

The vibrations of the MgO crystal structure and its infra-red absorption spectrum—Part I. The results of experimental study

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1. Introduction

The fundamental questions requiring an answer which arise in relation to the infra-red behaviour of crystals are the following: What is the nature of the vibration spectrum of the atomic nuclei in a crystal? How is this vibration spectrum related to its observed infra-red absorption spectra? What is the mechanism of the reflection and of the absorption of infra-red radiation by crystals? A precise and detailed experimental study of the infra-red behaviour of some crystals of simple structure may be expected to furnish an answer to these questions.

Magnesium oxide crystallises in the cubic system and, if the material is pure, the crystals are transparent and colourless. The structure of MgO is similar to that of rock-salt and is thus very simple. Moreover, the binding forces between the atoms being much stronger and their reduced mass much smaller for MgO than for NaCl, the infra-red absorption of MgO appears in a region much more readily accessible to precise investigation than that of rock-salt. Hence, MgO would be a most appropriate choice of material for a study of the kind referred to above.

A collection of MgO crystals came into the writer's hands many years ago as a gift from the Norton Company of Worcester, Mass., USA. Somewhat later, a single crystal of large size was received by him from AD Mackay, Inc. of Broadway, New York. It had long been the intention of the writer to make use of this material for a thorough investigation of the kind envisaged in the foregoing paragraphs. Only recently, however, has the availability at this Institute of an infra-red recording spectrograph by Messrs Leitz of Wetzlar provided with both NaCl and KBr optics enabled this desire to be fulfilled. The results of the experimental study made with this instrument are described and discussed in this first part of the memoir. In the subsequent parts of the memoir, their theoretical implications and their further consequences are worked out.

The reflecting power of a freshly cleaved surface of an MgO crystal relative to an aluminium mirror was determined by Burstein, Oberly and Plyler (1948) for the spectral region between $10\ \mu$ and $35\ \mu$ and the results were presented in a paper published in these *Proceedings* some years ago (*Proc. Indian Acad. Sci.*, 1948, A28, 388). The same authors also recorded the transmission of infra-red radiation in the wavelength range between $5\ \mu$ and $13\ \mu$ of five cleavage plates of MgO of thicknesses ranging from 9.2 to 0.9 mm. Graphs showing these five transmission curves (in part) and grouped together were reproduced as a figure in the same paper. As regards the reflecting power of MgO, the work of Burstein, Oberly and Plyler was complete and their results will be made use of and discussed in the present memoir. The position is rather different with reference to their studies of the transmission through MgO. Their work did not reveal all the significant features of the behaviour of MgO in this respect. A full and complete picture of the facts is clearly necessary before it is possible for their real significance to emerge. It was with a view to fill the lacunae in the published results of Burstein, Oberly and Plyler that the present experimental research was undertaken.

2. Some general considerations

In the spectrographic investigations with cleavage plates, we are interested in determining the percentage of transmission through the plate and of ascertaining the spectral composition of the transmitted radiation and the manner in which it varies with the thickness of the plate. The loss in transmission may be divided into three parts: (a) the loss by reflection at the surface of incidence, (b) the loss by absorption within the material and (c) the loss by reflection at the surface of emergence. The relative proportions of these three losses would evidently vary with the circumstances, including especially the thickness of the plate, as this would determine the magnitude of the true absorption loss. When the reflecting power is large, the three losses would add up and it would become difficult to extricate them from each other and evaluate them separately.

At wavelengths greater than $13\ \mu$, the reflecting power of MgO is small, as was shown by Burstein, Oberly and Plyler, and its alteration with wavelength would therefore not be significant. Hence in the spectral region between $5\ \mu$ and $13\ \mu$ covered by their studies of the transmission by MgO, the interpretation of the observations presents no particular difficulty. The position is, however, different in the wavelength range between $13\ \mu$ and $15\ \mu$ in which the reflecting power was shown by Burstein *et al.* to rise steeply from nearly zero to 75%. This rapid increase would make it difficult to determine how the absorption loss within the material varies with wavelength in the same range. However, by making observations with different thicknesses, the existence of a true absorption could be

demonstrated. The position would be much more difficult in the wavelength range between $15\ \mu$ and $25\ \mu$. The reflecting power in this range is very high and hence the percentage transmission would be small and difficult to determine, unless indeed the plate is itself so thin that the full reflecting power would be unable to manifest itself. Indeed, it is clear that for an elucidation of the infra-red behaviour of MgO in the wavelength range between $15\ \mu$ and $25\ \mu$, it would be necessary to work with extremely thin layers of the material, not exceeding a few microns.

A method of obtaining MgO films for the study of their transmission properties which has been frequently employed by the earlier investigators is that of the deposition of the fumes of burning magnesium on a plate transparent to infra-red radiation. It will suffice here to refer to the work of A O Momin published in these *Proceedings* in which references to the earlier literature will be found (*Proc. Indian Acad. Sci.*, 1953, A37, 254). Momin made a series of measurements with fourteen different thicknesses of MgO films prepared by fuming on to a KCl plate from a burning magnesium ribbon. Commencing with an extremely thin layer which was just visible, the thickness was progressively increased by adding more layers of MgO on the same plate by fuming up to a thickness of about 2.4 millimetres when the films begin to break away from the KCl plate. The readings were taken with a single-beam Beckman Model IR 2 infra-red spectrophotometer making point-to-point observations. Four typical graphs which between them cover the whole range of thicknesses employed have been reproduced with Momin's paper. They show some interesting features, but it is quite clear on an inspection of the graphs that they do *not* represent the real transmission curves of MgO at any of the thicknesses used and that on the other hand they depict a complex effect in which the scattering of infra-red radiation in its passage through the optically heterogeneous film produced by the deposition of the fumes and the extinction produced by such scattering play a highly important role.

The spurious and misleading nature of the results given by fumed films of MgO becomes evident when it is remarked that to exhibit an observable transmission in the wavelength range between $15\ \mu$ and $25\ \mu$, the thickness of the film cannot exceed a few microns. Films of this order of thickness should be fully transparent in the wavelength range between $1\ \mu$ and $13\ \mu$. Actually, Momin's graph for his thinnest film shows a transmission of only 17% at $1\ \mu$. This increases fairly rapidly to 70% at $5\ \mu$ and then more slowly to 80% at $13\ \mu$. The optical heterogeneity of the film has thus a notable effect on its transmission up to $13\ \mu$. Hence, to assume that it would cease to influence the behaviour of the film at still greater wavelengths is clearly unjustifiable. The falsity of the assumption is demonstrated by the comparative studies made at this Institute with fumed MgO films and with two other techniques presently to be described. The publications by earlier investigators who have based themselves and their theoretical discussions on the results obtained with fumed MgO films are vitiated by this error and are therefore entirely valueless.

3. Methods of the present investigation

Since MgO crystals exhibit an easy cleavage parallel to the cube faces, it is possible to obtain a whole series of plates suitable for the observation and of various thicknesses ranging from several millimetres down to about a tenth of a millimetre. It is desirable to use a fairly large crystal to start with. The area of the plates detached from it would then be sufficient to make a satisfactory recording of the transmission curves. The cleavage surfaces are not always optically as smooth as could be desired. It is necessary in such cases to grind and polish both the faces to as high a degree of optical perfection as practicable. To obtain plates thinner than about a tenth of a millimetre, two alternative techniques are available. That employed in the present investigation was to grind and polish both faces of a cleavage plate about a millimetre thick to start with and having made observations with it, to grind one of the faces with the finest grade of carborundum abrasive until the thickness is reduced to the extent desired. The ground face is then repolished and the transmission recorded. This process can be repeated and the transmission by plates which are progressively thinner and thinner can be studied until the practical limit to the applicability of the method is reached. This limit is set by the fragility of the material. With plates of fair size, it is possible to reduce the thickness to about 50 microns, while with smaller sizes one can go down to about 20 microns.

An alternative technique is to immerse a cleavage plate in hot concentrated hydrochloric acid and allow the acid to act until the thickness of the plate has been reduced to the desired extent. The defect of this technique is the unsatisfactory nature of the resulting surfaces.

To obtain the extremely thin absorption layers with which one could expect to find an observable transmission in the spectral range between $15\ \mu$ and $25\ \mu$, the following technique was adopted in the present investigation. A small fragment of an MgO crystal was reduced to the finest possible state of subdivision by prolonged grinding in an agate mortar. A little of the material thus obtained was stirred up into a thin paste with liquid paraffin. The transmission in the KBr range of the spectrograph by the thinnest possible layer of this paste held between two KBr plates was recorded, the absorption by the paraffin being compensated by a similar layer of the liquid alone held between two KBr plates. As a test of the satisfactory nature of the technique, the transmission in the NaCl range was also recorded.

Another technique which was also adopted was to mix a very small quantity of very finely divided MgO with one gram of finely powdered KBr and to compress the MgO-KBr mixture under high pressure in a vacuum into a flat tablet of which the transmission was recorded. By varying the quantity of MgO which was put into the tablet, the effective absorption path could be increased to the extent desired.

Since the paste and pellet techniques gave very similar results, it was not

considered necessary to try out still another possible procedure of obtaining thin films of MgO, viz., that of evaporating the material in a vacuum and depositing it on a suitable support.

4. Review of the results

The wavelength scale of the recording spectrograph for the NaCl optics covers the range between $1\ \mu$ and $15\ \mu$, while with the KBr optics it covers the range between $13\ \mu$ and $24\ \mu$. The overlap of the two scales over the range between $13\ \mu$ and $15\ \mu$ is a useful feature, since it provides a check on the proper functioning of the instrument and as it is also the range over which the reflecting power of MgO increases rapidly from nearly zero to some 75%.

Some 75 spectrographic records were made with the instrument, the majority with the NaCl optics and the rest in the KBr range. Some 25 different cleavage plates of various sizes and thicknesses were employed and numerous records were also obtained with the paste and pellet techniques already described. Before we proceed to discuss the results in detail, it appears useful to review the general features which emerge from the study, thereby enabling us to get a broad picture of the experimental situation and consider its significance.

The most striking feature exhibited by the records is that the infra-red behaviour of MgO is quite different in the three spectral ranges which we shall refer to as I, II and III respectively. Spectral range I extends from $6\ \mu$ to $10\ \mu$. Spectral range II extends from $10\ \mu$ to $15\ \mu$. Spectral range III extends from $15\ \mu$ to $24\ \mu$. Closely associated with this feature is the fact that the spectral character of the radiation transmitted by MgO depends greatly upon the absorption path. When the cleavage plate is a few millimetres thick, spectral region I exhibits a progressive change from complete transparency at $6\ \mu$ to complete opacity at $10\ \mu$, while spectral regions II and III are completely cut out. If the absorption path is a few tenths of a millimetre, spectral range I is almost completely transmitted and spectral region II exhibits a transmission spectrum with characteristic features, while spectral region III is cut out. If the absorption path is only a few microns, spectral region III exhibits an observable transmission, while spectral region I is completely transmitted and spectral region II is let through for the most part.

The facts stated above clearly indicate that the infra-red activities which manifest themselves respectively in the spectral regions I, II and III are of very different orders of magnitude. An explanation for this situation which suggests itself is that the same fundamental modes of vibration are responsible for the activities manifested in the three spectral regions, but that we are concerned with the fundamental modes and with their first and their second overtones respectively in the three cases. In other words, the fundamental absorption frequencies manifest themselves in spectral region I, their first harmonics in the spectral region II and their second harmonics in spectral region III. On this basis,

the great differences in the strength of the observed absorptions in the three regions would find an immediate explanation.

If what has been suggested above is correct, we should expect to find quantitative relationships between the specific features observed in the spectral regions I, II and III in the recorded transmission curves. We proceed, therefore, to describe and discuss these observed features.

5. Spectral region I: $6\ \mu$ to $10\ \mu$

We may begin with a few remarks on the transmission of infra-red radiation in the wavelength range between $1\ \mu$ and $5\ \mu$ by cleavage plates of MgO. Residual imperfections in the cleavage surfaces are unavoidable. Their effect manifests itself as a diminution in the percentage of the regularly transmitted radiation in the region of the near infra-red. If, however, a large-sized crystal is used and its cleavage is effected with due care, the effect of surface imperfections on the transmission which may be perceptible at $1\ \mu$ becomes small at $4\ \mu$ and negligible at $5\ \mu$. Transmissions as high as 95% may be obtained at $5\ \mu$.

The region between $5\ \mu$ and $6\ \mu$ is of particular interest. With a cleavage plate 7.5 millimetres thick, the transmission is observed to diminish by 8% between $5\ \mu$ and $6\ \mu$. With a plate thickness of 3 millimetres, the diminution is only 3%, while with a plate thickness of 1.6 millimetres, there is no observable fall of the transmission between $5\ \mu$ and $6\ \mu$, the curve running quite horizontally between these wavelengths. It is clear from these observations that while there is a sensible absorption of infra-red radiation between $5\ \mu$ and $6\ \mu$, it is extremely weak and of a lower order of magnitude than the absorption between $6\ \mu$ and $10\ \mu$ which we shall proceed to describe and discuss.

Figure 1 reproduces the record obtained with a cleavage plate 2.34 millimetres thick. We may draw attention here to the following features observed in it. The record runs horizontally between $5\ \mu$ and $6\ \mu$. Beyond $6\ \mu$, it dips down and becomes steepest at $6.8\ \mu$. It then takes a sharp turn and follows a different course in which the wavelength at which the transmission drops most steeply is $7.85\ \mu$. Between $8\ \mu$ and $9\ \mu$ the curve again changes its course. The slope is rather small at $8.5\ \mu$, beyond which it increases rapidly. The wavelength of steepest descent is $9\ \mu$. Between $9\ \mu$ and $10\ \mu$, the curve descends less quickly. Its slope diminishes until finally the curve touches the line of zero transmission at $10\ \mu$. Beyond $10\ \mu$, there is a complete cut-off.

Thus, the spectrographic record of transmission between $6\ \mu$ and $10\ \mu$ consists of three distinct sectors which exhibit quite different features, the transmission falling most steeply in the three sections at the wavelengths $6.8\ \mu$, $7.85\ \mu$ and $9\ \mu$ respectively. The three sectors can also be recognised in numerous other records which have been made with various thicknesses, viz., 7.5 mm, 3 mm, 1.6 mm, 1.34 mm, 1.04 mm and 1 mm. It has, however, not been thought necessary to

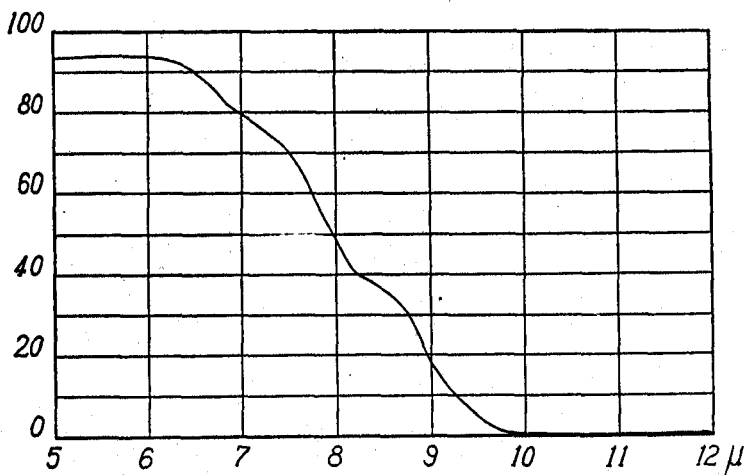


Figure 1. Transmission by an MgO plate 2.34 mm thick.

reproduce all these records here. That the three sectors exhibit the effect of specific absorptions is shown by the fact that each of them has a distinct absorption strength and that this results in altering the overall configuration of the graph in the wavelength range between 6μ and 10μ when the thickness is increased or diminished. Nevertheless, there is no difficulty in recognising the individual distinctive features described above in every case. In particular, the wavelengths of steepest descent, viz., 6.8μ , 7.85μ and 9μ , remain the same in all the records. Thus, these wavelengths possess a real significance in relation to the absorptive behaviour of MgO.

The wavelengths 6.8μ , 7.85μ and 9μ correspond to infra-red frequencies which expressed in wave-numbers are respectively 1470 cm^{-1} , 1275 cm^{-1} and 1110 cm^{-1} . Assuming these to be the second overtones of a set of fundamentals, the latter would be 490 cm^{-1} , 425 cm^{-1} and 370 cm^{-1} in wave-numbers and 20.40μ , 23.52μ and 27μ respectively in wavelengths. The first overtones would then have the frequencies 980 cm^{-1} , 850 cm^{-1} and 740 cm^{-1} in wave-numbers and the corresponding wavelengths would be 10.2μ , 11.76μ and 13.5μ . The frequencies of the fourth order would be 1960 cm^{-1} , 1700 cm^{-1} and 1480 cm^{-1} and the corresponding wavelengths 5.1μ , 5.9μ and 6.8μ respectively. We give below a table of these frequencies and wavelengths.

The figures listed in table 1 enable us immediately to explain various facts already known regarding the infra-red behaviour of MgO. For example, Burstein, Oberly and Plyler had observed that the reflecting power of MgO determined and represented graphically is highest in the wavelength region between 20μ and 24μ . We notice that this region includes the first two fundamental wavelengths shown in table 1. Then again, Burstein, Oberly and

Table 1. Vibrational frequencies and corresponding wavelengths

| Order | Frequencies in cm^{-1} | Wavelengths in μ |
|-----------------|---------------------------------|----------------------|
| Fundamental | 490, 425, 370 | 20.4, 23.52, 27 |
| Octave | 980, 850, 740 | 10.2, 11.76, 13.5 |
| Third Harmonic | 1470, 1275, 1110 | 6.8, 7.85, 9 |
| Fourth Harmonic | 1960, 1700, 1480 | 5.1, 5.9, 6.8 |

Plyler had noticed that in the transmission curves of MgO plates which were less than a millimetre thick, two well-defined absorption maxima appear whose wavelengths were given by them as 10.19μ and 11.82μ . These may be identified as the first two wavelengths of the octave series shown in table 1. The fact mentioned earlier in the present memoir, that there is an extremely weak infra-red absorption between 5μ and 6μ is also satisfactorily explained, since the first two wavelengths shown as the fourth harmonics in table 1 fall within this range. Thus, what is already known regarding the infra-red behaviour of MgO provides us with ample justification for accepting the basic idea which was put forward above and making use of it in interpreting the fresh experimental data which emerge from the present investigation.

6. Spectral region II: 10μ to 15μ

That the infra-red absorption appearing between 6μ and 10μ is of a higher order than that manifested between 10μ and 15μ is clearly proved by various facts of observation. In the first place, there is a total cut-off between 10μ and 15μ unless the absorption paths used are much smaller than those which are required to exhibit any sensible absorption in the 6μ to 10μ region. Then again, when such smaller thicknesses are used, the transmission is observed to be nearly complete over the range between 6μ and 10μ ; in these circumstances also, a steep fall is observed in the transmission curve near 10μ which is the dividing boundary between spectral ranges I and II (see figures 2, 3, 4 and 5).

On the long-wave side of the boundary between spectral regions I and II, the characteristic absorption at 10.20μ first clearly makes its appearance when the absorption path is rather less than one millimetre. This absorption evidently represents the octave of the highest fundamental frequency of vibration of the crystal structure of MgO. As the absorption path is progressively diminished, this absorption emerges more and more clearly from its background and becomes a very striking feature of the transmission curves. Its initial appearance is shown in figure 2 which was recorded with a cleavage plate 0.91 mm thick. A later stage in which the absorption at 10.2μ is very prominent and exhibits its characteristic

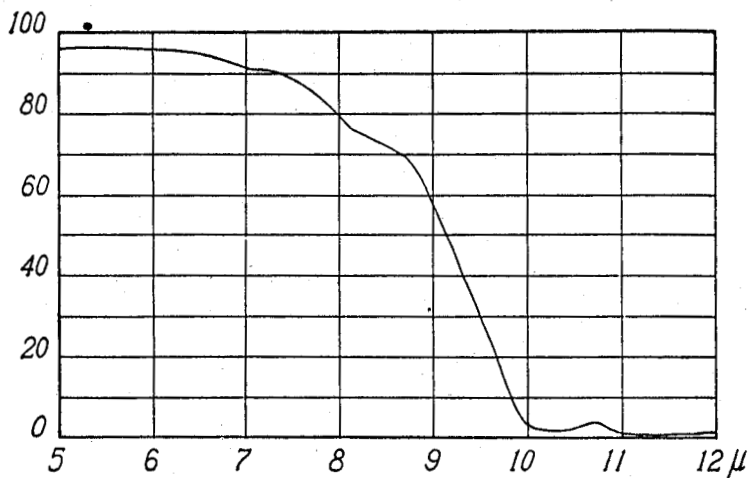


Figure 2. Transmission by an MgO plate 0.91 mm thick.

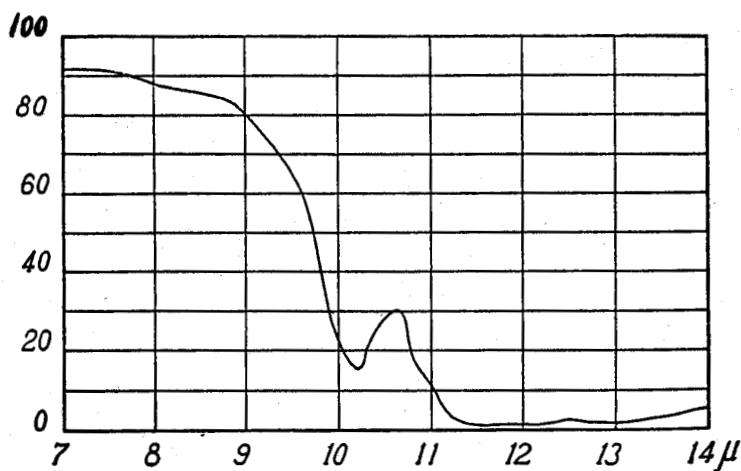


Figure 3. Transmission by an MgO plate 0.3 mm thick.

sharpness and V-shaped configuration is represented in figure 3 recorded with a cleavage plate 0.3 mm thick. With diminishing thickness of the plate, the V-shaped dip in transmission retains both its sharpness and its position on the wavelength scale at 10.2μ but moves upwards in the figure, as is to be expected from the diminishing strength of the absorption which it represents (see figures 4, 5, 6, 7, 8 and 9).

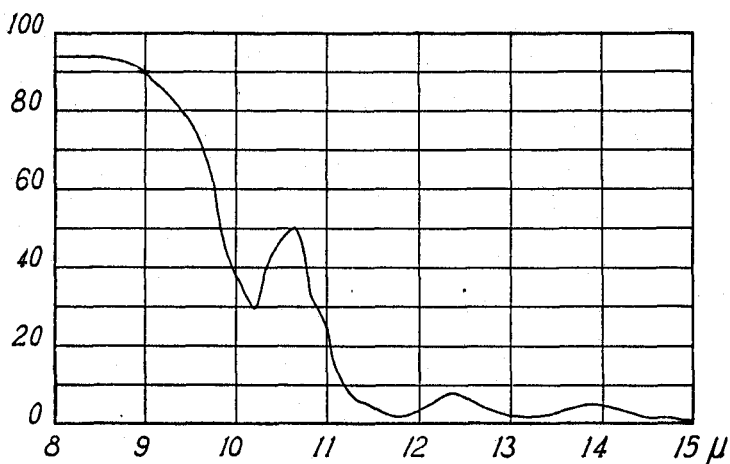


Figure 4. Transmission by an MgO plate 0.128 mm thick.

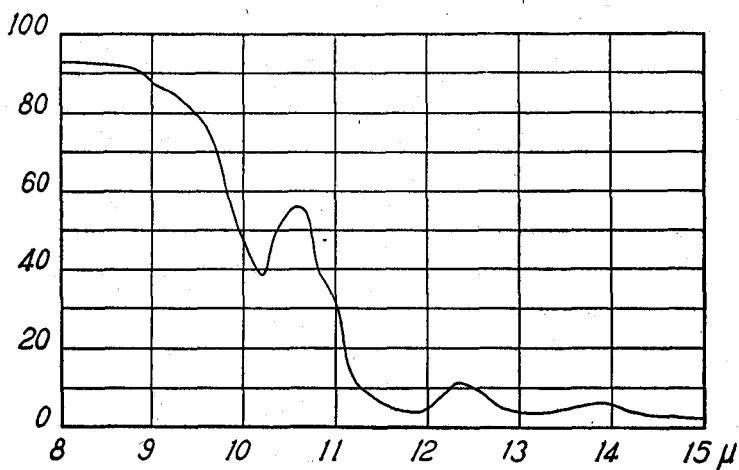


Figure 5. Transmission by an MgO plate 0.114 mm thick.

The second minimum of transmission located at $11.76\ \mu$ and shown in table 1 as an octave of a fundamental mode makes its appearance rather inconspicuously in figure 3. But as the thickness of the plate is progressively diminished, it becomes more and more conspicuous, as will be seen from the series of records, until it becomes even more conspicuous than the minimum at $10.2\ \mu$ (figures 4, 5, 6, 7 and 8). Like the minimum at $10.2\ \mu$, the minimum at $11.76\ \mu$ retains its position on the wavelength scale but moves upwards as the absorption path is diminished.

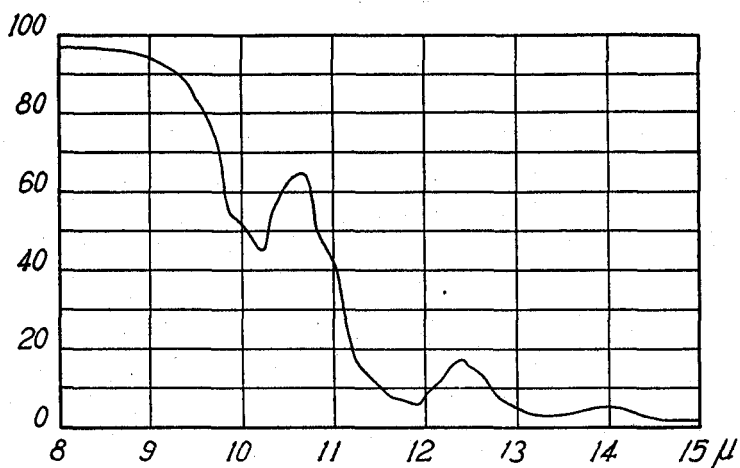


Figure 6. Transmission by an MgO plate 0.088 mm thick.

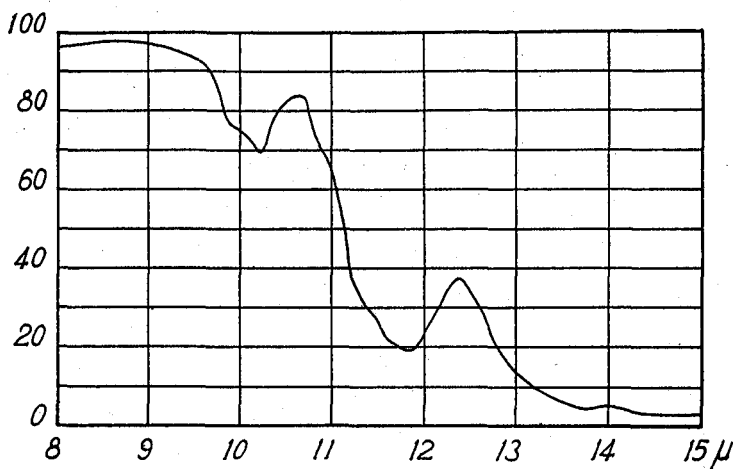


Figure 7. Transmission by an MgO plate 0.06 mm thick.

Referring to the spectrographic records reproduced as figures 4, 5 and 6, we find that in each of them, the transmission reaches a maximum at about 12.4μ and then drops down to a much lower value at about 13.3μ . The actual transmission at 13.3μ is small in figure 4 and is distinctly larger in figures 5 and 6. That there is a real absorption at 12.4μ and that this goes up to a much higher value at 13.3μ is thus abundantly clear. We are therefore justified in stating that there is a minimum of transmission at about the wavelength 13.5μ which was

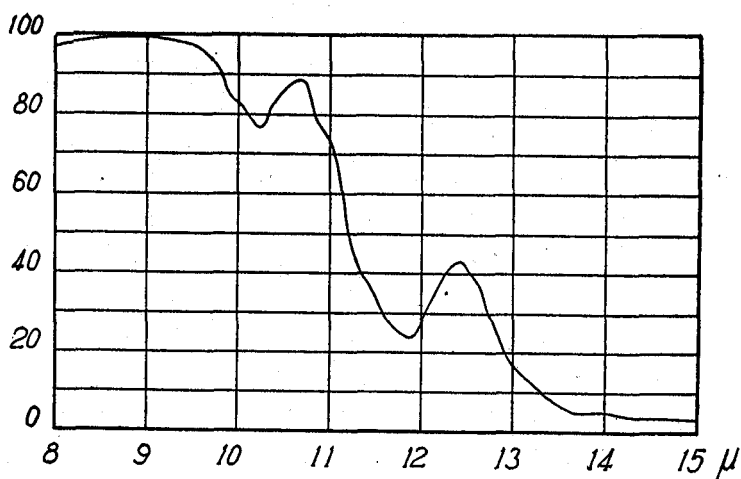


Figure 8. Transmission by an MgO plate 0.057 mm thick.

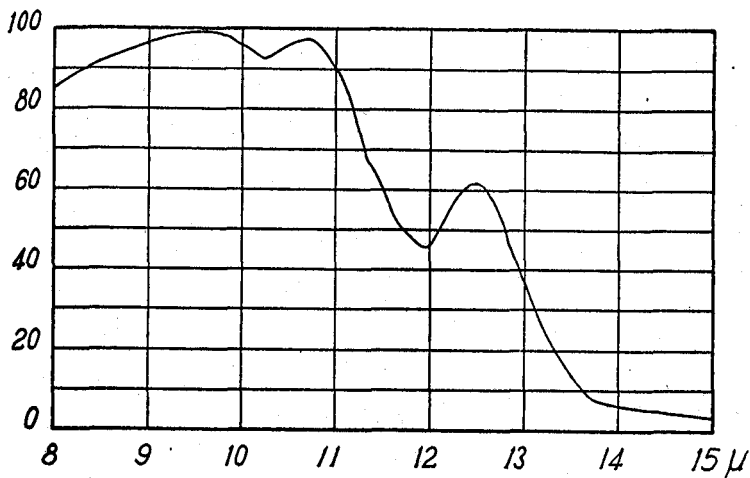


Figure 9. Transmission by an MgO plate 0.021 mm thick.

listed in table 1 as the third in the series of octaves. The reason why the existence of this minimum is not made more conspicuous by a progressive rise of the curve in the region between 13.5μ and 15μ with diminishing thickness is to be found in the enormous increase in the reflecting power of MgO which occurs in the same region of wavelength. The fall in transmission arising therefrom more than sets off the increase in the transmission due to the diminishing thickness of absorbing material.

That the percentage transmission through a plate of MgO in the wavelength region between $13.7\ \mu$ and $15\ \mu$ is almost entirely determined by the reflection losses is evident on a comparison of the records for this region appearing in figures 8 and 9. The absorbing path in the two cases was respectively 57 microns and 21 microns. It will be noticed that in spite of this great difference in the thickness of the absorbing material, the percentage transmission between $13.7\ \mu$ and $15\ \mu$ remains substantially unaltered, whereas between $12\ \mu$ and $13.7\ \mu$, it has increased enormously.

Thus, the inference from the observations made in spectral region I that three absorptions which we now locate at $10.2\ \mu$, $11.82\ \mu$ and $13.7\ \mu$ respectively should appear in spectral region II is abundantly confirmed by the actual facts of observation. The conclusion follows irresistibly that the MgO crystal structure has the three fundamental modes of vibration with the respective frequencies which have been listed in table 1.

7. Spectral region III: $15\ \mu$ to $24\ \mu$

The techniques used to study the transmission in this region using the KBr optics have already been explained. Figure 10 shows two transmission records obtained with the paste technique: the upper of the two curves was obtained without any spacer to hold apart the two KBr plates between which the thin film of paraffin containing the finely divided MgO was located. The thickness of the film was hence the very smallest possible and presumably of the same order of magnitude as the size of the MgO particles contained in it. The second record in the figure was with a spacer 30 microns thick separating the two KBr plates. The two records reproduced in figure 11 are those recorded with NaCl optics for the

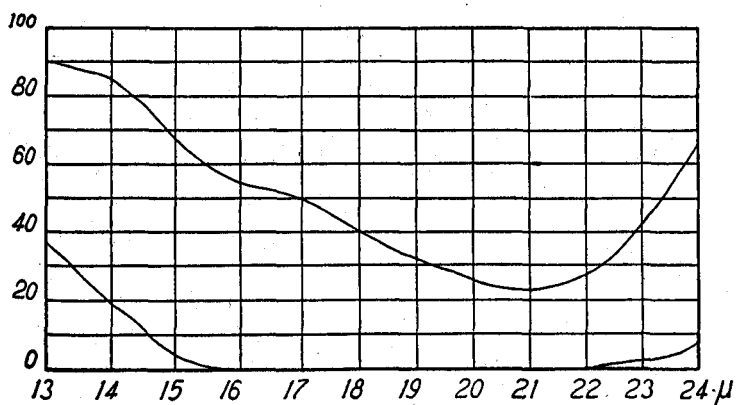


Figure 10. Transmission curve of MgO films (paste technique).

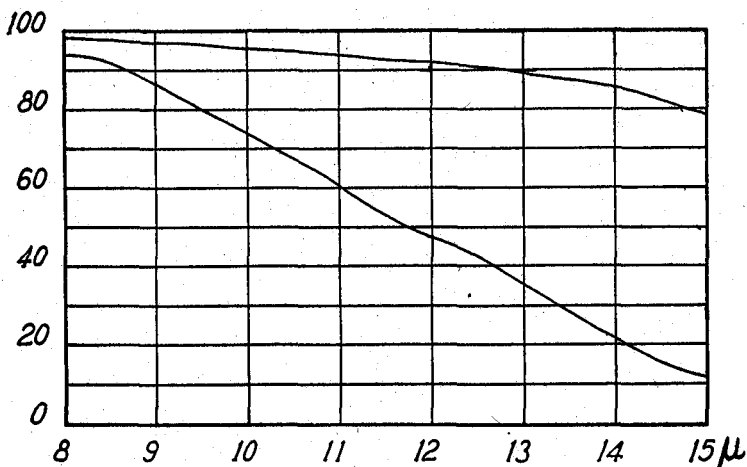


Figure 11. Transmission curve of MgO films (paste technique).

wavelength region between $8\ \mu$ and $15\ \mu$ in the same two cases. We shall return presently to a consideration of the features appearing in figures 10 and 11.

Figure 12 below reproduces four records for the KBr range of the spectrograph obtained with the pellet technique already described. The pellet was a circular disc of 1 centimetre radius containing one gram of KBr and four different quantities of finely divided MgO, viz., 1 milligram, 1.2 milligrams, 2 milligrams and 5 milligrams respectively. The effective absorption paths through MgO would thus be respectively in the four cases $3.2\ \mu$, $3.8\ \mu$, $6.4\ \mu$ and $16\ \mu$. As is to be expected, the four records exhibit a rapid and progressive change as the effective thickness of the MgO layer is increased.

We may make the following remarks on the data presented in figures 10, 11 and 12. It is evident that the results obtained with the two different techniques are very similar and that they fit into each other perfectly when the differences in the effective absorption paths are taken into consideration. Indeed, the curves in figures 10 and 12 form a regular sequence showing how the transmission alters with a progressive increase in absorption path. The upper curve in figure 10 represents the behaviour of the thinnest possible layer; the first three curves in figure 12 represent the subsequent alterations with increasing thickness, while the second curve in figure 10 and the fourth curve in figure 12 represent the final stages in which the layers are practically opaque to all radiations in the wavelength region between $15\ \mu$ and $24\ \mu$.

The first of the two curves reproduced in figure 10 is particularly important. It depicts the absorptive behaviour of an MgO film when it is so thin that the losses due to reflection at its two surfaces can be disregarded. It is significant that the

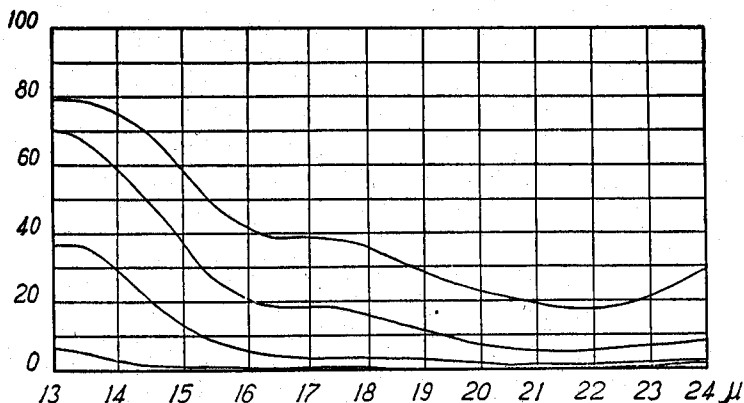


Figure 12. Transmission curve of MgO films (pellet technique).

absorption is greatest at about 21μ and falls off quickly at greater wavelengths. This is the behaviour which we might expect to observe if the fundamental mode of highest frequency of which the characteristic wavelength is 20.4μ is the only mode which is infra-red active, while the numerous other modes whose characteristic wavelengths are larger and have been listed in table 1 are either totally inactive or active only in a very minor degree. The shift of the maximum from the theoretical value 20.4μ to the observed value of 21μ is readily understood on that basis.

The two curves reproduced in figure 11 are also highly significant. They show that the films studied were completely transparent at 8μ . The two upper curves in figure 10 and in figure 11 respectively agree in showing a transmission of 90% at 13μ while the two lower ones similarly agree in showing a transmission of 35% at 13μ . The transparency of the films at 8μ is an indication that the losses due to scattering at all greater wavelengths are negligible. In other words, it is a demonstration of the satisfactory nature of the technique employed. In this respect, the results provide a very striking contrast with the behaviour of fumed MgO films. As has already been remarked, the fumed MgO films exhibit the effect of scattering very markedly. Hence the results obtained with them are erroneous and totally misleading.

We may also remark on a feature shown by the upper curve in figure 10 and also by the two upper curves in figure 12, viz., the downward bulge of the transmission curve in the region of wavelengths between 15μ and 17μ . This is a clear indication that there is a specific absorption which we shall locate at 16μ and which is clearly the octave of still another fundamental mode whose characteristic wavelength is 32μ and characteristic frequency is therefore 313 cm^{-1} .

8. Summary

Records have been made of the infra-red absorption spectra between $5\ \mu$ and $24\ \mu$ of magnesium oxide in the form of polished cleavage plates of various thicknesses ranging from 7.5 millimetres down to 20 microns. Films with an effective absorption path ranging from 1 micron to 16 microns have also been prepared by two different techniques and studied. They give results in close agreement with each other.

A critical comparative study of the data reveals that the infra-red absorption by MgO has its origin in a set of distinct modes of vibration of the crystal structure possessing discrete frequencies. The highest of these frequencies corresponds to an infra-red wavelength $20.4\ \mu$. It is strongly active as a fundamental and also as overtones. The infra-red absorption spectra enable us to recognize the presence of three other modes with lower frequencies which are inactive as fundamentals but are strongly active as overtones. The characteristic frequencies of MgO (including the highest) revealed by the investigation are respectively in wave-numbers $490\ \text{cm}^{-1}$, $423\ \text{cm}^{-1}$, $365\ \text{cm}^{-1}$ and $313\ \text{cm}^{-1}$. The corresponding wavelengths are $20.4\ \mu$, $23.64\ \mu$, $27.4\ \mu$ and $32\ \mu$.

The present investigation shows that the results reported earlier by other authors which were obtained with fumed MgO films are spurious and hence that all theoretical discussions based thereon are valueless.