

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 rock-salt 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 6μ and 15.5μ , 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 formulæ 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 formulæ 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 cm.^{-1} and 812 cm.^{-1}

TABLE I

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 Wave-length
ν_1	Normal oscillation of cubic planes, Mg and O atoms in same phase.	3	$0.1037P - 0.036T$	cm.^{-1} 704	μ 14.2
ν_2	Tangential oscillation of cubic planes, Mg and O atoms in opposite phases.	6	$0.1037P + 0.397T$	680	14.7
ν_3	Oscillation of Mg and O lattices in opposite phases.	3	$0.1037P + 0.830T$	652	15.35
ν_4	Normal oscillation of octahedral layers of O atoms, Mg being at rest.	4	$0.0625P - 0.5T$	584	17.1
ν_5	Tangential oscillation of octahedral layers of O atoms, Mg being at rest.	8	$0.0625P + 0.25T$	527	19.0
ν_6	Normal oscillation of octahedral layers of Mg atoms, O being at rest.	4	$0.0412P - 0.33T$	474	21.1
ν_7	Tangential oscillation of octahedral layers of Mg atoms, O being at rest.	8	$0.0412P + 0.165T$	428	23.4
ν_8	Normal oscillation of cubic planes, Mg and O atoms in opposite phases.	3	$-0.794T$	258	38.8
ν_9	Tangential oscillation of cubic planes, Mg and O atoms in same phase.	6	$-0.397T$	184	54.4

in the lower state and 668 cm.^{-1} and 771 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 14.2μ (704 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 I above shows the nine eigenfrequencies of MgO as calculated from the simplified formulæ 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 ν_3 which is the oscillation 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 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 ν_3 , but also the higher and lower frequencies to be active in infra-red absorption. ν_8 and ν_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 ν_3 .

Barnes and Brattain studied the reflecting power of an MgO crystal and found that it rises steeply from about 13μ and shows a double maximum at 14.8μ and 15.3μ of about 65% in each case and then drops down again sharply. That the peak at 14.8μ is itself the joint effect of more than one active frequency between 14μ and 15μ 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 14.15μ and 14.55μ respectively besides a third at 15.35μ , in agreement with the indications of theory shown in Table I.

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

TABLE II
Percentage Transmission by MgO Film

Wavelength in μ	6.7	8.7	20.75	22.9	27.3	29.4	32.8
Percentage Transmission	88	36	04	02	90	93	87

TABLE III
Percentage Reflection from MgO Crystal

Wavelength in μ	20.7	23	27.3	29.4	32.8	41	52	63
Percentage Reflection	80	72	44	42	35	33	32	31

In the same paper, Strong recorded the percentage of reflection by an MgO crystal at 22.9μ and 32.8μ as 80% and 33% respectively. In a later paper (1931 *b*) he gives fresh determinations over these and many more wave-lengths, and these are listed in Table III. The results obtained by Strong, *viz.*, practically complete absorption for 20.75μ and 22.9μ , and nearly total reflections at the same wave-lengths are what should be expected if there are fundamental frequencies at 21.1μ and 23.4μ as shown in Table I. The practically complete transparency for longer wave-lengths and the near identity of the reflecting power for such wave-lengths with the theoretical value of 27% given by the dielectric constant 9.8 are also significant. They are fully consistent with the *absence* of any fundamental frequency between 24μ and 38μ and the *inactivity* of the two lowest frequencies at 38.8μ and 54.4μ respectively.

Since Strong's observations indicate that the fundamental frequencies at 21.1μ and 23.4μ are strongly active, and since this activity is an induced effect, we should expect the fundamentals at 17.1μ and 19.0μ appearing in Table I to be still more strongly active, especially the one at 17.1μ 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 wave-length region between 2μ and 40μ is at the wave-length 17.3μ , and that the absorption falls off rapidly both towards longer and shorter wave-lengths. This observation shows clearly enough that 17.3μ is very close to an active fundamental. But it seems at first sight rather surprising that the activity of ν_4 should exceed that of ν_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 ν_1 instead of at ν_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 ν_8 and ν_9 is possible since they are inactive. The fifth fundamental ν_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 ν_4 is very high.

4. ANALYSIS OF THE ABSORPTION CURVES

The range of wave-lengths 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 wave-lengths, these limits are 14.2μ , 7.1μ and 4.7μ respectively. We do not therefore have to look for any fundamentals between 14.2 and 7.1μ or for second-order lines between 7.1μ and 4.7μ . 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 wave-lengths greater than $10\ \mu$, but for the wave-lengths 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 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

TABLE IV
Calculated and Observed Absorption Frequencies

Sl. No.	Plate thickness	Wave-length Observed	Frequency Observed	Assignment	Calculated Frequency
	mm.	μ	cm.^{-1}		cm.^{-1}
1	0.075	15.4	651	ν_2	652
2	0.075	15.2	658	$\nu_6 + \nu_9$	658
3	0.075	14.7	680	ν_2	680
4	0.075	14.4	694	$\nu_7 + \nu_8$	686
5	0.075	14.2	704	ν_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

curve of the plate 0.12 mm. thick. $2\nu_7$ is indicated by a complete cut-off in a small region of wave-lengths on either side of 11.7μ . $2\nu_6$ is indicated by a very prominent dip in the curve at 10.5μ . $2\nu_5$ is marked by a sharp and fairly prominent absorption line at 9.5μ . $2\nu_4$ may also be made out at 8.5μ , but appears much better developed as a deep trough at that position with the next thicker plate (0.47 mm.). A trough appears in the same curve at 7.6μ which is the position of $2\nu_3$. A dip at 7.3μ in the absorption curve for the plate of 1.75 millimetre thickness may be identified with $2\nu_2$, and the dip at 7.1μ 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 IV 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 wave-lengths, they are respectively 14.2, 14.7, 15.35, 17.1, 19.0, 21.1, 23.4, 38.8 and 54.4μ . 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 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°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 electronic transition at $\lambda 6991$ with vibrational transitions in the MgO structure, as is proved by the fact that at low temperatures the bands at shorter wave-lengths vanish, while those at longer wave-lengths persist. As the result of the cooling

the principal emission shifts to $\lambda 6981$ and becomes sharper, while the bands appearing at longer wave-lengths are resolved into a group of lines of varying intensities and widths in close juxtaposition. Other weaker electronic lines are also noticed in the vicinity of $\lambda 6981$. These are found to be stronger with some samples of the luminescent material than with others differently prepared. Deutschbein's data for the samples which do *not* show these weaker lines at room temperature indicate that *all the subsidiaries exhibited at liquid air temperature* (other than the weak electronic transitions) are due to combination of the principal emission at $\lambda 6981$ with vibrational transitions in the MgO structure. The eigenfrequencies of MgO thus deduced are found to agree closely with the frequencies theoretically derived in the present paper. The diffuseness of the vibrational lines is accounted for by the width of the electronic line and the loading of the MgO lattice by the heavy atoms of chromium.

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