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Neutron Diffraction Refinement of the Crystal Structure of Aragonite

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Summary

The crystal structure of aragonite ($a = 4.9611(4)$, $b = 7.9672(6)$, $c = 5.7407(4)$ Å, cell content: $4 \times CaCO_3$, space group: *Pmcn*) was refined with 1180 neutron diffraction data to $R_w = 0.014$. The atomic parameters of earlier X-ray refinements were essentially confirmed, but were now determined with considerably higher accuracy. The aplanarity of the carbonate group is 0.0280(5) Å, a value greater by 0.010 Å than that in dolomite.

Zusammenfassung

Neutronenbeugungsverfeinerung der Kristallstruktur des Aragonits

Die Kristallstruktur des Aragonits ($a = 4{,}9611(4)$, $b = 7{,}9672(6)$, $c = 5{,}7407(4)$ Å, Zellinhalt: $4 \times CaCO_3$, Raumgruppe: *Pmcn*) wurde mit 1180 Neutronenbeugungsdaten zu einem $R_w = 0.014$ verfeinert. Die Atomparameter früherer Röntgenverfeinerungen wurden im Prinzip bestätigt, nun jedoch mit beträchtlich höherer Genauigkeit bestimmt. Die Aplanarität der Karbonatgruppe beträgt 0.0280(5) Å, ein Wert, der um 0.010 Å größer ist als der im Dolomit.

Introduction

The crystal structure of aragonite was first determined by *Bragg* (1924). Three careful refinements of the atomic arrangement with X-ray methods yielded very similar results (*de Villiers*, 1971; *Dal Negro* and *Ungaretti*, 1971; *Dickens* and *Bowen*, 1971); the carbonate group was found to be slightly aplanar, with a distance d of the atom from the plane of the three O atoms of $d = 0.020(6)$, 0.027(4) and 0.026(4) Å (according to the above authors).

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The aplanarity of the carbonate group in aragonite as determined by *Dal Negro* and *Ungaretti* (1971) is larger than that in the vast majority of examples for this effect known by now (cf. *Zemann*, 1981 for a review article, further *Effenberger* et al., 1981; *Hesse* and *Simons*, 1982; *Effenberger* et al., 1983a; *Effenberger* and *Langhof*, 1984), and a greater aplanarity is reported in literature for thaumasite only ($d = 0.060(9)$ Å, *Effenberger* et al., 1983b)[1].

In connection with systematic work on the aplanarity of zO_3 groups (z = B, C, N) in inorganic crystal structures carried out in the "Institut für Mineralogie und Kristallographie der Universität Wien" it seemed to be interesting to refine the structure of aragonite with neutron data to determine the d-value for this mineral very accurately.

Experimental

Aragonite from Hořenz/Czechoslovakia was used for the investigations. Because of the twinning of the crystal a single crystal piece with a size of $2.05 \times 2.50 \times 2.55$ mm was cut out. A microprobe analysis of the sample gave a small content of 0.15 wt.% SrO which was not taken into account in our structure refinement. To increase the mosaic structure and reduce extinction effects the crystal was chilled in liquid nitrogen.

Lattice constants were determined with a four circle X-ray diffractometer (Mo-radiation): $a = 4.9611(4)$, $b = 7.9672(6)$, $c = 5.7407(4)$ Å; space group: $Pmcn$ (D_{2h}^{16}), $Z = 4$.

Intensities were measured at room temperature with the four circle neutron diffractometer P110 at the Orphee reactor in Saclay/France. The wavelength was 0.8314 Å. Intensities for 1256 reflexions (in two symmetry-equivalent regions) – to a limit of $\sin \vartheta/\lambda = 0.84$ Å^{-1} (corresponding to $2\vartheta = 88°$) were collected. The technique of measurement was a ω-scan for reflexions with $2\vartheta \leqslant 70°$ and a ω-2ϑ-scan for reflexions with $2 > 70°$.

A Lorentz correction was applied and the data were reduced by averaging the intensity values of equivalent reflexions. Using the atomic parameters of the earlier structure refinements as starting point least squares refinements with the computer programs SHELX76 (*Sheldrick*, 1976) and RFINE4 (*Finger* and *Prince*, 1975) were carried out.

Neutron scattering lengths were taken from *Koester* (1977): $b_{\mathrm{Ca}} = 4.90$, $b_{\mathrm{C}} = 6.6484$, $b_{\mathrm{O}} = 5.8030 \times 10^{-13}$ cm. At this point of the refinement a factor for isotropic extinction correction was applied. The result was an unweighted value for R of 0.034 for all reflexions. In order to improve the agreement of F_o and F_c the refinement was continued with the origin data (non reduced data) and a correction for anisotropic extinction (based on *Coppens* and *Hamilton*, 1970). The observed intensities were corrected with the results of this refinement and reduced by averaging one more time. Now the internal

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[1] The large aplanarity of the CO_3 group in buetschliite of $d = 0.038$ Å as quoted in *Zemann* (1981) was shown to be incorrect by *Effenberger* and *Langhof* (1984).

R-value for the reduced data was R_i = 0.023 (instead of R_i = 0.040 the first time). The final refinement was done using 666 independent reflections (for refining 29 free parameters) without any extinction correction. During the last cycles 31 reflexions with $I = 2.5\ \sigma\ (I)$ ("unobserved reflexions") and additional two reflexions which still had $\Delta(F)/\sigma(F) \geqslant 13.0$ (supposed as reflexions with extraordinary extinction effects) were rejected.

The final R-values are: for all reflexions: $R = 0.024, R_w = 0.022$ (weight for $1/\sigma^2(F)$); and for the non rejected reflexions: $R = 0.021, R_w = 0.014$.

Table 1. *Final Atomic Coordinates and Anisotropic Thermal Parameters* ($\times 10^5$)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	25000	41508 (5)	24046 (8)	676 (12)	264 (5)	505 (9)	0	0	11 (6)
C	25000	76211 (4)	8518 (6)	450 (8)	226 (3)	304 (6)	0	0	4 (4)
O1	25000	92224 (4)	9557 (8)	1152 (12)	213 (4)	664 (8)	0	0	−32 (5)
O2	47347 (5)	68065 (3)	8726 (5)	518 (7)	365 (3)	700 (6)	114 (4)	−12 (6)	46 (3)

Anisotropic temperature factors are in the form: $T = \exp[-(h^2\beta_{11} + \ldots + 2\,hk\beta_{12}\ \ldots)]$.

The atomic coordinates and the anisotropic thermal parameters calculated from the last least squares cycle are listed in Table 1. A list of observed and calculated structure factors is available from the "Institut für Mineralogie und Kristallographie der Universität Wien" upon request.

Discussion

The atomic parameters of aragonite found by our neutron refinement correspond to those given by *Dal Negro* and *Ungaretti* (1971), *de Villiers* (1971) and *Dickens* and *Bowen* (1971) within their limits of accuracy. The weighted shift of the positions according to *Dal Negro* and *Ungaretti* to ours is 0.0047 Å, to *de Villiers* to ours 0.0050 Å, and according to *Dickens* and *Bowen* to ours 0.0033 Å; the maximum atomic shifts are 0.0081 Å, 0.0067 Å and 0.0070 Å.

Selected bond lengths and bond angles according to our refinement are given in Table 2. As compared with the two earlier X-ray refinements, their standard errors have deceased by a factor of 5 to 10. Geometrical calculations were carried out with the computer program KRISTALLCHEMIE (*Nowotny* and *Zobetz*, 1982).

Although the two crystallographically different kinds of O atoms in the carbonate group are both coordinated by three Ca^{2+} ions, the two C–O bond lengths differ by 0.0075(4) Å. The atom with the shorter C–O bond, O1, has the longer average O–Ca^{2+} distance, i.e. 2.5744(4) Å, the one with the longer C–O bond, O2, has the shorter average O–Ca^{2+} distance, i.e. 2.5051(5) Å. Such a correlation is in accordance with general experience in stereochemistry.

Table 2. *Interatomic Distances* [Å] *and Bond Angles* [°], *Uncorrected for Thermal Vibration**

Ca – O1	2.4157 (6)	O1 – C – O2	120.28 (2) 2×
– O1	2.6538 (3) 2×	O2 – C – O2	119.30 (3)
– O2	2.5454 (5) 2×		
– O2	2.4502 (5) 2×		
– O2	2.5197 (4) 2×		
C – O1	1.2772 (5)		
– O2	1.2847 (3) 2×		

Aplanarity of the CO$_3$-group: 0.0280 (5) Å

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* Standard deviations in brackets include the errors of lattice constants.

Table 3. *Ellipsoids of Thermal Vibration*

		Angle [°] with		
Atom	R.M.S.-amplitude [Å]	*a*	*b*	*c*
Ca	0.091 (1)	90	132.8	42.8
	0.092 (1)	0	90	90
	0.093 (2)	90	42.8	47.2
C	0.071 (1)	90	92.1	2.1
	0.075 (1)	0	90	90
	0.085 (1)	90	2.1	87.7
O1	0.082 (1)	90	9.6	80.4
	0.106 (2)	90	80.4	170.4
	0.120 (2)	0	90	90
O2	0.075 (1)	21.6	111.0	84.9
	0.105 (1)	74.7	61.4	146.8
	0.115 (1)	75.1	36.7	57.3

The average C–O bond length, C–O$_{\text{av}}$ = 1.2822(4) Å, compares well with the C–O = 1.2809(5) Å as determined in dolomite by *Effenberger* et al. (1983a), also by neutron diffraction; it might be, however, slightly larger. It is also in good agreement with the average bond lengths found in the same mineral by the earlier X-ray refinements which yielded C–O$_{\text{av}}$ = 1.285(4), 1.282(4) and 1.285(2), according to *Dal Negro* and *Ungaretti*, *de Villiers* and to *Dickens* and *Bowen*.

The ellipsoids of thermal vibration are given in Table 3. For calcium and carbon they are nearly spherical; for the two oxygens the smallest axis is approximately in the direction of the C–O bond, the longest is approximately parallel to the plane of the carbonate group (see also *de Villiers*, 1971, Fig. 1).

The value for the aplanarity of the carbonate group, d = 0.0280(5) Å, corresponds well with results of *Dal Negro* and *Ungaretti* and *Dickens* and *Bowen*, but the accuracy of the values has increased by almost an order of magnitude. It is now established that it is larger than that in dolomite by 0.0100(15) Å. For a tentative interpretation of the aplanarity of the carbonate group in aragonite cf. *Zemann* (1981), for electrostatic lattice energy computations considering this effect *Heiss* and *Zemann* (1985).

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