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Crystal structure refinements of magnesite, calcite, rhodochrosite, siderite, smithonite, and dolomite, with discussion of some aspects of the stereochemistry of calcite type carbonates

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Abstract. The crystal structures of magnesite, calcite, rhodochrosite, siderite, smithonite and dolomite were refined by standard single crystal X-ray methods using diffraction data up to $\sin\vartheta/\lambda = 1.0\,\text{Å}^{-1}$. The C–O bond lengths are essentially the same. Attention is drawn to short O–O contacts (2.85 Å in both magnesite and smithonite) outside the coordination figures. The MeO_6 octahedra are always elongated parallel [00.1]; the distortion is not a monotone function of the Me–O distance. The approximation of four point charges for the $[CO_3]^{2-}$ ion for calcite gives good agreement between observation and classical electrostatic calculation when charges of 1+ for carbon and 1− for oxygen are used.

Introduction

The main features of the atomic arrangement in the calcite and in the dolomite structure type have been known since the early days of X-ray crystallography (calcite: Bragg, 1914; dolomite: Bragg, 1914; Wyckoff and Merwin, 1924), and modern refinements have been published for some of the representatives (calcite: Sass et al., 1957; Inkinen and Lahti, 1964; Chessin et al., 1965; Finger, 1975; Petersen et al., 1979; magnesite: Oh et al., 1973; Finger, 1975; rhodochrosite: Brown and Forsyth, 1967; dolomite: Steinfink and Sans, 1959; Althoff, 1977; Beran and Zemann, 1977; ankerite: Beran and Zemann, 1977). Although results of neutron diffraction investigations of the spin ordering in siderite have been published (Alikhanov, 1959; Pickart,

1960) modern structure refinements for this mineral and for smithonite could not be found in the literature.

In view of our interest in the crystal chemistry of carbonates, we decided to refine the crystal structures of several members of the calcite type and of dolomite using exactly the same method of data collection and refinement to learn more about a possible variation of the C−O bond length in the carbonate group and about the exact geometry of the MeO_6 polyhedra. The final choice of the examples was influenced by the easy availability of the title minerals.

Experimental and structure refinements

Optically homogenous material from natural minerals was used for this investigation. The origin of the specimens and the results of partial microprobe analyses are given in Table 1.

After preliminary X-ray work, spheres of diameters between 0.27 and 0.29 mm were ground, except for calcite where a sphere diameter of only 0.23 mm was chosen in order to keep extinction effects low. Lattice parameters and diffraction intensities were obtained on a Philips PW1100 diffractometer. Data were collected with Mo$K\alpha$-radiation (graphite monochromator) from $2\vartheta = 6°$ to $2\vartheta = 90°$ using $\omega - 2\vartheta$-scan; they were corrected with the Lorentz and polarization factors to obtain F_0's. Absorption corrections for the spherical shape were applied. The complex scattering functions for neutral atoms were taken from the "International Tables for X-ray Crystallography", Vol. IV (1974). The structures were refined with the full-matrix least-squares programm CRYLSQ (X-Ray-72, Stewart et al., 1972). An isotropic extinction correction according to Larson (1967) was applied.

Table 1. Localities and chemical compositions of the minerals used. Partial electron-microprobe analyses in weight-% (analyst: A. Beran)

Locality	$MgCO_3$ Oberdorf, Styria, Austria	$CaCO_3$ Iceland	$MnCO_3$ Alicante, Spain	$FeCO_3$ Ivigtut, Greenland	$ZnCO_3$ Tsumeb	$MgCa(CO_3)_2$ Oberdorf, Styria, Austria
CaO	0.1	55.7	0.1	0.1	n.d.	30.1
MgO	47.1	0.2	0.2	0.2	0.3	20.4
FeO[a]	0.6	0.1	4.0	58.8	0.9	1.8
MnO	0.1	n.d.	57.3	2.9	0.2	0.5
ZnO	n.d.	n.d.	n.d.	n.d.	63.3	n.d.

[a] Total iron as FeO
n.d. = not detected

Table 2 gives the crystallographic data. Unit cell parameters were obtained with the measuring routine LAT and least-squares refinements by PARAM. Table 3 gives the results of the structure refinements. A list with the F_0's and F_c's is available upon request from the Institut für Mineralogie und Kristallographie der Universität Wien, Vienna.

In order to depend not just on the standard deviations of the least-squares refinements for the estimation of the errors, we also carried out refinements with partial data sets. All six structures were refined with the reflections for which $0.5 < \sin\vartheta/\lambda < 1.0\,\text{Å}^{-1}$, the five calcite type carbonates also with data sets containing only the ($l = 2n + 1$) reflections. With the one exception of calcite, these results agreed with those for the complete data set (Table 3) within 2σ, very often within 1σ. The refinement with the higher order reflections for calcite, however, yielded the positional parameter of oxygen $x = 0.25735(13)$, 0.00053 off the value given in Table 3. As a consequence, we consider the standard deviations of Table 3 as very reliable for magnesite, rhodochrosite, siderite, smithonite, and dolomite, while the error of the x-parameter of calcite is probably larger. We consider oxygen positional parameters up to $x = 0.2573$ to be possible for this mineral.

Our results of magnesite, rhodochrosite and dolomite agree well with earlier modern refinements (magnesite: Oh et al., 1975; Finger, 1975; rhodochrosite: Brown and Forsyth, 1967; dolomite: Althoff, 1977; Beran and Zemann, 1977) but seem to be somewhat more accurate. As to calcite, our refinement is in good agreement with those of Chessin et al. (1965) and of Finger (1975), but for the reasons given we can not claim a greater accuracy.

Stereochemical discussion of the refined structures

Interatomic distances are given in Table 4. Important results of our refinements:

(1) The variation of the C–O bond length in this group of minerals is very slight, if at all real. The most extreme values obtained were C–O = 1.2811(10) Å (calcite, refinement with $l = 2n + 1$ data) and C–O = 1.2875(6) Å (siderite, refinement with high-order reflections). Even when comparing the results with the high-order reflections for these two minerals in both cases the C–O bond length difference is 0.0033(13) Å and is therefore probably significant. This holds, of course, only for the distances between the centers of vibration – a rigid body refinement or a correction for riding motion (cf. Table 4) can overcompensate this difference. The anisotropic temperature factors for calcite are significantly larger than those for the five other structures, whereas the parameters for dolomite are between those for calcite and magnesite. Physically more significant is the comparison of two representatives in which the tensors of the thermal vibration are very similar. One such pair is magnesite – siderite; in this case the C–O bond length

Table 2. Crystallographic data. Standard deviations (in units of last digit) in parentheses

	Magnesite	Calcite	Rhodochrosite	Siderite	Smithonite	Dolomite
a [Å]	4.6328(2)	4.9896(2)	4.7682(2)	4.6916(4)	4.6526(7)	4.812(1)
c [Å]	15.0129(5)	17.0610(11)	15.6354(8)	15.3796(16)	15.0257(22)	16.020(3)
V [Å^3]	279.05(3)	367.85(5)	307.86(4)	293.17(8)	281.68(13)	321.06(9)
Space group	$R\bar{3}\frac{2}{c}$	$R\bar{3}\frac{2}{c}$	$R\bar{3}\frac{2}{c}$	$R\bar{3}\frac{2}{c}$	$R\bar{3}\frac{2}{c}$	$R\bar{3}$
Z	6	6	6	6	6	3
μ(Mo$K\alpha$) [cm^{-1}]	6	22	60	72	133	15

Table 3. Results of least-squares structure refinements for the complete data sets. Standard deviations (in units of the last digit) in parentheses. Hexagonal cell. ATF = $\exp\left[-2\pi^2\left(U_{11}\,a^{*2}h^2 + \ldots + 2\,U_{23}\,b^*c^*kl\right)\right]$

Calcite-type compounds							Dolomite-type		
		Magnesite	Calcite	Rhodochrosite	Siderite	Smithonite		Dolomite	
6 Me^{2+} on 6(b)	U_{11}	0.00532(10)	0.00989(8)	0.00662(8)	0.00580(6)	0.00520(6)	3 Ca on 3(a)	U_{11}	0.00846(6)
(0, 0, 0) etc.	U_{33}	0.00617(13)	0.00972(10)	0.00624(9)	0.00514(8)	0.00513(7)	(0, 0, 0) etc.	U_{33}	0.00804(8)
							3 Mg on 3(b)	U_{11}	0.00414(8)
							(0, 0, $\frac{1}{2}$) etc.	U_{33}	0.00582(11)
6 C on 6(a)	U_{11}	0.00471(14)	0.00851(22)	0.00632(22)	0.00571(22)	0.00384(22)	6 C on 6(c)	z	0.24287(4)
(0, 0, $\frac{1}{4}$) etc.	U_{33}	0.00519(20)	0.01161(35)	0.00572(35)	0.00511(31)	0.00399(31)	(0, 0, z) etc.	U_{11}	0.00655(11)
								U_{33}	0.00763(16)
18 O on 18(e)	x	0.27740(7)	0.25682(11)	0.26986(9)	0.27427(10)	0.27636(11)	18 O on 18(f)	x	0.24802(7)
(x, 0, $\frac{1}{4}$) etc.	U_{11}	0.00486(11)	0.01108(16)	0.00634(12)	0.00586(12)	0.00446(13)	(x, y, z) etc.	y	−0.03471(7)
	U_{33}	0.00834(14)	0.02057(24)	0.01024(16)	0.00915(16)	0.00711(16)		z	0.24401(2)
	U_{12}	0.00355(6)	0.01088(14)	0.00485(8)	0.00425(9)	0.00319(9)		U_{11}	0.00782(9)
	U_{13}	−0.00058(4)	−0.00411(11)	−0.00108(6)	−0.00077(7)	−0.00071(7)		U_{22}	0.01130(10)
								U_{33}	0.01359(11)
								U_{12}	0.00634(7)
								U_{13}	−0.00208(7)
								U_{23}	−0.00324(7)
g (extinction coefficient according to Larson [1967])		0.00055(2)	0.00086(2)	0.00023(1)	0.00006(1)	0.00009(1)			0.00019(1)
Number of observed reflections		263	340	288	274	264		596	
Number of refined reflections (m)		253	340	288	274	264		596	
$R = \Sigma(F_o - F_c)/\Sigma F_o$		0.020	0.022	0.015	0.013	0.013		0.021	
$R_w = [\Sigma_w(F_o - F_c)^2/\Sigma_w F_o{}^2]^{1/2}$		0.022	0.023	0.019	0.017	0.016		0.024	
$s = [\Sigma_w(F_o - F_c)^2/(m-n)]^{1/2}$		1.07	0.92	1.01	0.97	0.98		1.27	
Number of variables (n)		11	11	11	11	11		18	

Table 4. Some interatomic distances [Å] according to the refinements with the complete reflection data sets (cf. Table 3). Standard deviations (in units of last digit) in parentheses. The C–O bond distances corrected for riding motion are given in brackets (Busing and Levy, 1964)

	Magnesite	Calcite	Rhodochrosite	Siderite	Smithonite	Dolomite
C–O	1.2852(4) [1.2873]	1.2815(6) [1.2902]	1.2867(5) [1.2898]	1.2869(5) [1.2895]	1.2859(6) [1.2881]	1.2853(4) [1.2895]
Me–O	2.1018(4)	2.3598(6)	2.1900(5)	2.1445(5)	2.1107(6)	2.3822(5) 2.0877(4)
d_1	3.0188(5)	3.4107(7)	3.1447(6)	3.0864(6)	3.0263(6)	3.4377(6) 2.9940(6)
d_2	2.9252(7)	3.2623(10)	3.0489(8)	2.9781(9)	2.9430(9)	3.2987(8) 2.9103(7)
$\Delta = d_1/d_2$	1.0320(4)	1.0455(5)	1.0314(5)	1.0364(5)	1.0283(5)	1.0421(5) 1.0288(4)
d_3	2.8485(5)	3.1883(5)	2.9531(5)	2.9080(5)	2.8524(5)	3.0696(7) 2.9966(6)

In the dolomite column the upper values refer to the CaO_6 polyhedron or the "Ca sheet" and the lower values to the MgO_6 polyhedron or the "Mg sheet".

d_1 = Edge of the MeO_6 polyhedra inclined to (00.1); d_2 = edge of the MeO_6 polyhedra parallel to (00.1); d_3 = shortest O–O distances outside the coordination figures.

difference according to the refinements is 0.0017(9) Å (refinement with all data, Table 4), 0.0024(14) Å (refinement with $l = 2n + 1$ reflections) and 0.0021(14) Å (refinement with high-order reflections); sigma is taken as the sum of the standard deviations of the two respective bond lengths. Therefore it seems probable that the C–O bond length in siderite is 0.002(1) Å longer than in magnesite.

(2) All seven MeO_6 octahedra in our compounds are somewhat elongated parallel [00.1] as was known previously; the ratios Δ = (longer edge)/(shorter edge) are given in Table 4. It should be noted that these ratios are not a monotone function of the distance Me–O.

(3) The weakly pyramidal shape of the carbonate group in dolomite (cf. Steinfink and Sans, 1959; Althoff, 1977; Beran and Zemann, 1977) is definitely confirmed. The new value for the distance of the C atom from the plane of the oxygen atoms is 0.018(1) Å for both the refinement with the complete data set and with only the high-order reflections.

(4) The result of Althoff (1977) and of Beran and Zemann (1977) that the Mg–O distance in dolomite is shorter than in magnesite, while the Ca–O distance is longer than in calcite, is confirmed.

(5) Attention is drawn to the calcite type compounds with their short O–O distances which are not edges of coordination figures, Such a distance

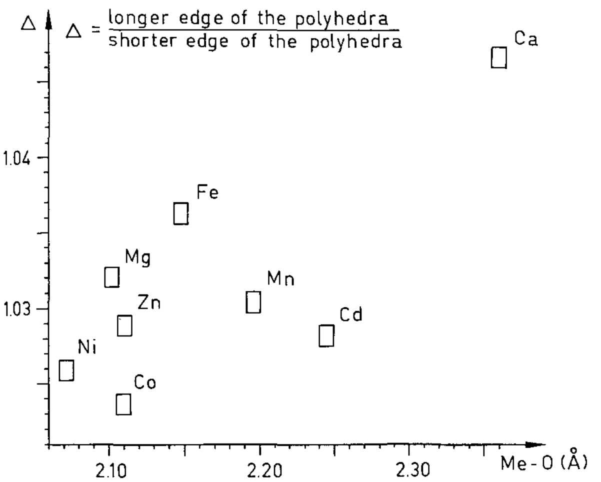

Fig. 1. Distortion index Δ [=(longer edge)/(shorter edge) of the MeO_6polyhedron] for theoretical calcite-type structures. Lattice parameters according to Graf (1961), C—O = 1.285 Å

occurs e.g. between the oxygen atoms on $(x, 0, 0)$ and on $(\frac{2}{3}-x, \frac{1}{3}, \frac{1}{6})$; in Table 4 they are listed as d_3. These O—O distances are always shorter than any of the edges in the MeO_6 octahedra. They may be as short as 2.85 Å (magnesite and smithonite) and thus belong to the shortest known non-bonding O—O contacts between two oxygens outside a coordination polyhedron; according to our knowledge the shortest such distance occurs in the high-pressure modification of $AlBO_3$ with O—O = 2.67 Å (cf. for this structure Vegas et al., 1977; this distance is not given in their paper). No notice seems to have been taken so far of the stereochemical role of these short O—O contacts in the calcite type compounds with small cations.

Some more general problems of calcite type compounds

The nearly uniform C—O bond length in trigonal carbonates also allows one to predict reasonably accurately the structures for those members of the calcite type for which only the lattice parameters are known. We have derived theoretical $MeCO_3$ structures from the lattice parameters given by Graf (1961) assuming C—O to be 1.285 Å and have computed the O—O edges of the MeO_6 octahedra. The distortion indices $\Delta = d_1/d_2$ are plotted in Figure 1 as a function of the Me—O distance. The distortion index is definitely not a monotone function of Me—O. This shows clearly that the stereochemistry of the calcite type carbonates cannot be treated merely by applying electrostatic forces and radial symmetric repulsion forces, but that other spherical effects of the bond between Me(II) and oxygen must also be considered; this is definitely so for the transition metals (cf. also Rosenberg and Foit, 1979).

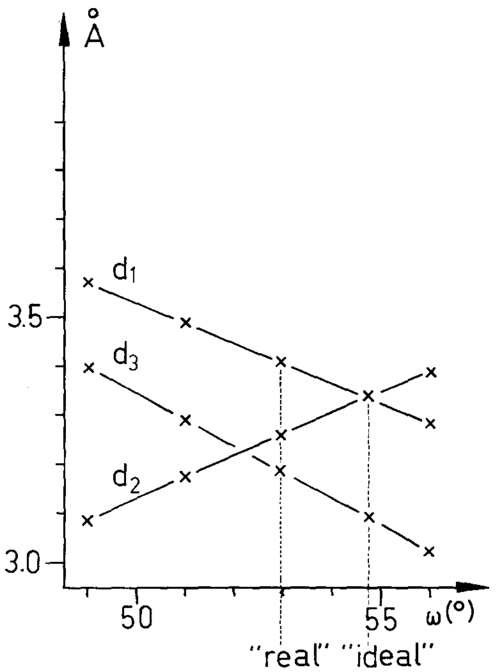

Fig. 2. Edges of the CaO_6 polyhedron (d_1 and d_2) and short inter-polyhedral O – O distance (d_3) in theoretical calcite structures as a function of ω. Ca – O and C – O were kept constant

Nevertheless electrostatic computations seem to be very important for this class of compounds. They have been carried out repeatedly in the past, often considering radial symmetric repulsion forces also (Bragg and Chapman, 1924; Chapman et al., 1926; Lennard-Jones and Dent, 1927; Jenkins and Waddington, 1971a and b; Ladd, 1972a and b; Jenkins et al., 1976; Yuen et al., 1978). The main goals of these computations were (a) to gain a detailed understanding of the geometry of calcite type carbonates, and (b) to obtain information on the charge distribution within the $[CO_3]^{2-}$ ion. At variance with older results, Yuen et al. (1978) found the following charges within the frame of the four point charges model in the carbonate ion: $\varphi(C) = +0.96(26)$ and $\varphi(O) = -0.98(9)$.

We have considered theoretical calcite and magnesite models built of Me^{2+} and $[CO_3]^{2-}$ ions in which the Me – O and C – O bond lengths within the coordination figures were kept constant, while the shape of the MeO_6 polyhedron was allowed to vary. ω, the angle between the Me – O bond and the [00.1] direction, was chosen as the variable. With $\omega = \arcsin \sqrt{\frac{2}{3}} \sim 54.7356°$ the MeO_6 octahedron is geometrically ideal; smaller values of ω correspond to a stretching of this octahedron parallel [00.1].

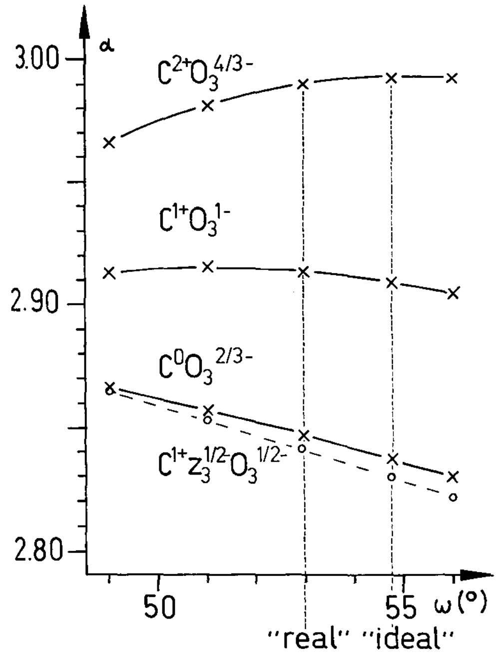

Fig. 3. Madelung constants α of theoretical calcite-type carbonates as a function of ω. Ca – O and C – O were held constant. Reference length was for all four models the distance C – O. The internal potential of the $[CO_3]^{2-}$ ions was subtracted

Of all our computations we have presented only a few, all of them for calcite models which seem to be particulary interesting for crystal chemistry. Figure 2 gives the three shortest O – O distances outside the carbonate group as a function of ω. (Within the carbonate group O – O is held constant because C – O is kept constant.) It can be clearly seen that deviations of ω within three degrees of the experimental value do not reduce any O – O distance below 3.0 Å, a value distinctly greater than the sum of two oxygen van der Waals radii, i.e. 2.80 Å (cf. Pauling, 1960). Therefore, non-Coulomb repulsion forces can to a first approximation be neglected in this range of distortion, and the change of the electrostatic part of the lattice energy seems to be decisive for the direction of the distortion. Madelung constants were computed by the method of Bertaut (1952) as a function of ω. Within the $[CO_3]^{2-}$ ion, models with four charge distributions were considered; three with four point charges ($C^{2+}O_3^{4/3-}$, $C^{1+}O_3^{1-}$ and $C^0O_3^{2/3-}$) and one with seven point charges (carbon bears the charge 1 + and charges $\frac{1}{2}$ – are placed at the positions of the oxygen as well as on the exact center of the C – O bond). The results are plotted in Figure 3.

Let us first consider the results for the models with four point charges. The model with a neutral C atom results in an ω below the experimental value, while the model with C^{2+} would cause it to get larger; for the model with C^{1+} the optimum of the electrostatic lattice energy is close to the experimental value for ω. A slightly higher charge for the C atom [$\varphi(C) \sim 1.1+$] would probably shift the maximum even closer to the observed value. But as the maximum is very flat, no significance should be attributed to such detailes. In any case our results are in good agreement with those of Yuen et al. (1978) for the charge distribution in the carbonate ion.

A word of warning would be appropriate. Neither the results of Yuen et al. (1978) nor ours prove that the charge distribution within the carbonate group is such that 1+ point charges are located at the carbon position and 1− point charges at the oxygen position. They show only that within the framework of the model with four point charges this is a fair approximation. This is nicely demonstrated by our results for the model with seven point charges. The curve for this model is so close to that for $[C^0O_3^{2/3-}]$ that the two models cannot be differentiated. Without any doubt, the model $[C^{1+}O_3^{1-}]$ can also be replaced by other charge distributions.

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