American Mineralogist, Volume 58, pages 1029–1033, 1973

The Crystal Structure of Magnesite

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Abstract

The crystal structure of synthetic magnesite has been studied by X-ray and infrared methods Magnesite is trigonal $R\bar{3}c$, with a = 4.637 Å, c = 15.023 Å, and Z = 6. Intensity data were collected with a Rigaku automated diffractometer and Mo$K\alpha$ radiation. The structure was refined by the full-matrix least-squares method using anisotropic thermal parameters. The final R index for 234 reflections is 0.037.

The C-O and Mg-O bond lengths were 1.283 and 2.105 Å, respectively. The interatomic angles of three kinds of O-Mg-O were 88.25, 91.75 and 180.00°, respectively. It is clarified that the distortion of the Mg-O_6 octahedron in magnesite is smaller than that of Ca-O_6 in calcite.

The force constants of the Urey-Bradley force field were calculated from the infrared absorption frequencies. For magnesite the stretching force constant $\mathbf{K}$ = 5.41, the bending force constant $\mathbf{H}$ = 0.46, the repulsive force constant $\mathbf{F}$ = 1.97, and the force constant for the out-of-plane vibration $f\theta$ = 0.65 md/Å. For calcite they are $\mathbf{K}$ = 5.51, $\mathbf{H}$ = 0.38, $\mathbf{F}$ = 1.88 and $f\theta$ = 0.64 md/Å.

Introduction

The crystal structure of magnesite has been said to be similar to that of calcite, but no previous single crystal structure analysis of magnesite is available. The present authors (1973) synthesized rhombohedral single crystals of magnesite about 100 μ in size by the hydrothermal method. Using these crystals, the present study was carried out to determine the crystal structure of magnesite and to compare it with the structure of calcite, which was first studied by Bragg (1914) and recently by Chessin, Hamilton, and Post (1965).

Data Collection and Refinement

The cell dimensions obtained using the powder method are a = 4.637(1) and c = 15.023(3) Å. Photographic experiments confirmed that magnesite has the same space group as calcite, $R\bar{3}c$. The only variable positional parameter is the x-coordinate of oxygen.

Intensities were measured on a Rigaku automated four-circle diffractometer equipped with a scintillation detector plus pulse height analyzer using Zr-filtered Mo$K\alpha$ radiation. A $\theta - 2\theta$ scan mode with a scanning speed of 1°/2 min was employed. Measurements of three reference reflections were carried out every 52 reflections. No systematic drift was observed. The indices of measured reflections were in the range, h: 0 to 11, k: -11 to 11, and l: 0 to 32 with $-h + k + l = 3\text{n}$ in the trigonal system. Observed structure factors were corrected for Lorentz polarization factors. Absorption corrections were not applied in view of the small value (0.03) of μR.

Refinement of the structure was carried out on 234 independent reflections using the full-matrix least squares program of UNICS (Sakurai, 1967) and the scattering factors for the neutral atoms given in *International Tables for X-ray Crystallography*, vol. 3 (1962). Refinements with anisotropic thermal parameters were carried out using the x-coordinate of oxygen, deduced from a prior set of film data, as the starting value. The weighting scheme used was w = 1.0 for all structure factors.

There are only 10 variable parameters: a scale factor, the x-coordinate of oxygen, its four independent thermal parameters, the two thermal parameters of carbon, and the two thermal parameters of magnesium. The final conventional R was 0.037, and the final weighted R was 0.038. Table 1 gives the positional and thermal parameters with their standard errors. The observed and calculated structure factors are compared in Table 2. Table 3 gives the interatomic distances and angles, and Table 4 the r.m.s. displacements of thermal motions and

TABLE. 1. Positional and Thermal Parameters of Magnesite*

Parameters	Atoms		
	Mg	C	O
x	0	0	0.2767(2)
y	0	0	0
z	0	1/4	1/4
β11	0.0063(4)	0.0072(8)	0.0059(3)
β22	--	--	0.0091(4)
β33	0.00060(3)	0.00052(6)	0.00083(3)
β23	--	--	-0.00027(9)

*Standard deviations are shown in parentheses.

their orientations together with those of calcite reported by Chessin *et al* (1965) for comparison.

Infrared

The infrared spectrum of magnesite was obtained by using a Japan Spectrometer (JASCO) IR-G with gratings. Magnesite showed strong absorption bands at 880, 1440, and 745 cm^{-1} for ν_2, ν_3, and ν_4 modes, respectively.

ν_3 and ν_4 modes of vibration can be analyzed theoretically by Wilson's method using the GF matrices (Wilson *et al*, 1955; Omori, 1971). The

TABLE 2. Observed and Calculated Structure Factors

h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c	h	k	ℓ	F_o	F_c
					4	7	6	-6.96	-7.47	1	1	15	23.46	23.96
1	1	0	27.76	29.33	0	9	6	6.93	8.35	2	2	15	-10.79	-10.57
2	2	0	25.76	26.17	2	1	7	24.78	25.03	5	5	15	9.25	8.70
0	3	0	83.91	84.65	5	1	7	19.44	19.17	1	0	16	37.91	38.24
3	3	0	28.41	29.30	3	2	7	-18.54	-18.81	4	0	16	38.53	39.57
1	4	0	27.55	29.34	6	2	7	-12.50	-12.86	7	0	16	25.13	24.81
4	4	0	27.13	27.39	2	4	7	8.83	9.61	2	1	16	20.33	21.01
2	5	0	14.89	14.72	3	5	7	-9.28	-7.59	5	1	16	7.60	6.59
0	6	0	19.20	19.24	2	0	8	33.01	32.23	0	2	16	20.57	20.58
3	6	0	7.28	5.96	5	0	8	18.57	18.86	3	2	16	11.72	11.59
1	7	0	19.45	19.82	8	0	8	18.66	18.00	1	3	16	30.28	31.03
4	7	0	20.24	18.72	0	1	8	74.59	73.85	4	3	16	25.53	25.85
2	1	1	-33.39	-32.57	3	1	8	46.46	47.20	2	4	16	11.34	11.68
5	1	1	-19.70	-20.74	6	1	8	17.14	17.99	0	5	16	14.37	14.07
8	1	1	-11.62	-8.55	1	2	8	33.70	33.63	3	5	16	11.12	11.59
3	2	1	19.67	21.19	4	2	8	16.56	17.02	1	6	16	14.49	13.93
6	2	1	12.99	13.52	2	3	8	15.92	16.43	0	8	16	14.65	14.81
1	3	1	8.05	7.87	5	3	8	14.32	14.03	1	2	17	-12.57	-12.64
2	4	1	-10.76	-10.57	0	4	8	56.76	57.84	2	3	17	12.67	12.17
3	5	1	8.39	7.93	3	4	8	33.67	33.40	1	5	17	-14.54	-15.92
2	0	2	54.75	54.26	6	4	8	12.40	10.87	0	0	18	-14.62	-14.35
5	0	2	17.46	17.74	1	5	8	10.26	9.82	3	0	18	-7.93	-5.74
1	2	2	40.19	39.92	2	6	8	7.22	7.13	1	1	18	20.70	21.61
4	2	2	15.76	16.72	5	6	8	9.02	7.93	4	1	18	7.01	6.32
2	3	2	29.10	29.38	0	7	8	30.58	31.13	2	2	18	14.31	15.05
0	4	2	-14.59	-13.78	3	7	8	15.70	15.33	2	1	19	10.27	10.79
3	4	2	-9.73	-9.03	1	1	9	-42.48	-41.75	5	1	19	13.27	12.62
1	5	2	21.18	21.75	4	1	9	-8.29	-7.66	3	2	19	-12.03	-11.29
4	5	2	10.83	10.11	2	2	9	14.94	14.70	2	0	20	14.93	14.84
2	6	2	11.67	11.90	5	2	9	-5.61	-5.23	5	0	20	11.30	10.45
0	7	2	-12.73	-12.59	3	3	9	8.49	6.37	0	1	20	27.99	28.38
1	1	3	72.04	67.23	1	4	9	-7.92	-8.03	3	1	20	23.85	24.71
4	1	3	8.56	9.16	2	8	9	-6.04	-6.95	6	1	20	12.92	11.85
2	2	3	-18.62	-18.85	1	0	10	12.29	13.37	1	2	20	15.74	16.04
5	2	3	6.98	5.68	4	0	10	-11.65	-11.50	4	2	20	10.96	10.20
3	3	3	-7.69	-7.21	7	0	10	-9.91	-11.64	2	3	20	8.57	8.43
6	3	3	-9.81	-8.93	2	1	10	27.35	28.07	5	3	20	11.38	9.35
1	4	3	8.94	9.19	5	1	10	16.89	17.87	0	4	20	31.51	31.74
2	5	3	6.31	5.51	0	2	10	36.51	36.58	3	4	20	20.54	21.57
5	5	3	11.54	11.08	3	2	10	21.39	22.19	0	7	20	20.99	21.07
1	0	4	99.05	98.90	6	2	10	10.55	10.23	1	1	21	-14.95	-15.55
4	0	4	63.94	65.67	4	3	10	-9.03	-8.58	2	2	21	7.23	7.59
7	0	4	32.87	33.31	2	4	10	13.23	13.45	2	1	22	10.18	9.61
2	1	4	39.59	38.62	0	5	10	12.16	13.22	5	1	22	9.74	10.00
5	1	4	10.66	10.60	3	1	11	-5.22	-5.98	0	2	22	11.06	11.80
0	2	4	36.91	37.56	1	2	11	18.54	19.03	3	2	22	10.49	10.02
3	2	4	18.20	18.51	4	2	11	10.02	8.94	4	3	22	-6.35	-6.24
6	2	4	10.00	7.85	2	3	11	-15.71	-15.93	2	4	22	8.17	6.94
1	3	4	52.93	54.20	1	5	11	17.13	17.30	0	5	22	7.09	5.85
4	3	4	36.27	36.11	2	6	11	-10.59	-11.57	2	3	23	-8.74	-8.93
7	3	4	14.49	16.20	0	0	12	94.48	93.01	1	5	23	9.95	10.50
2	4	4	18.09	18.30	3	0	12	51.39	52.78	0	0	24	34.94	34.99
0	5	4	20.88	21.32	6	0	12	15.81	14.94	3	0	24	24.44	24.67
3	5	4	15.45	15.37	1	1	12	22.20	22.19	6	0	24	9.71	8.54
6	5	4	9.40	8.42	4	1	12	20.78	21.76	1	1	24	9.48	9.28
1	6	4	19.88	19.32	7	1	12	16.64	16.83	2	2	24	9.76	8.58
4	6	4	12.08	11.71	2	2	12	18.85	18.96	0	3	24	25.24	24.87
0	8	4	20.11	19.19	5	2	12	10.59	11.04	3	3	24	12.84	12.56
3	1	5	7.36	7.59	0	3	12	52.22	52.99	1	4	24	11.50	11.21
1	2	5	-28.82	-28.63	3	3	12	22.34	22.43	4	4	24	15.47	13.97
4	2	5	-9.64	-10.29	1	4	12	20.80	21.56	0	6	24	10.55	9.40
2	3	5	19.27	19.78	4	4	12	21.94	22.65	2	1	25	-8.29	-7.49
5	3	5	8.25	7.52	2	5	12	11.72	11.57	5	1	25	-8.20	-9.35
1	5	5	-20.47	-20.03	0	6	12	14.75	15.68	3	2	25	8.40	8.20
4	5	5	-7.84	-6.08	1	7	12	16.32	16.43	2	0	26	8.97	8.68
2	6	5	13.20	13.11	2	1	13	-15.88	-16.15	2	3	26	8.63	8.25
0	0	6	-69.77	-68.11	5	1	13	-16.04	-16.13	1	1	27	11.24	10.59
3	0	6	-8.55	-7.83	3	2	13	14.89	14.91	1	0	28	14.85	15.61
9	0	6	11.51	8.80	6	2	13	9.70	11.26	4	0	28	19.94	19.69
1	1	6	60.08	59.49	2	4	13	-7.52	-7.89	2	1	28	9.41	8.97
4	1	6	13.26	14.37	2	0	14	24.92	26.21	0	2	28	9.45	8.55
2	2	6	33.26	33.49	5	0	14	11.98	11.24	1	3	28	14.14	14.79
5	2	6	10.80	10.83	0	1	14	9.82	10.18	4	3	28	14.16	14.33
0	3	6	-8.39	-7.98	1	2	14	19.65	20.04	1	5	29	-6.97	-7.40
3	3	6	9.53	6.99	4	2	14	10.12	10.46	1	1	30	8.61	7.58
1	4	6	14.16	14.59	2	3	14	19.04	17.96	2	2	30	8.87	6.14
2	5	6	10.57	10.99	0	4	14	-11.34	-10.93	3	1	32	11.09	11.63
3	6	6	11.47	9.84	1	5	14	14.13	14.84	0	4	32	14.83	15.21
					2	6	14	10.39	9.21					

elements of the **G** and **F** matrices of the ν_3 and ν_4 modes of vibration for the CO_3 ion were calculated by using the following relations:

$$\mathbf{G}_{11} = \mu_{(C)} + \mu_{(O)} - \mu_{(C)} \cos \alpha$$

$$\mathbf{G}_{12} = -\frac{2\mu_{(C)}}{r}\cdot\frac{\cos \alpha(1 - \cos \alpha)}{\sin \alpha} + \frac{\mu_{(C)}}{r}\cdot\sin \alpha$$

$$\mathbf{G}_{22} = \frac{2}{r^2}[\mu_{(O)} + \mu_{(C)}(1 - \cos \alpha)] - \left[\frac{\mu_{(O)}}{r^2}\cdot\frac{\cos \alpha}{1 + \cos \alpha} + \frac{\mu_{(C)}}{r^2}\cdot\frac{(1 + 3\cos \alpha)(1 - \cos \alpha)}{1 + \cos \alpha}\right]$$

$$\mathbf{F}_{11} = \mathbf{K} + \left[\sin^2\frac{\alpha}{2} - (0.3)\cos^2\frac{\alpha}{2}\right]\mathbf{F}$$

$$\mathbf{F}_{12} = -(0.9)r\cdot\mathbf{F}\cdot\sin\frac{\alpha}{2}\cdot\cos\frac{\alpha}{2}$$

$$\mathbf{F}_{22} = r^2\left[\mathbf{H} + \mathbf{F}\left\{\cos^2\frac{\alpha}{2} + (0.1)\sin^2\frac{\alpha}{2}\right\}\right]$$

where $\mu_{(O)}$ and $\mu_{(C)}$ were the reciprocal mass of the oxygen and carbon atoms, respectively; r was the bond length between the oxygen and carbon atoms; α was equal to 120°; and **K**, **H**, and **F** are the force constants in the Urey-Bradley force field (Urey and Bradley, 1931). For the CO_3 ion **K** is the stretching force constant between C–O; **H** is the bending force constant between O–C–O; and **F** is the repulsive force constant between two oxygens O . . . O.

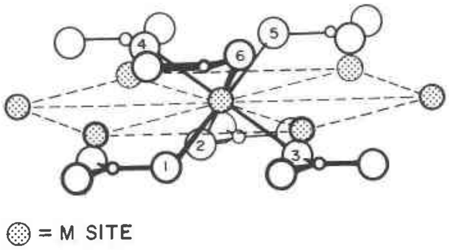
The force constants $\mathbf{K} = 5.41$, $\mathbf{H} = 0.46$, and $\mathbf{F} = 1.97$ md/Å were determined from calculations applying the Jacobian matrix, using $r = 1.283$ Å. The calculated frequencies $\nu_3 = 1440$ and $\nu_4 = 745$ cm^{-1} are identical to the observed values.

The force constants of calcite $\mathbf{K} = 5.51$, $\mathbf{H} = 0.38$, and $\mathbf{F} = 1.88$ md/Å were also determined using the infrared spectral data reported by Huang and Kerr (1960) and the C–O bond length reported by Chessin *et al* (1965). The calculated frequencies for calcite, $\nu_3 = 1435$ and $\nu_4 = 713$ cm^{-1}, are the same as the reported values. The out-of-plane vibration force constant, $f\theta$, was directly calculated using the wave number of the ν_2 mode. These values are summarized in Table 5.

Discussion

It is interesting to compare the results of magnesite with those of calcite reported by Chessin *et al* (1965).

TABLE. 3. Interatomic Distances and Angles in Magnesite and Calcite



	magnesite	calcite*
M - O	2.105(1)Å	2.356(1)Å
C - O	1.283(1)	1.283(1)
$O_1 - O_2$	2.850(1)	3.261(2)
$O_1 - O_6$	3.022(1)	3.402(1)
$O_1 - M - O_2$	88.25(2)°	87.57(3)°
$O_1 - M - O_6$	91.75(2)	92.43(3)
$O_1 - M - O_5$	180.00(2)	180.00(3)

**After Chessin <u>et al</u>. Standard deviations are given in parentheses.*

Shape of the Octahedron

The three independent O–Mg–O interatomic angles of magnesite are 88.25, 91.75, and 180.00°, respectively, while those of O–Ca–O are 87.57, 92.43, and 180.00°, as listed in Table 3. Thus the octahedron in magnesite is closer to the ideal than that in calcite. This can be explained by the fact that the Mg^{2+} has a more suitable size for octahedral

TABLE. 4. The r.m.s. Component of Thermal Displacement (Å) of Magnesite and Calcite*

	Magnesite			Calcite**
	Mg	C	O	O
R_1	0.072(4)	0.077(8)	0.063(7)	0.032(9)
R_2	0.072(4)	0.077(8)	0.084(5)	0.089(7)
R_3	0.083(4)	0.077(8)	0.099(3)	0.155(4)
α(°)	--	--	19(2)	48(2)

* R_1 and R_2 of Mg and C are on the plane normal to the c axis. R_3 of Mg and C, and R_1 of O coincide with the c axis, and the a axis, respectively. An angle α is defined as the angle which R_3 of O makes with the c axis, and this is measured from the positive c direction towards the negative b^* direction.

** The parameters of oxygen atoms in calcite were determined from the reflections with $h\neq0$, $k\neq0$ and $l=2n+1$ (after Chessin et al.).

TABLE 5. Summary of Infrared Analyses

Interatomic distance(Å)		Magnesite		Calcite
C-O		1.283		1.283
Force constant(md/Å)				
Stretching (K)		5.41		5.51
Bending (H)		0.46		0.38
Repulsive (F)		1.97		1.88
Out of plane vibration (fθ)		0.65		0.64
Absorption band(cm^{-1})	Calc	Obs	Calc	Obs
ν_1 (Raman)	--	1096*	--	1087*
ν_2	--	880	--	877+
ν_3	1440	1440	1435	1435+
ν_4	745	745	713	713+

* D.Krishnamurti; + C.K.Huang and P.F.Kerr.

coordination by oxygen ions. The principal axes of the thermal ellipsoid of oxygen are 0.063, 0.084, and 0.099 Å in magnesite and 0.032, 0.089, and 0.155 Å in calcite. The thermal ellipsoid of oxygen in magnesite is an oblate spheroid as in orthorhombic carbonates (de Villiers, 1971; dal Negro, 1971). However, the thermal ellipsoid in calcite is compressed along the *a* axis and is elongated along one direction (Table 4). Since Ca^{2+} has nearly the upper-limit size that fits into the octahedron, Ca^{2+} is not sufficiently shielded by oxygen. Therefore, the electron clouds of oxygens in calcite are strongly stretched to screen the cation-cation interaction.

C–O Bond Length

The length of the C–O bond, which is 1.283 Å in both magnesite and calcite, has been the subject of many experimental investigations, especially in the field of infrared absorption. The infrared absorption frequencies are influenced by surrounding metallic ions. Recently Elderfield and Chester (1971) reported the variations of the ν_4 mode of many normal anhydrous carbonate minerals. The wavelengths of the ν_4 modes reported by them and the lengths of the C–O bonds in the literature are listed in Table 6. The C–O bond lengths in trigonal carbonates are almost identical with one another, but different from those in orthorhombic carbonates. It is apparent that a correlation exists between the length of the C–O bond and the shifting frequency of the orthorhombic carbonate within the same group of the periodic table. Namely, the ν_4 wavelength increases with increasing mean C–O bond length. In contrast, the C–O bond length in trigonal carbonates is almost constant regardless of variations of the shifting frequency.

TABLE 6. Relationships between ν_4 Mode and C–O Bond Length (Å)

	Wavelength* (μm)	C-O bond length (Å) Average			References**
		Trigonal Carbonates			
Magnesite	13.40, *13.42*	1.283 (1)	--	--	This study
Dolomite	13.76	1.283	--	--	S and S
Calcite	14.08	1.283 (1)	--	--	C, H, and P
		Orthorhombic Carbonates			
Aragonite	14.08, 14.39	1.282,	1.279 (5),	1.284 (3)	dV
		1.284,	1.280 (5),	1.287 (3)	dN and U
Strontianite	14.24, 14.34	1.285,	1.269(10),	1.287 (3)	dV
Witherite	14.56	1.287,	1.282(12),	1.289 (7)	dV

**Wavelength values from Elderfield and Chester (1971), except that in italics which is from this study.*
***S and S = Steinfink and Sans (1959); C, H, and P = Chessin, Hamilton, and Post (1965); dV = deVilliers (1971); dN and U = dal Negro and Ungaretti (1971).*

Results of Infrared Analyses

The stretching force constant **K** is the largest among the force constants in both minerals. From a potential energy consideration, movements of oxygen are more restricted along the *a* axis than perpendicular to it. As a result, the thermal ellipsoid of oxygen in the CO_3 ion is compressed along the *a* axis. Concerning the shape of the thermal ellipsoid, the results obtained by infrared analyses are in qualitative conformity with the results obtained by X-ray analyses.

Acknowledgments

The authors wish to thank Professor K. Ohmori of Tohoku University, Japan, who directed the calculation for the infrared analysis. X-ray data collections with the 4-circle diffractometer were performed at Iidaka Laboratory, Faculty of Pharmacy, University of Tokyo, Japan, under the direction of Professor Y. Iidaka. The computations were carried out using UNICS program at The Computer Center of Tokyo Institute of Technology using HITAC 8500.

References

BRAGG, W. L. (1914) An analysis of crystals by the X-ray spectrometer. *Proc. Roy. Soc. London,* **A89,** 468–469.

CHESSIN, H., W. C. HAMILTON, AND B. POST (1965) Position and thermal parameters of oxygen atoms in calcite. *Acta Crystallogr.* **18,** 689–693.

DAL NEGRO, A., AND L. UNGARETTI (1971) Refinement of the crystal structure of aragonite. *Amer. Mineral.* **56,** 768–772.

DE VILLIERS, J. P. R. (1971) Crystal structures of aragonite, strontianite, and witherite. *Amer. Mineral.* **56,** 758–767.

ELDERFIELD, H., AND R. CHESTER (1971) The effect of periodicity on the infrared absorption frequency ν_4 of anhydrous normal carbonate minerals. *Amer. Mineral.* **56,** 1600–1606.

HUANG, C. K., AND P. F. KERR (1960) Infrared study of the carbonate minerals. *Amer. Mineral.* **45,** 311–324.

KRISHNAMURTI, D. (1956) Raman spectrum of magnesite. *Proc. Indian Acad. Sci.* **43A,** 210–212.

MACGILLAVRY, C. H., AND G. D. RIECK (1962) *International Tables for X-ray Crystallography,* Vol. 3, p. 202. Kynoch Press, Birmingham, England.

OH, K., H. MORIKAWA, S. IWAI, AND H. AOKI (1973) Hydrothermal growth of single magnesite. *Amer. Mineral.* **58,** 339–340.

OMORI, K. (1971) Analysis of the infrared absorption spectrum of almandine-pyrope garnet from Nijosan, Osaka prefecture, Japan. *Amer. Mineral.* **56,** 841–849.

SAKURAI, T., Ed. (1967) *Universal Crystallographic Computation Program System.* Crystallographic Society, Japan.

STEINFINK, H., AND F. T. SANS (1959) Refinement of the crystal structure of dolomite. *Amer. Mineral.* **44,** 679–682.

UREY, H. C., AND C. A. BRADLEY (1931) The vibrations of pentatonic tetrahedral molecules. *Phys. Rev.* **38,** 1969–1978.

WILSON, E. B., J. C. DECIUS, AND P. C. CROSS (1955) *Molecular Vibration.* McGraw-Hill, New York.

Manuscript received, November 17, 1972; accepted for publication, June 5, 1973.