

## The vibration spectra of crystals—Part IV. Magnesium oxide

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### 1. Introduction

Magnesium oxide crystallises in the cubic system and X-ray diffraction studies show that its structure is similar to that of rocksalt. The high values of its density and elastic constants indicate, however, that the atomic interactions are far stronger in magnesium oxide than in rocksalt. This circumstance taken in conjunction with the low atomic weights of magnesium and oxygen has a notable influence on the vibration frequencies of the structure. Instead of being crowded together in the remote infra-red as in the case of rocksalt, the spectral frequencies are high and widely separated from each other and by the same token are very little influenced by thermal agitation. Magnesium oxide is accordingly a perfect choice for a material that would demonstrate by its spectral behaviour the monochromatic character of the atomic vibration frequencies in crystals. This indication of theory is strikingly borne out by the observations of Barnes and Brattain (1935) on its infra-red absorption spectrum. Employing plates of five widely different thicknesses obtained by cleavage from a large synthetically prepared single crystal, they recorded their absorption curves with a rocksalt spectrometer, using an amplifying arrangement which gave a 150-fold magnification of the galvanometer deflections. The results showed the presence of some 40 well-defined absorption lines between  $6\mu$  and  $15.5\mu$ , those of shorter wavelengths being most clearly exhibited by the thicker plates and those of longer wavelengths by the thinnest of the five plates.

In view of the similarity of structure, the nine fundamental frequencies of MgO may be evaluated with the aid of the same formulae as in the case of rocksalt considered in the preceding paper. The three fundamentals with the highest frequencies are found to fall within the region investigated by Barnes and Brattain, and their positions can be checked from the absorption curves published by these authors. The positions of the other six fundamentals as evaluated from the formulae find experimental support in the observations made by Strong (1931*a, b*) and by Fock (1934) in the region of wavelengths beyond the reach of a rocksalt spectrometer. The numerous other absorption lines noticed by Barnes and Brattain are evidently the overtones and summations of the nine fundamental frequencies.

## 2. Evaluation of the nine fundamental frequencies

Some idea of the magnitude of the forces which hold the magnesium and oxygen atoms together in the crystal may be obtained from the results of the analysis of the band spectra of MgO in the state of vapour (P C Mahanti 1932). The vibration frequencies as deduced from the "red" and "green" systems of bands are respectively  $822\text{ cm}^{-1}$  and  $812\text{ cm}^{-1}$  in the lower state and  $668\text{ cm}^{-1}$  and  $771\text{ cm}^{-1}$  in the upper state. We may reasonably expect to find frequencies of this order of magnitude also in the vibration spectrum of the crystal. Actually, all the investigators [Tolksdorf (1928), Fock (*loc. cit.*), Barnes and Brattain (*loc. cit.*)] have found a strong absorption at about  $14.2\ \mu$  ( $704\text{ cm}^{-1}$ ). Taking this to represent the fundamental of highest frequency, we may at once evaluate P, the larger of the two constants which we need to know. The second constant T may, as in the case of rocksalt, be expected to be quite small in comparison with P. The frequencies of the two lowest fundamentals are determined exclusively by the value of T, but as they are not directly accessible to observation, we have to choose T so as to fit the facts best over the whole range of the spectrum. Table 1 above shows the nine eigenfrequencies of MgO as calculated from the simplified formulae of the preceding paper, with the atomic weights of oxygen and magnesium substituted for those of sodium and chlorine. The values of P and T adopted are shown at the head of the table.

## 3. Their infra-red activities

If all the eigenvibrations are completely independent normal modes, only  $\nu_3$  which is the oscillating of the Mg and O lattices of atoms against each other would be active in infra-red absorption, and the rest would be inactive. As remarked already in the cases of diamond and rock-salt, such independence of the normal modes does not, as a matter of fact, subsist. On the other hand, there is clear evidence of the existence of a strong coupling between them due to

**Table 1.** Calculated eigenfrequencies of magnesium oxide  
( $P = 2.82 \times 10^5$  dynes per cm,  $T = -0.05 \times 10^5$  dynes per cm,  $m_H$  = mass of hydrogen atom.)

Designation	Description of mode	Degeneracy	$4\pi^2\nu^2c^2m_H$	Calculated frequency	Calculated wavelength
$\nu_1$	Normal oscillation of cubic planes, Mg and O atoms in same phase.	3	$0.1037P - 0.036T$	$\text{cm}^{-1}$ 704	$\mu$ 14.2
$\nu_2$	Tangential oscillation of cubic planes, Mg and O atoms in opposite phases.	6	$0.1037P + 0.397T$	680	14.7
$\nu_3$	Oscillation of Mg and O lattices in opposite phases.	3	$0.1037P + 0.830T$	652	15.35
$\nu_4$	Normal oscillation of octahedral layers of O atoms, Mg being at rest.	4	$0.0625P - 0.5T$	584	17.1
$\nu_5$	Tangential oscillation of octahedral layers of O atoms, Mg being at rest.	8	$0.0625P + 0.25T$	527	19.0
$\nu_6$	Normal oscillation of octahedral layers of Mg atoms, O being at rest.	4	$0.0412P - 0.33T$	474	21.1
$\nu_7$	Tangential oscillation of octahedral layers of Mg atoms, O being at rest.	8	$0.412P + 0.165T$	428	23.4
$\nu_8$	Normal oscillation of cubic planes, Mg and O atoms in opposite phases.	3	$-0.794T$	258	38.8
$\nu_9$	Tangential oscillation of cubic planes, Mg and O atoms in same phase.	6	$-0.397T$	184	54.4

anharmonicity and the finite amplitudes of vibration. As a consequence of this coupling, the activity of any mode results in an induced activity of the modes having frequencies not too greatly differing from it. On this basis, we should expect not merely  $\nu_3$ , but also the higher and lower frequencies to be active in infra-red absorption.  $\nu_8$  and  $\nu_9$  in the table may however be expected to be more or less completely inactive by reason of their very low frequencies in comparison with  $\nu_3$ .

Barnes and Brattain studied the reflecting power of an MgO crystal and found that it rises steeply from about  $13 \mu$  and shows a double maximum at  $14.8 \mu$  and  $15.3 \mu$  of about 65% in each case and then drops down again sharply. That the peak at  $14.8 \mu$  is itself the joint effect of more than one active frequency between  $14 \mu$  and  $15 \mu$  is clearly shown by their absorption curve for this region recorded with the thinnest of their five plates, as well as by that obtained with a layer of MgO fumed on to a plate of NaCl. As we shall see later, three summational frequencies ( $\nu_5 + \nu_9$ ), ( $\nu_7 + \nu_8$ ) and ( $\nu_6 + \nu_9$ ) also fall in the vicinity, and it is therefore not surprising that a good deal of detail is observed in this region. There is however no difficulty in recognising the presence in the absorption curves of two closely adjacent fundamental frequencies at about  $14.15 \mu$  and  $14.55 \mu$  respectively besides a third at  $15.35 \mu$ , in agreement with the indications of theory shown in table 1.

Strong (1931*a*) studied the transmission through a film of MgO of infra-red radiations of selected wavelengths obtained by means of crystal reflections. Table 2 exhibits his results.

In the same paper, Strong recorded the percentage of reflection by an MgO crystal at  $22.9 \mu$  and  $32.8 \mu$  as 80% and 33% respectively. In a later paper (1931*b*) he gives fresh determinations over these and many more wavelengths, and these are listed in table 3. The results obtained by Strong, viz., practically complete absorption for  $20.75$  and  $22.9 \mu$ , and nearly total reflections at the same wavelengths are what should be expected if there are fundamental frequencies at  $21.1 \mu$  and  $23.4 \mu$  as shown in table 1. The practically complete transparency for longer wavelengths and the near identity of the reflecting power for such wavelengths with the theoretical value of 27% given by the dielectric constant 9.8

Table 2. Percentage transmission by MgO film

Wavelength in $\mu$	6.7	8.7	20.75	22.9	27.3	29.4	32.8
Percentage transmission	88	36	04	02	90	93	87

Table 3. Percentage reflection from MgO crystal

Wavelength in $\mu$	20.7	23	27.3	29.4	32.8	41	52	63
Percentage reflection	80	72	44	42	35	33	32	31

are also significant. They are fully consistent with the *absence* of any fundamental frequency between  $24 \mu$  and  $38 \mu$  and the *inactivity* of the two lowest frequencies at  $38.8 \mu$  and  $54.4 \mu$  respectively.

Since Strong's observations indicate that the fundamental frequencies at  $21.1 \mu$  and  $23.4 \mu$  are strongly active, and since this activity is an induced effect, we should expect the fundamentals at  $17.1 \mu$  and  $19.0 \mu$  appearing in table 1 to be still more strongly active, especially the one at  $17.1 \mu$  in view of its being adjacent in frequency to the "active" third fundamental. This indication is strikingly supported by the observations of Fock (1934). This author, working with a film of MgO found that by far the strongest absorption in the whole wavelength region between  $2 \mu$  and  $40 \mu$  is at the wavelength  $17.3 \mu$ , and that the absorption falls off rapidly both towards longer and shorter wavelengths. This observation shows clearly enough that  $17.3 \mu$  is very close to an active fundamental. But it seems at first sight rather surprising that the activity of  $\nu_4$  should exceed that of  $\nu_3$  so notably. It may be recalled, however, that in the case of rocksalt, a similar situation but in the opposite direction arises, viz., the peak of infra-red absorption by thin films is situated at  $\nu_1$  instead of at  $\nu_3$ . One may therefore hazard the suggestion that the explanation is the same in both cases, the reversal as between NaCl and MgO being due to the fact that the metallic atom is the lighter in one case and the heavier in the other.

It may be remarked that no direct observation of the two lowest fundamentals  $\nu_8$  and  $\nu_9$  is possible since they are inactive. The fifth fundamental  $\nu_5$  falls on the steeply rising part of the transmission curve of Fock but is not indicated by any distinct peak of absorption. It is to be presumed therefore that its activity is rather low, possibly for the same reason that the activity of  $\nu_4$  is very high.

#### 4. Analysis of the absorption curves

The range of wavelengths covered by the observations of Barnes and Brattain includes besides 3 out of the 9 fundamentals, also 7 out of the 9 octaves, 34 out of the 36 possible summations of the frequencies taken two at a time, and nearly all of the 93 frequencies appearing in the third-order spectrum. It might seem at first sight scarcely possible to analyse an absorption spectrum including such a crowd of distinct frequencies. Various factors however simplify the task considerably, especially since the nine fundamental frequencies are known in advance with some precision. Firstly, the fundamental of highest frequency and its overtones fix the upper limits of frequency for the successive orders of spectra. Expressed in infra-red wavelengths, these limits are  $14.2 \mu$ ,  $7.1 \mu$  and  $4.7 \mu$  respectively. We do not therefore have to look for any fundamentals between  $14.2$  and  $7.1 \mu$  or for second-order lines between  $7.1 \mu$  and  $4.7 \mu$ . Intensity considerations are also very helpful. In a particular region of the spectrum, a fundamental may be expected to appear more strongly than an octave, an octave more strongly than a summation

of two frequencies, a second-order frequency more strongly than one of the third-order, and so forth. Considerations of this kind are strongly supported by the observations recorded with the five plates of widely different thicknesses which enable us to assess the activity in absorption of the various frequencies. Comparison of the different absorption curves shows, for instance, that with the thinnest plate of all (0.075 mm), the first-order spectrum is strongly developed, the second-order spectrum appears rather weakly and the third-order spectrum still more weakly. With the next thicker plate (0.12 mm), the first-order is completely blocked out, the second-order is very strongly developed, and the third-order is quite definitely present. With the plate of thickness 0.47 mm, the second-order spectrum is blocked out for wavelengths greater than  $10\mu$ , but for the

Table 4. Calculated and observed absorption frequencies

Sl. no.	Plate thickness	Wavelength observed	Frequency observed	Assignment	Calculated frequency
	mm	$\mu$	$\text{cm}^{-1}$		$\text{cm}^{-1}$
1	0.075	15.4	651	$\nu_3$	652
2	0.075	15.2	658	$\nu_6 + \nu_9$	658
3	0.075	14.7	680	$\nu_2$	680
4	0.075	14.4	694	$\nu_7 + \nu_8$	686
5	0.075	14.2	704	$\nu_1$	704
6	0.075	14.0	714	$\nu_5 + \nu_9$	711
7	0.075	13.8	725	$\nu_6 + \nu_8$	732
8	0.075	13.1	763	$\nu_4 + \nu_9$	768
9	0.075	12.8	781	$\nu_5 + \nu_8$	785
10	0.075	12.1	826	$\nu_3 + \nu_9$	836
11	0.12	11.7	855	$2\nu_7$	856
12	0.075	11.6	862	$\nu_2 + \nu_9$	864
13	0.12	11.15	897	$\nu_1 + \nu_9$	888
14	0.12	10.9	917	$\nu_6 + \nu_7$	902
15	0.075	10.7	935	$\nu_2 + \nu_8$	938
16	0.12	10.5	952	$2\nu_6$	948
17	0.075	10.2	980	$\nu_1 + \nu_8$	962
18	0.12	10.0	1000	$\nu_5 + \nu_6$	1001
19	0.12	9.5	1053	$2\nu_5$	1054
20	0.12	9.3	1075	$\nu_3 + \nu_7$	1080
21	0.12	9.0	1111	$\nu_4 + \nu_5$	1111
22	0.075	8.8	1136	$\nu_1 + \nu_7$	1132
23	1.75	8.7	1149	$\nu_2 + \nu_6$	1154
24	0.12	8.5	1177	$2\nu_4$	1168
25	0.12	8.3	1205	$\nu_2 + \nu_5$	1207
26	1.75	8.15	1227	$\nu_1 + \nu_5$	1231
27	0.12	7.9	1266	$\nu_2 + \nu_4$	1264
28	0.47	7.6	1316	$2\nu_3$	1304
29	1.75	7.3	1370	$2\nu_2$	1360
30	3.05	7.1	1408	$2\nu_1$	1408

wavelengths between  $7\ \mu$  and  $9\ \mu$  where all the absorptions are necessarily weak, the observations with this plate as well as with the still thicker plate ( $1.75\ \text{mm}$ ) are distinctly helpful.

The octaves of the fundamental frequencies are those most easily recognised in the absorption curves, and their observed positions furnish welcome confirmation of the correctness of the theoretically determined fundamental frequencies.  $2\nu_7$ ,  $2\nu_6$ ,  $2\nu_5$  and  $2\nu_4$  are seen very clearly in the absorption curve of the plate  $0.12\ \text{mm}$  thick.  $2\nu_7$  is indicated by a complete cut-off in a small region of wavelengths on either side of  $11.7\ \mu$ .  $2\nu_6$  is indicated by a very prominent dip in the curve at  $10.5\ \mu$ .  $2\nu_5$  is marked by a sharp and fairly prominent absorption line at  $9.5\ \mu$ .  $2\nu_4$  may also be made out at  $8.5\ \mu$ , but appears much better developed as a deep trough at that position with the next thicker plate ( $0.47\ \text{mm}$ ). A trough appears in the same curve at  $7.6\ \mu$  which is the position of  $2\nu_3$ . A dip at  $7.3\ \mu$  in the absorption curve for the plate of  $1.75\ \text{millimetre}$  thickness may be identified with  $2\nu_2$ , and the dip at  $7.1\ \mu$  in the absorption curve of the thickest plate with  $2\nu_1$ .

The second-order combinations are much more numerous than the octaves, and hence it is not quite so easy to identify their appearance in the absorption curves. Especially, however, in the case of the two thinnest plates where the confusion arising from the superposition of the still more numerous third order combinations is not so serious, assignments may be made of the features observed in the absorption curves with some measure of confidence. Table 4 is a collected list of 30 absorption lines in the first and second order spectra with their respective interpretations in terms of the nine fundamental frequencies.

## 5. Summary

The nine fundamental frequencies of the magnesium oxide structure are theoretically evaluated. Expressed as infra-red wavelengths, they are respectively  $14.2$ ,  $14.7$ ,  $15.35$ ,  $17.1$ ,  $19.0$ ,  $21.1$ ,  $23.4$ ,  $38.8$  and  $54.4\ \mu$ . All except the last two are active in the infra-red and their positions check very closely with the absorptions observed by Barnes and Brattain, by Strong and by Fock. The octaves of the first seven fundamentals and numerous summational frequencies including also the two inactive fundamentals have been identified with the lines recorded by Barnes and Brattain in the absorption spectrum of cleavage plates of various thicknesses.

*Note added, 26th November 1947*—Deutschbein (*Annalen der Physik*, 1932, 14 712) found that a small percentage of chromic oxide can be successfully incorporated in  $\text{MgO}$ , thereby causing it to become luminescent when irradiated. The spectrum of this luminescence with the phosphor at room temperature, as also when it is cooled down to  $-195^\circ\text{C}$  has been investigated by him. At room temperature, a strong emission appears at  $\lambda\ 6991$  in the red, with subsidiary bands symmetrically disposed about it on either side. These bands are due to the combination of the