THE INFRA-RED SPECTRUM OF MAGNESIUM OXIDE BETWEEN 1 AND 21 MICRONS

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1. INTRODUCTION

The infra-red spectrum of magnesium oxide in the form of thin cleavage plates as well as of thin films fumed on to nitrocellulose films and NaCl plates, has been the subject of study by several workers. While there appears to be some disagreement between the earlier workers in the results obtained, recent work has brought out a more consistent picture of the spectrum of magnesium oxide. The results of previous workers may be summarised as follows:

Tolksdorf (1928) studied the transmission of thin layers of powdered MgO held between thin plates of NaCl and found absorptions at 3.85, 7.65 and 14.2 microns. The residual ray technique of Strong (1931) has revealed the existence of a strong absorption in the region of 23 microns in fumed films of MgO and a strong reflection of almost 80% in the same region in the case of a freshly cleaved plate of MgO. Barnes, Brittain and Seitz (1935) who made a detailed study both of thin cleavage plates as well as of films of MgO evaporated on to nitrocellulose films in vacuum found a considerable amount of fine structure consisting of a number of weak lines between 6 and 12 microns. Fock (1934) studying films fumed on to nitrocellulose found a strong absorption maximum at 17.3 microns and two weaker absorptions at 14.9 and 25 microns. Of the recent studies, Elias Burstein, J. J. Oberly and Plyler (1948) have studied the absorption spectra of thin cleavage plates between 5 and 14 microns and the reflection spectra between 15 and 37 microns. They report absorption bands at 8.3, 10.18 and 11.82 microns and a reflection which starts at about 13 microns and rises rapidly to a peak of almost 100% at about 21 microns except for a small kink between 15 and 16 microns and decreases rapidly beyond 24 microns and is about 40% at 37 microns. Wilmott (1950) has studied both plates and films.

The work of Strong clearly establishes the selective reflection of MgO about 23 microns, but his reststrahlen technique is not capable of giving any details regarding the structure of these bands and only indicates the rough
position of the band. The measurements of Barnes, Brittain and Seitz appear to suffer from errors which may be attributed to instrumental factors, viz., an unregulated infra-red source or their method of making point by point measurements. Although their general results have been confirmed by later work, the considerable amount of secondary structure reported by them has not found confirmation in recent work carried out with more refined techniques.

In view of the lack of agreement on some points between the various previous workers, and the fact that a new model of infra-red spectrophotometer which the writer felt was a more advanced instrument than those used by other workers, became available to him, it was felt that it may be worthwhile to repeat these measurements of MgO films. Another important reason for undertaking this investigation was that thin layers of MgO are in use in this laboratory for the purpose of filtering out the visible portion of the spectrum in an instrument for the measurement of infra-red radiation from the atmosphere developed by Kale and it was important to know the exact transmission characteristics of this material in the form of thin films with various thicknesses in the infra-red region between 1 and 20 microns.

Before presenting the results obtained it may be useful briefly to describe the experimental arrangement used in these measurements as it will help in making a comparative study of the measurements made with other types of instruments by previous workers.

2. EXPERIMENTAL

The Beckman model IR-2 Infra-red spectrophotometer used in this investigation uses a potassium bromide prism and optics and covers the range from 1 to 25 microns. The lay-out of the instrument is indicated in Fig. 1. The optical path of the infra-red radiation through the spectrophotometer is as follows and is indicated by an arrow line in Fig. 1:

![Fig. 1. Schematic optical path of Beckman Model IR-2 infra-red spectrophotometer](Courtesy of National Technical Laboratories)

Light from the Nernst glower A is modulated at 10 cycles per second by the rotating shutter B, passes through the KBr window C and is focussed
by the condensing mirror D, forming an image of the source in the focal plane of the concave KBr lens E. The collimated beam passes through the filter slide and shutter F and the liquid cell compartment G. The lens H converges the beam through the gas cell compartment I and the lens K, forming an image of the source on the entrance slit L. Light from the slit is collimated by the spherical mirror M (5·5° off axis) and dispersed by the KBr prism N (6 cm. base and 4 cm. height). It is reflected by the rotatable Littrow mirror O, dispersed a second time by the prism and focussed by the collimator M on the plane of the exit slit, which lies just below the entrance slit. The beam is directed by the plane mirror J against the condensing mirror P which focuses an image of the exit slit on the thermocouple Q. The phototube R monitors the source to maintain constant output; its received light is adjustable by a shutter so that the glower current may be regulated to the proper value.

The radiation source is a Nernst glower operating on 60 Watts of power at about 0·8 ampere. The glower is self-starting and its output is automatically held constant within 0·1% by the special photoelectronic monitor. The watercooled housing maintains a constant temperature.

Two interchangeable shutters, one of metal for use up to 9 microns and the other of glass for use beyond 9 microns, are provided for modulating the beam. The glass shutter eliminates the effects of contamination of the longer wave-lengths by the scattered short-wave radiations which are concentrated in the energy peak of the glower near about 2 microns. Since this scattered radiation is not modulated by the glass shutter it is ignored by the tuned amplifier which only responds to radiation modulated at 10 c/s.

3. PREPARATION OF THE MgO FILMS

The MgO films were prepared by fuming on to a KCl plate from a burning magnesium ribbon. The measurements were first started with an extremely thin layer which was just visible and then the thickness increased by adding more layers of MgO on the same plate by fuming. As the KCl plate is almost completely transparent up to about 21 microns these measurements cover the region 1 to 21 microns.

4. DISCUSSION OF THE RESULTS

Measurements have been made on 14 different thicknesses starting from a layer which was just visible to a thickness of about 2·4 mm. when the film begins to break away from the KCl plate. Fig. 2 shows four curves giving the infra-red spectrum of MgO films for selected thicknesses, for the region 1 to 21 microns. The other curves have been omitted for the purposes of clarity as they lie in between the curves given in this figure.
The most obvious conclusion that can be drawn from a study of these curves is that infra-red absorption spectrum of MgO is not a continuous one but consists of a series of well defined bands. The strongest of these absorption bands lies between 18 and 19 micron. There is another strong absorption band between 14 and 16 and it is clear that this is not a single band but consists two or more bands very close together. As we go towards the shorter wave-lengths a number of bands can be seen developing as the thickness of the film is increased, until we reach a region near about 7 microns where the transmission begins to decrease rapidly. This is obviously due to the reflection and scattering of the shorter wave-lengths by the MgO film. More broadly speaking a film of MgO has a broad transmission from about 1 to 2 microns to beyond 21 (except for a band at about 18 microns) with its peak at about 10 microns and its short and long wave-length cut off points are functions of the thickness of the film. This transmission characteristic of MgO films is of great use in measurements of atmospheric radiation in the infra-red region, during daytime where we are dealing with emission sources with effective temperatures of about 300° A which have their energy peaks in the 10 micron region. The use of MgO films by Kale for his instrument for the measurement of atmospheric infra-red radiation appears to be fully justified, if a film of correct thickness is chosen so that the short-wave cut off
is at about 2 to 3 microns and the 18 microns band is not very strong. It may be pointed out that MgO films reflect and scatter away almost 100% of the energy in the visible region while remaining almost completely transparent in the 10 \( \mu \) region and therefore if a layer of this material is coated on a blackened thermopile or other receiver, it becomes sensitive to the atmospheric infra-red radiations while remaining completely unaffected even by bright sunlight.

5. APPLICATIONS TO THEORY OF VIBRATION SPECTRA OF CRYSTALS

The infra-red spectrum of magnesium oxide is of great interest to the crystal physicist. According to the theory of vibration spectra of crystals put forward by Sir C. V. Raman, a magnesium oxide crystal has nine fundamental modes of vibrations whose frequencies are listed below:

<table>
<thead>
<tr>
<th>Frequency in ( \text{cm}^{-1} )</th>
<th>704</th>
<th>690</th>
<th>632</th>
<th>584</th>
<th>527</th>
<th>474</th>
<th>428</th>
<th>258</th>
<th>184</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wave-length in microns</td>
<td>14.2</td>
<td>14.7</td>
<td>15.25</td>
<td>17.1</td>
<td>19.0</td>
<td>21.1</td>
<td>23.4</td>
<td>38.8</td>
<td>54.4</td>
</tr>
<tr>
<td>Assignment</td>
<td>( \nu_1 )</td>
<td>( \nu_2 )</td>
<td>( \nu_3 )</td>
<td>( \nu_4 )</td>
<td>( \nu_5 )</td>
<td>( \nu_6 )</td>
<td>( \nu_7 )</td>
<td>( \nu_7 )</td>
<td>( \nu_8 )</td>
</tr>
</tbody>
</table>

Of these all frequencies except the last two, i.e., 38.8 and 54.4 microns are expected to be infra-red active.

The results of the present investigation permit an experimental verification of these discrete vibration frequencies predicted by the theory. As the region covered in this investigation is from 1 to 21 microns only the 23.4 band cannot be verified by the present measurements, the last two frequencies being inactive in the infra-red.

Fig. 3 gives a chart showing the predicted active fundamentals for magnesium oxide on the basis of Raman theory and the clear absorption
bands found in these measurements. As there are a number of well-developed bands in the overtone region these are compared with the second harmonics of the fundamentals. A fairly good agreement between theory and experimental result is obtained. There are indications that some of the bands have additional structure which is either beyond the resolving power of the instrument used or is incapable of being resolved on account of the overlapping or broadening of the bands due to coupling between the modes of vibrations.

The author intends to further investigate this region with a NaCl prism which has a higher dispersion in this region than the KBr used in the present measurements and with a new recording technique which it is hoped will resolve the additional structure of which there are strong indications, if it is resolvable at all.

6. ACKNOWLEDGMENTS

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