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RAMAN SPECTRUM OF MAGNESITE

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1. Introduction

According to Dana,[1] magnesite ($MgCO_3$) commonly occurs in massive and compact forms but clear single crystals are rare. It is not surprising therefore that few investigations have been made on its Raman spectrum. The only study reported in the literature was by Schæfer and others[2] who, using a single crystal, have reported a line at a frequency shift of 1096 cm.$^{-1}$ The opportunity for the present study arose due to the fact that some clear crystals from Brumadas, Bahia, Brazil were made available to us through the kindness of Dr. C. S. Pichamuthu. The density of a clear specimen was determined and found to be 3·02 gm./c.c., in fair agreement with the value 3·037 given in the *International Critical Tables.*

As the specimens were colourless, it was thought that the complete Raman spectrum could be readily recorded using the λ 2536·5 resonance line of mercury for excitation. Actually however, the crystals were found to be opaque to radiations of shorter wave-length than λ 2652. Hence the visible radiations of the mercury arc and a glass spectrograph had to be used, and the recording of the complete Raman spectrum was found to be far from easy, since in the first place the crystals were of rather small size and not completely free from flaws and since they also exhibited a faint luminescence. A strong and sharp line at a shift of 332 cm.$^{-1}$ and a strong but slightly diffuse line at 1096 cm.$^{-1}$ with a width of about ten wave-numbers were the principal features recorded on all the plates. By interposing a filter of $NaNO_2$ solution to suppress λ 4046 from the incident radiation and by placing a thin opaque strip just before the photographic plate to screen the exciting radiation λ 4358, clearer spectra were recorded in which could be observed and measured a line with a frequency shift of 212 cm.$^{-1}$ In some particularly clear spectrograms, a weak and rather diffuse line was found with a frequency shift of 735 cm.$^{-1}$ By analogy with the Raman effect in calcite one should expect one more line with a frequency shift in the vicinity of 1450 cm.$^{-1}$ A faint trace of such a line was found on one of the plates with an estimated frequency shift of 1460 cm.$^{-1}$

2. Discussion of Results

Magnesite has the same crystal structure as calcite belonging to the space-group D^6_{3d} of the trigonal system. Dolomite has also a similar structure, though it belongs to the space-group C^2_{3i}. In view of the similarity of crystal structure and chemical composition it is of interest to compare their Raman spectra. Table I shows the observed frequency shifts and their relative intensities in the case of calcite, dolomite and magnesite. The data for calcite are from a paper by Krishnan[3] while those for dolomite are due to Couture[4] by whom the Raman effect in dolomite has been investigated in detail.

Table I

Raman Frequencies

Substance	Frequency shifts in cm.$^{-1}$					
$CaCO_3$ ..	156 (8)	284 (15)		712 (2)	1086 (20)	1434 (5)
$CaMg(CO_3)_2$	176 (9)	301 (10)	335 (0·3)	724 (2)	1099 (23)	1444 (1·4)
$MgCO_3$ ..	212 (w)	332 (st)		735 (w)	1096 (st)	1460 (?)

As is to be expected, Table I exhibits a close similarity between the Raman spectra of calcite, dolomite and magnesite. All the frequencies of magnesite are definitely higher than those observed with calcite, this feature being more pronounced for the lattice oscillations than for the internal frequencies of the CO_3 group. An explanation of this feature is to be sought for in the fact that the lattice constants of calcite and magnesite are respectively 6·36 A.U., and 5·61 A.U., indicating a notable decrease in the interionic distances in the latter case. This would result in an increase of the interionic forces and hence also of the vibration frequencies involving the CO_3 groups.

Schæfer *et al.*[5] have studied the infra-red reflection and absorption spectra of magnesite and observed the following frequencies amongst others: Reflection Spectrum: 726, 889 and 1495 cm.$^{-1}$; Absorption Spectrum: 730, 877, 899 and 1430 cm.$^{-1}$ The only study on the far infra-red reflection spectrum of magnesite was by Coblentz[6] who observed a reflection maximum at 30·7 μ, *i.e.*, 326 cm.$^{-1}$ It will be noticed from the data that the frequency observed at 889 cm.$^{-1}$ in the infra-red does not appear in the Raman effect, whereas the frequency 1096 cm.$^{-1}$ observed in the Raman effect does not

appear in infra-red absorption. These facts are in accordance with the theoretical analysis of the vibrations of the calcite structure by Bhagavantam and Venkatarayudu.[7]

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SUMMARY

The Raman spectrum of magnesite ($MgCO_3$) has been investigated and found to be analogous in its features to that of calcite, as is to be expected in view of the similarity of structure. The frequency shifts observed are: 212 (*w*), 332 (*st*), 735 (*w*), 1096 (*st*) and 1460 (?) cm.$^{-1}$ All the frequencies and especially the two lowest are notably higher than for calcite and this is explicable as due to the smaller interionic distances and correspondingly larger force constants.

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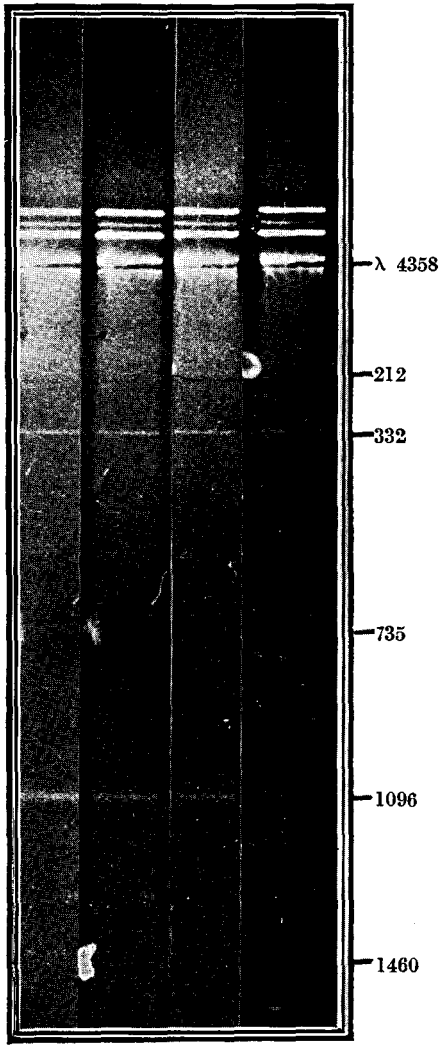

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