

# The vibrations of the MgO crystal structure and its infra-red absorption spectrum—Part III. Comparison of theory and experiment

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## 1. Introduction

Part I of this memoir dealt with the observed infra-red behaviour of MgO over the spectral range covered by the instruments at the disposal of the author. In part II, the normal modes of vibration of the atomic nuclei in the crystal about their positions of equilibrium were deduced from the principles of classical mechanics and expressions were given for the frequencies of the nine modes which were shown to be possible. In the present part, we shall concern ourselves with a comparison of the results of experiment and the consequences of the theory. Such a comparison has necessarily to be based on the nature of the relationship between infra-red activity and the modes of vibration of the atomic nuclei. We shall freely make use of the ideas and principles which have emerged from studies on the infra-red behaviour of diatomic, triatomic and polyatomic molecules, as also of crystals having more complex structures. It will be found that these ideas and principles when applied to the particular circumstances of the case enable a highly satisfactory concordance to be established between the facts of experiment recorded in part I of the memoir and the dynamical theory developed in part II.

## 2. Infra-red activity of the first order

A fact which emerges very clearly from the experimental studies described in part I is that the normal mode which is strongly active as a fundamental has also the highest frequency of all the active normal modes. The theoretical formulae for the frequencies obtained and set out in part II also show that the mode of vibration in which the Mg and the O atoms oscillate in opposite phases and in which the oscillation repeats itself from cell to cell without change of phase has a higher frequency than all the other eight modes. This is obvious from the approximate formulae given in section 4 of part II and the situation is not altered when the

higher approximations set out in section 5 are considered. It is further evident that this normal mode would exhibit a powerful infra-red activity of the first-order. For, the displacements of electric charge resulting from the approach to or recession from each other of the two dissimilar atoms Mg and O would occur in the same phase in the successive cells of the structure and hence their effects would be cumulative.

Considering now the eight other normal modes, they can all be described as movements of the Mg atoms or of the O atoms alone or of both sets of atoms together in one or another of the different directions permitted by the symmetry of the structure. But a common feature of all the eight modes is that these movements alternate in phase along one or two or all three of the directions which are the edges of the unit rhombohedral cell of the lattice. Hence, the displacements of charge in the successive cells of the structure are in alternate phases. Therefore, when summed up over an element of volume including a block of eight contiguous cells in the structure, the displacements of charge would cancel out. It follows that all the eight modes under reference would fail to exhibit any infra-red activity of the first-order. In other words, we cannot expect their fundamental frequencies to manifest themselves as absorption maxima in the spectrographic records. This again is in agreement with what is actually observed.

Here a distinction must be drawn between the four normal modes which involve simultaneous movements of the Mg and O atoms in directions which are either normal or tangential to the cubic planes of the crystal and the four other normal modes in which the Mg atoms alone or the O atoms alone oscillate in directions which are normal or tangential to the octahedral planes of the crystal. As has already been remarked in part II, the Mg atoms and the O atoms appear in distinct layers in the octahedral planes in such manner that each Mg layer has O layers on either side of it at the same distance and each O layer has likewise Mg layers situated symmetrically on either side. Further, in the normal modes of these four species, the Mg layers on either side of the O layers, or the O layers on either side of the Mg layer oscillate in opposite phases. As a consequence, the displacements of electric charge on either side of the middle layer are in opposite directions. When summed up over the volume element containing eight unit cells of the structure, they cancel out. Such cancellation is clearly *absolute*; in other words, it is not limited to the case in which the movements of charge are regarded as of very small amplitude and therefore strictly harmonic in character.

Thus, the two categories of normal modes, viz., those in which the Mg and O atoms oscillate simultaneously and those in which they oscillate separately stand on a different footing. The former are inactive in the first-order absorption by reason of the alternation of phase in the successive cells of the structure. The absence of activity depends on the oscillation being of small amplitude and the displacements of charge resulting therefrom being of equal magnitude but opposite in phase in successive cells. On the other hand, in the second category, the cancellation is effective irrespective of the actual amplitude of the oscillations.

### 3. Infra-red activity of higher orders

The considerations set forth above naturally lead us to consider the possibility of the normal modes exhibiting infra-red activity of higher orders, in other words of manifesting themselves in the absorption spectra as overtones of the fundamentals. The appearance of overtones in the infra-red absorption spectra of diatomic and polyatomic molecules is a familiar fact of experience. It is also well known that they are much weaker than the fundamentals, which is indicated by the fact that their observation needs the use of much thicker absorbing layers. The explanation usually given for their appearance is based on the hypothesis of the anharmonicity of the molecular vibrations of which the effect comes into prominence when the oscillations of the atomic nuclei are of very large amplitude. In these circumstances, the periodic displacements of electric charge which give rise to the absorption of infra-red radiation include components not only of the fundamental frequencies but also the overtones of those frequencies. Absorption of the energy of radiations having the overtone frequencies and its transformation to the energy of nuclear vibrations is thereby made possible.

The important point regarding the infra-red activity of higher orders is that the amplitudes of nuclear vibration should be large. Even when this condition is satisfied, considerations regarding the symmetry of the modes of vibration may, in particular cases, totally exclude the manifestation of the effect of the periodic displacements of charge and hence also the possibility of the infra-red activity of all orders. We have already noticed such a situation in the case of the modes involving oscillation of the Mg atoms alone or of the O atoms alone in directions normal or tangential to the octahedral layers. Hence these four modes could not be expected to manifest themselves as overtones in the infra-red absorption spectra. The position is different in regard to the five other modes which involve simultaneous movements of the Mg and the O atoms. No such restriction based on considerations of the symmetry appears in their cases. Hence we may expect overtones of all these five modes to manifest themselves in the absorption spectra, provided the necessary condition of the largeness of the amplitudes of the nuclear vibrations is satisfied.

The dynamical theory set out in part II of the memoir is based on the well known theorem in classical mechanics regarding the small vibrations of a connected system of particles about their positions of equilibrium. The theorem enables the relative magnitudes of the amplitudes of their vibration in any particular normal mode to be evaluated. But it leaves their absolute magnitudes undetermined. But, since we are now concerned with the absorption of radiation, the introduction of the ideas of the quantum theory, which is inevitable, results in making the amplitudes of vibration fully determinate. The incident radiation consists of energy quanta of magnitude  $h\nu$ . Assuming for the sake of simplicity that the oscillators are strictly harmonic with a frequency  $\nu_0$ , their energy would go up with increasing amplitude by successive equal steps of

$h\nu_0$ . The successive orders of absorption would then appear as a consequence of equating  $h\nu$  to  $h\nu_0$ , or  $2h\nu_0$  or  $3h\nu_0$  or  $4h\nu_0$ . Mechanical anharmonicity of the oscillators would only result in the energy values deviating from this regular harmonic sequence. What is needed for the possibility of infra-red activity of higher orders is that the oscillations of electric charge associated with the nuclear movements should include a harmonic series of components having the frequencies  $2\nu_0$ ,  $3\nu_0$ ,  $4\nu_0$ , etc. The energy of radiation having those frequencies can then be taken up by the moving charges and transferred to the atomic nuclei as energy of mechanical movement, in other words, as heat energy.

From what has been stated, it is clear that if we identify the mechanical oscillators in the crystal as *domains of macroscopic size*, infra-red absorptions of orders higher than the first would be impossible. For, when the oscillatory energy of such a domain is quantised, the actual amplitudes of oscillation of the atomic nuclei and therefore also the movements of electric charge associated with them would be infinitesimal. The only possibility would then be the absorption of the first-order in which  $h\nu = h\nu_0$  and absorptions of higher order cannot arise. Thus, for absorptions of higher order to be at all possible, we must assume the oscillators in the crystal to be of extremely small dimensions, in other words to be the unit cells of the crystal structure or small groups of such unit cells. The oscillators whose normal modes were listed and enumerated in part II of the memoir were twice as large in each direction as the unit cells of the crystal structure. If their energies are quantised, the amplitude of the atomic oscillations in domains of such small size would be sufficiently large to permit of infra-red absorption of higher orders than the first.

We may sum up the results of this discussion by the statement that of the nine normal modes listed in table 2 of part II of the memoir, mode I would be active both as a fundamental and as overtones, modes II, III, VIII and IX would be inactive as fundamentals but could be active as overtones, while modes IV, V, VI and VII would not be active either as fundamentals or as overtones.

#### 4. Frequencies of the active modes

The frequencies of the normal modes of vibration were derived in section 4 of part II on the assumption that the only interactions which need be taken into account are those between unlike atoms in the structure. This assumption is valid only in respect of the active mode of the highest frequency. The approximate formulae derived on that basis are however useful as they enable the frequencies of the five active modes to be expressed in terms of each other. Two force-constants appear in the formulae, viz.,  $\alpha$  and  $\beta$ ,  $\alpha$  being the longitudinal and  $\beta$  the transverse component of the interaction between adjacent unlike atoms. It may be presumed that  $\alpha$  is greater than  $\beta$ , but the ratio of  $\alpha$  to  $\beta$  is not known. We

Table 1. Frequencies of the normal modes: Observed and calculated ( $\text{cm}^{-1}$ )

	Mode I	Mode II	Mode III	Mode VIII	Mode IX
Observed	490	423	365	313	277
Calculated	490	428	380	309	237
$\alpha = 2\beta$					
Calculated	490	441	393	293	212
$\alpha = 3\beta$					
Calculated	490	408	408	271	270
$\alpha = \beta$					

assume the highest frequency of the five to be  $490 \text{ cm}^{-1}$  and compute the others for various values of the ratio  $\alpha/\beta$ , viz.,  $\alpha = \beta$ ,  $\alpha = 2\beta$  and  $\alpha = 3\beta$ . Table 1 above shows the results thus obtained.

It will be seen that the five frequencies follow each other in the same order for all three  $\alpha/\beta$  ratios, though the actual magnitudes of the calculated frequencies are different. The best agreement between the calculated and the spectroscopically determined frequencies results from the most reasonable assumption for the  $\alpha/\beta$  ratio, viz., that  $\alpha = 2\beta$ . The mode of lowest frequency, viz., mode IX, is however seen to be an exception. Mode IX, it may be remarked here, is an oscillation of the cubic planes tangential to themselves, the Mg and the O atoms in those planes moving in the same phase. Like all the other modes listed in table 1 except the first, it is inactive as a fundamental but active as an octave. By the nature of the case, however, such activity would be feeble. Referring to the absorption curves of the thinnest MgO film reproduced as the upper of the two records in figure 10 of part I of this memoir, it will be noticed that the transmission falls off more steeply in the region of wavelengths greater than  $20 \mu$  than towards shorter wavelengths. The form of the graph between  $16 \mu$  and  $20 \mu$  indicates that a specific absorption is operative which is located midway between them, viz., at about  $18 \mu$ . We are, therefore, justified in adding  $277 \text{ cm}^{-1}$  and the wavelength  $36 \mu$  to the list of normal modes and their characteristic wavelengths in the summary of experimental results which concludes part I.

## 5. Relation between reflectivity and infra-red absorption

We may now proceed to discuss the manner in which the reflecting power of the surface of an MgO crystal changes with wavelength in the spectral range between  $13 \mu$  and  $36 \mu$ . The experimental results obtained and reported by Burstein,

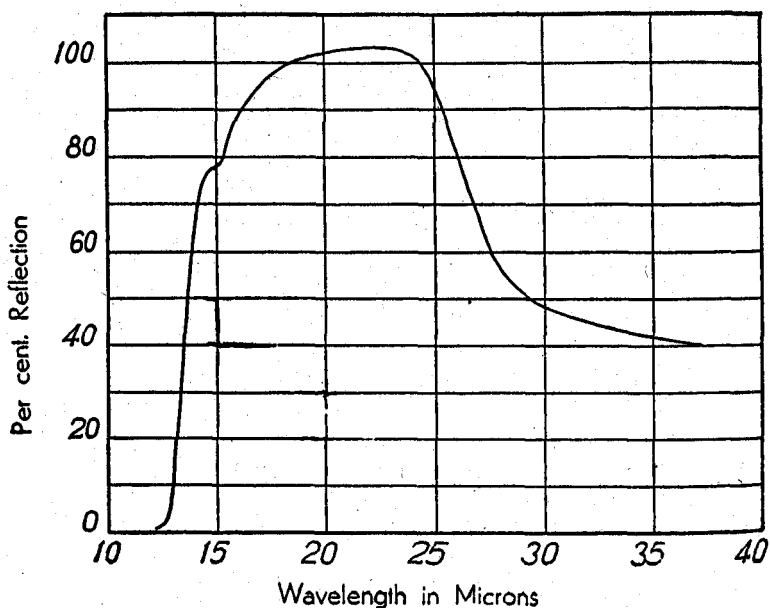


Figure 1. Reflecting power of MgO surface.

Oberly and Plyler (1948) have already been referred to in part I of this memoir. Their figure which shows the reflecting power as compared with an aluminium mirror is reproduced as figure 1 above in the text. One might expect that the peak of the reflecting power would appear at the wavelength  $20.4 \mu$  which corresponds to the active fundamental frequency of  $490 \text{ cm}^{-1}$ . However, we have also to consider in this connection, the other normal modes of vibration of the crystal. Besides the active fundamental at  $20.4 \mu$ , there is the inactive fundamental close to it in frequency which has a characteristic wavelength at  $23.64 \mu$  and a series of other inactive fundamentals at still greater wavelengths, viz.,  $27.4 \mu$ ,  $32 \mu$  and  $36 \mu$ . Then again, in the region of wavelengths less than  $20.4 \mu$ , octaves of the normal modes appear which have their characteristic wavelengths at  $10.2 \mu$ ,  $11.82 \mu$ ,  $13.7 \mu$ ,  $16 \mu$  and  $18 \mu$  respectively. All these octaves have been shown to be active in absorption. The possibility therefore arises of their making an observable contribution to the reflecting power of an MgO surface.

As already noticed, the absorptions located at  $10.2 \mu$  and  $11.82 \mu$  are so weak that they can only be recorded with comparatively thick plates. We may, therefore, exclude them from consideration and need only take note of the absorptions located at  $13.7 \mu$ ,  $16 \mu$  and  $18 \mu$ . It is significant that the reflective power of MgO reaches large values in this range of wavelengths. It rises very steeply at about  $13.7 \mu$  and after exhibiting an inflexion or arrest at  $15 \mu$ , goes up

again in the wavelength range between  $16\ \mu$  and  $18\ \mu$  before it reaches the peak reflectivity beyond  $20\ \mu$ . Indeed, the course of the reflectivity curve is itself the clearest demonstration that the octaves at  $13.7\ \mu$ ,  $16\ \mu$  and  $18\ \mu$  contribute notably to the reflecting power; the arrest at  $15\ \mu$  arises from the frequency gap between the first two.

Figure 1 shows that the reflecting power continues to increase a little beyond  $20.4\ \mu$  and is greatest at about  $24\ \mu$ . Beyond  $24\ \mu$ , it falls rather quickly at first and then more slowly, but remains large up to  $35\ \mu$  and beyond. These facts find a natural explanation if we assume that the second fundamental having its characteristic wavelength at  $23.64\ \mu$  makes a notable contribution to the reflecting power. This is indeed to be expected. For, when the frequency of the radiation is equal to or near the frequency of the active fundamental, the movements of electric charge at and near the surface of the crystal would be large. In these circumstances, the different normal modes of vibration may be expected to influence each other in such a manner that a mode which is ordinarily inactive could be excited to activity. That the observed powerful reflection extends up to  $24\ \mu$  and even beyond it is therefore not surprising.

## 6. Frequencies of the inactive modes

The approximate formulae given in section 4 of part II enable us also to evaluate the frequencies of the inactive modes, viz., those in which the O atoms alone or the Mg atoms alone oscillate in terms of the highest active frequency, viz.,  $490\ \text{cm}^{-1}$ . We obtain  $380\ \text{cm}^{-1}$  and  $309\ \text{cm}^{-1}$  respectively as the frequencies of vibration of the O and of the Mg atoms. It is evident, however, that these figures are an underestimate of the actual frequencies of these modes. For, as is also clear from the formulae of section 5 of part II, the frequencies of these modes are determined by the interaction of each oscillating atom with the six like atoms in its immediate vicinity as well as with the six unlike atoms which are its nearest neighbours. As the distance between like atoms is only  $\sqrt{2}$  times the distance between unlike atoms, we may safely assume that the two sets of interactions would be of comparable magnitudes and hence that the vibration frequencies would be definitely greater than  $380\ \text{cm}^{-1}$  and  $309\ \text{cm}^{-1}$  indicated by the first approximation.

The neglect of the interactions between like atoms also results in the frequencies of oscillations of the Mg and of the O atoms normal to the octahedral planes having the same frequency as oscillations tangential to them. Actually, however, oscillations normal to the octahedral planes may be expected to have frequencies noticeably greater than the modes tangential to those planes.

Earlier, it was remarked that by reason of their geometric symmetry, modes IV, V, VI and VII would be totally inactive, in other words, that they would be wholly

inaccessible to observation by the methods of infra-red spectroscopy. This statement was, however, based on the assumption that the normal vibrations of the structure are completely independent of each other. Since, however, we are concerned with the infra-red activity of higher orders than the first, the amplitudes of vibrations involved are not small and the normal modes cannot therefore be completely independent of each other. The possibility thus arises of the inactive modes or rather of their overtones revealing themselves in the spectroscopic records by a species of induced activity resulting from the contiguity of their frequencies to the frequencies of strongly active modes.

Referring to the spectrographic records reproduced as figures 3, 4, 5, 6, 7 and 8 in part I of this memoir, it will be noticed that the transmission curve in the region between  $10.2\ \mu$  and  $11.82\ \mu$  exhibits certain curious features appearing in all of them and at precisely the same spectral wavelengths. The transmission which is a minimum at  $10.2\ \mu$  rises to a maximum and then drops to the second minimum at  $11.82\ \mu$ ; but between the two minima, the graph does not follow a smooth curve but bends inwards more or less sharply in the vicinity of two wavelengths, one on either side of the  $11\ \mu$  ordinate. One such bend may be located at  $10.8\ \mu$  and the other at  $11.2\ \mu$ . The sharp bends at these two positions appear very clearly, for example, in figure 6 of part I. The frequencies in wave-numbers at which these singularities appear are respectively  $925\ \text{cm}^{-1}$  and  $893\ \text{cm}^{-1}$ . If we assume that they represent the octaves of two normal modes exhibiting induced activity, their frequencies would be  $463\ \text{cm}^{-1}$  and  $446\ \text{cm}^{-1}$ , substantially greater than the  $380\ \text{cm}^{-1}$  indicated by the rough calculation in which the interactions between the oxygen atoms nearest to each other are totally ignored. But the increases are not greater than what might be expected to result from such interactions being taken into account.

The induced activity of modes VI and VII in which the magnesium atoms alone oscillate is not so conspicuously exhibited in the spectrograms reproduced in part I of this memoir. Indications of them, however, appear in the wavelength range between  $12\ \mu$  and  $13\ \mu$  in figures 6, 7 and 8 of part I. The sharp bends in the transmission curve at  $12.5\ \mu$  and at  $12.9\ \mu$  noticed in figure 8 are perhaps their clearest manifestation. Interpreting these singularities as arising from the octaves of the normal modes VI and VII, we obtain their characteristic wavelengths at  $25\ \mu$  and  $25.8\ \mu$  respectively and their characteristic frequencies as  $400\ \text{cm}^{-1}$  and  $387\ \text{cm}^{-1}$ . These are substantially higher than the rough value of  $309\ \text{cm}^{-1}$  which results when we neglect the interactions between each magnesium atom and the six nearest magnesium atoms which appear in the more exact expressions for the frequencies of these modes. The observed frequencies indicate that these interactions are far from being weak or negligible. The electron atmospheres of the magnesium atoms extend further from their nuclei and hence would come into closer contact with each other in the unit cells of the structure than would be the case for the oxygen atoms. Hence the forces of interaction as between like atoms may be expected to be even more powerful for Mg than for O atoms.



## 7. Some concluding remarks

Our purpose so far has been to show how closely the consequences of the dynamical theory set out in part II and the observed infra-red behaviour of MgO in absorption and in reflection described in part I fit into each other and how we are thereby enabled to obtain a clear and comprehensive view of the subject. Formal considerations based on the concept of interatomic forces, of displacements of electric charge resulting from atomic movements and of their symmetry characters were sufficient for that purpose. It would not, however, be superfluous to add a few remarks here regarding other fundamental aspects of the infra-red behaviour of crystals.

A question of some importance is the role played respectively by the atomic nuclei and by the electrons in the infra-red activity of crystals. The displacements of the massive atomic nuclei from their positions of equilibrium are necessarily involved, since the frequency of the absorbed radiation is identical with or approximates to a frequency of vibration of the atomic nuclei about their positions of equilibrium or to a small multiple thereof. But we have also to emphasise the part played by the electrons which hold the nuclei together and determine the magnitude of the interatomic forces and hence also effectively determine the frequencies of the nuclear vibrations. There can be little doubt that it is the displacement of these electrons induced by the field of the incident radiation which is the effective cause of infra-red absorption. The nuclear movements can make no direct contribution of importance to the displacements of electric charge. For, the oscillations of some of the atomic nuclei are in opposition of phase to the oscillations of the others and hence their effects would cancel out.

It follows from what has been stated above that the dynamic theory of the vibrations of the atomic nuclei and its consequences represent only one aspect of the subject of the infra-red behaviour of crystals. The other aspect is the behaviour of the electrons which hold the nuclei together in their places. These two aspects are closely related to each other. Hence, while there should be an easily observable correlation between the features of the vibration spectra of the atomic nuclei deduced from the theory and the spectral characters of the absorption and reflection of infra-red radiation as found in experiment, a complete agreement in respect of all details of their features is scarcely to be expected.

## 8. Summary

The description of the nine normal modes of vibration and their frequency formulae given in part II enable them to be grouped together in respect of infra-red activity and arranged in each group in diminishing order of frequency. A

detailed comparison then becomes possible between the consequences of the theory and the experimental results set out in part I. A comprehensive and satisfactory agreement emerges from the comparison. The modes can be identified and their frequencies determined directly from the spectroscopic records. The manner in which the reflectivity of an MgO surface varies with the wavelength of the infra-red radiation also receives a satisfactory elucidation.