stated above, very striking changes appear in the form of the transmission curve when the thickness is greatly reduced and is of the order of a few millimetres only. Figures 6 to 9 are the records respectively for plates of thickness 8 mm., 4 mm., 2·5 mm. and 1·5 mm. The cut-off in the region of the longer wavelengths has now disappeared and is replaced by a transmission which increases from 25% at $19\,\mu$ to 72% at the same wavelength as the thickness is diminished from 8 to 1·5 mm.

We may here draw attention to the remarkable fact that the percentage transmission curves are by no means always smooth graphs showing a progressive and continuous fall in transmission with increasing wavelength. Dips and sudden changes in direction are a noticeable feature. That they represent genuine features and not accidental faults in recording is shown by their appearance in the graphs for different thicknesses at the same wave-
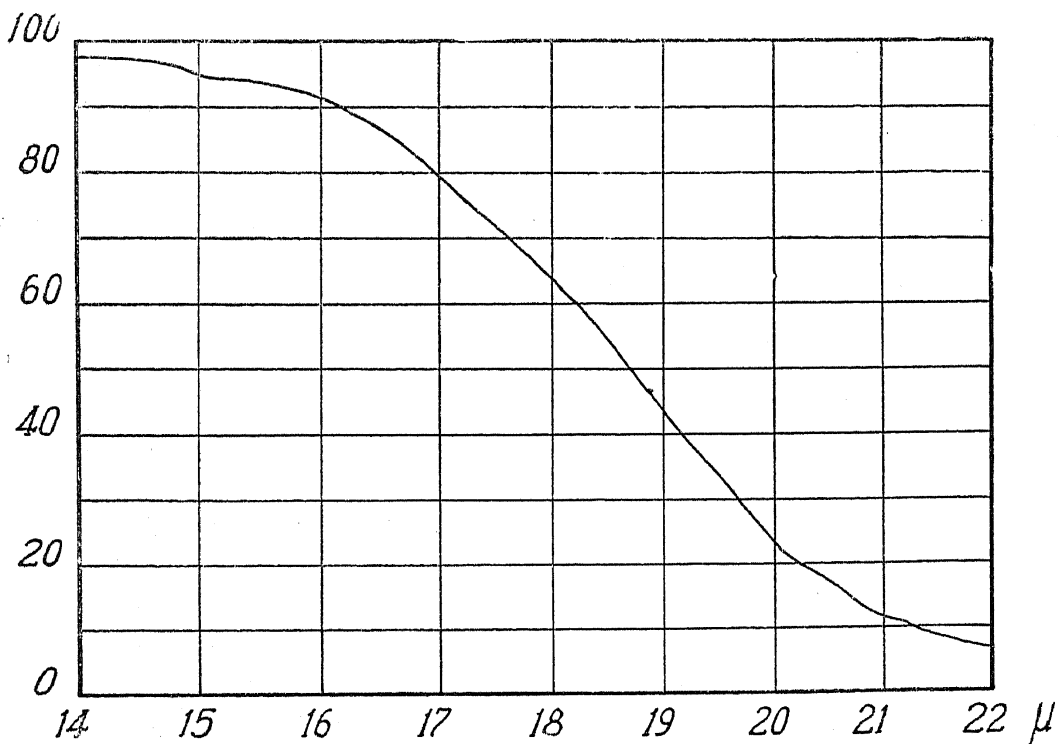

FIG. 7. Infra-Red Absorption by Rock-Salt : 0·4 cm.

lengths. It will suffice here to draw special attention to Fig. 8 which is the record for a plate 2·5 mm. thick. The curve as reproduced commences
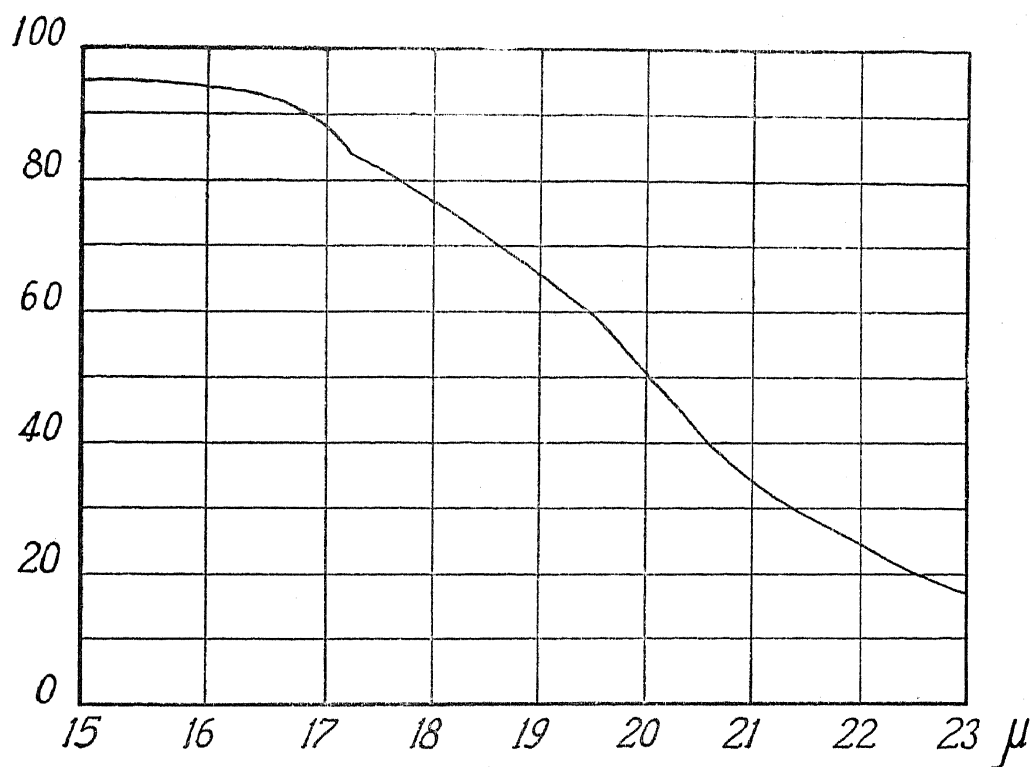
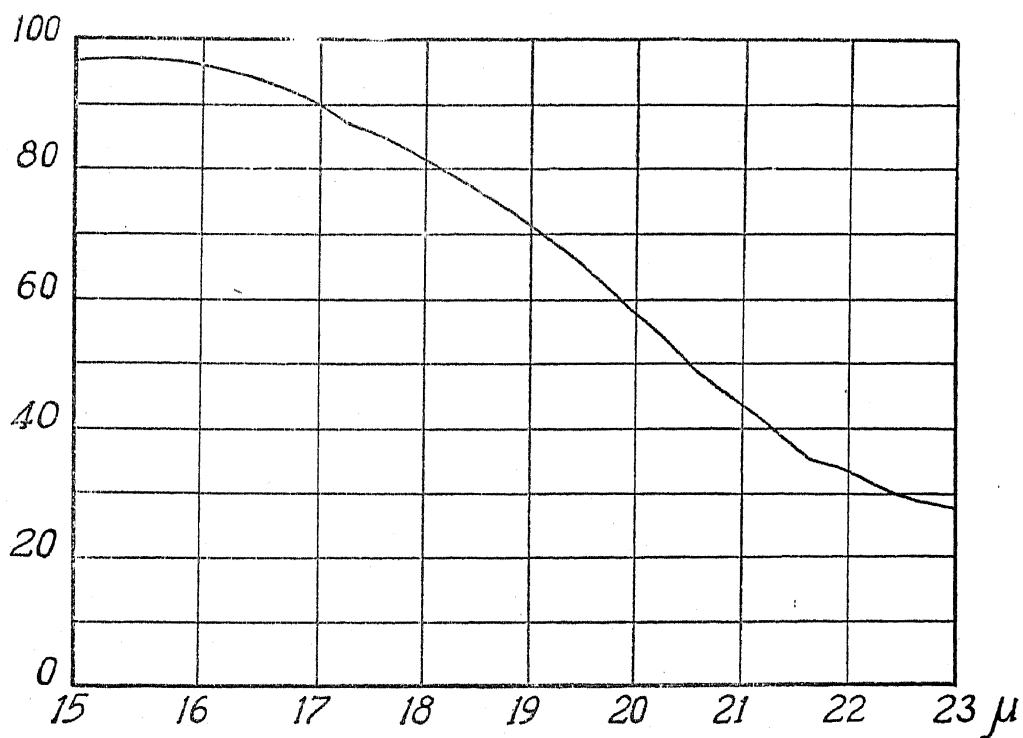FIG. 8. Infra-Red Absorption by Rock-Salt : 0·25 cm.

FIG. 9. Infra-Red Absorption by Rock-Salt : 0·15 cm.

with a 90% transmission at 15 μ. This drops down rapidly and takes a sudden turn at 17·2 μ. Another change in direction is noticeable at 19·5 μ, still another at 20·7 μ and finally a small but distinct change in direction at 22 μ.

6. SIGNIFICANCE OF THE RESULTS

We shall now proceed to show that the experimental results set forth above and also the results of the published studies of Barnes and Czerny, and of Mentzel cited in the first part of this memoir find an intelligible explanation in the light of the theoretical considerations expounded earlier in this memoir. We shall commence by assuming that the frequencies of the five modes of coupled oscillation of the Na and the Cl nuclei in rock-salt at room temperature are as shown below in Table I, both as wavelengths and as wave-numbers. The figures find their justification in the theoretical calculations presented in the first part of the memoir and corrected on the basis of the spectrographic data emerging from Rasetti's investigation. Table I also shows the overtones of the five frequencies up to and inclusive of the fifth order.

TABLE I

Vibration frequencies of rock-salt

Mode		I Order	II Order	III Order	IV Order	V Order
I	cm.$^{-1}$	180	360	540	720	900
	μ	55·6	27·8	18·5	13·9	11·1
II (a)	cm.$^{-1}$	150	300	450	600	750
	μ	66·7	33·3	22·2	16·7	13.3
II (b)	cm.$^{-1}$	129	258	387	516	645
	μ	77·5	38·8	25·8	19·4	15·5
II (c)	cm.$^{-1}$	110	220	330	440	550
	μ	90·9	45·5	30·3	22·7	17·9
II (d)	cm.$^{-1}$	92	184	276	368	460
	μ	109	54·5	36·2	27·2	21·7

A scrutiny of the figures in Table I enables us to understand the absorptive behaviour of rock-salt in the various ranges of frequency. In the wave-length range between $13\,\mu$ and $18\,\mu$, the absorptions that could manifest themselves are the fourth-order absorptions of modes I and II (*a*) and the fifth-order absorptions of modes II (*a*), II (*b*) and II (*c*). These would necessarily be very weak and would need large absorption paths to enable them to be observed. They would also disappear quickly when the path is diminished. In the wavelength range between $18\,\mu$ and $24\,\mu$ the third-order absorptions of modes I and II (*a*) would appear, supplemented by the fourth-order absorptions of modes II (*b*) and II (*c*) and the fifth-order absorptions of mode II (*d*). The strength of the third order absorptions would naturally be far greater than of those of higher orders appearing between $13\,\mu$ and $18\,\mu$. It is, therefore, not surprising that thicknesses which allow a notable transmission in that region are completely opaque to greater wavelengths.

The vibrations of the structure responsible for the absorptions of the third, fourth and fifth orders would necessarily be of large amplitude. In consequence, the vibrations excited would be a superposition of the various normal modes approximating to each other in frequency and not the individual modes by themselves. In these circumstances, we could scarcely expect to find any observable evidence of the discreteness of the normal modes. Nonetheless, some indications of it do appear. The remarkable features noticed in the absorption curve reproduced in Fig. 8 for a thickness of $2 \cdot 5$ mm. may be cited as an example.

The absorptions of the second order would be far more powerful than those of the third order. Hence, much thinner layers, of the order of a hundred microns or less, would be needed to obtain any observable transmission in the region where the second-order absorptions operate. There is however much less crowding up of the normal modes. Hence it should be possible to find observational evidence of the discreteness of the absorption frequencies. The arrest in the absorption curve at about $34\,\mu$ noticed by Mentzel with rock-salt plates some 30 microns thick is clearly identifiable with the second-order absorption of mode II (*a*) listed in Table I. Likewise, the arrest extending from $40\,\mu$ to $44\,\mu$ and observed with plates 8 microns thick by Barnes and Czerny is clearly a superposition of the second-order absorptions of modes II (*b*) and II (*c*) shown in Table I.

Using evaporated films of NaCl only a few microns thick, Barnes and Czerny succeeded in obtaining an observable transmission in the spectral region where the infra-red activity is strongest and intense reflections appear. They studied the spectral character of the transmitted radiation for various

thicknesses of the films employed by them. The results which they reported, as also Czerny's observations on the variations of the reflecting power with wavelength, form a study in themselves. They are more appropriately discussed in a later part of this memoir.

SUMMARY

Infra-red activity is shown to be a consequence of the periodic movements of the electron clouds in the crystal excited by the field of the incident radiation. The accompanying oscillations of the positively charged nuclei determine the frequencies but are not themselves the cause of the activity.

It is shown that of the nine modes of free vibration of the rock-salt structure, the mode of highest frequency is intensely active both in the first and the higher orders. Four other modes are inactive in the first order but active in higher orders. The remaining four are totally inactive. Spectrographic records of the absorption of rock-salt over a wide range of thicknesses are presented and explained in terms of the activity of these modes. The results reported by Mentzel and by Barnes and Czerny on the transmission spectra of rock-salt are explained on the same basis.