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Neutron single-crystal refinement of cerussite, $PbCO_3$, and comparison with other aragonite-type carbonates

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Abstract. The crystal structure of cerussite, $PbCO_3$, was refined with 669 merged single-crystal neutron data [$F_o > 3\sigma(F_o)$] to $R = 0.032$, $R_w = 0.025$ (space group *Pmcn*; $a = 5.179(1)$, $b = 8.492(3)$, $c = 6.141(2)$; $Z = 4$). – Cerussite belongs to the aragonite-type compounds. The weak aplanarity of the carbonate group, $d = 0.026(1)$ Å, is of the same order of magnitude as in aragonite, $CaCO_3$, and strontianite, $SrCO_3$, and the direction of the deviation from planarity is the same. The minor details of the stereochemistry differ slightly from the expectations to be drawn from the structures of the alkaline earth carbonates on the basis of the effective ionic radii of the twovalent metals.

Introduction

It is well known from the old days of morphological crystallography that cerussite, $PbCO_3$, is isomorphous with aragonite, $CaCO_3$, strontianite, $SrCO_3$, and witherite, $BaCO_3$. Zachariasen (1928) confirmed this by X-ray methods and derived coordinates of the Pb atom for this mineral. Colby and LaCoste (1933) determined the atomic arrangement of cerussite from X-ray oscillation photographs, and Sahl (1974) refined the structure using

Table 1. Atomic coordinates and anisotropic displacement parameters for $PbCO_3$ with e.s.d's in units of the last digit in parentheses. U_{ij} are given in pm^2. ATF = exp $[-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja_i{}^*a_j{}^*]$. $U_{\mathrm{iso}} = 1/3\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$.

	Pb	C	O1	O2
x/a	1/4	1/4	1/4	0.46445(14)
y/b	0.41702(7)	0.76221(11)	0.91299(14)	0.68597(9)
z/c	0.24560(12)	0.08718(15)	0.09649(20)	0.08893(14)
U_{11}	115(2)	98(4)	206(5)	110(3)
U_{22}	101(2)	107(4)	116(4)	181(3)
U_{33}	110(2)	87(3)	183(5)	216(4)
U_{12}	0	0	0	32(3)
U_{13}	0	0	0	11(3)
U_{23}	1(3)	0(3)	28(5)	−33(3)

an automatic four-circle X-ray diffractometer ($R = 0.07$ for 331 observed reflections).

In connection with our longstanding interest in the stereochemistry of carbonates (e.g. Effenberger et al., 1981; Zemann, 1981, 1989) and with our previous neutron refinements of aragonite (Jarosch and Heger, 1986) and strontianite (Jarosch and Heger, 1988), it seemed worth-while to refine also the structure of cerussite by single-crystal neutron work.

Experimental

For the structure investigation an untwinned part of a crystal from Příbram, CSFR, (collection of the Institut für Mineralogie und Kristallographie, Universität Wien; reference number 5968) was cut to a size of $\approx 2 \times 2 \times 2$ mm. The remainder of the crystal was used to determine the lattice parameters. They were refined using 20 reflections from an X-ray powder diffraction pattern with Si as internal standard: $a = 5.179(1)$ Å, $b = 8.492(3)$ Å, $c = 6.141(2)$ Å.

On the four-circle diffractometer P110 at the Orphee reactor/C.E.N. Saclay, France, Bragg intensities were measured normally for three symmetry equivalent reflections at a neutron wavelength of $\lambda = 0.8307$ Å. The resulting 1827 intensity data (up to $\sin\theta/\lambda = 0.85$ Å^{-1}) were corrected for Lorentz effects and averaged according to crystal symmetry; since absorption is almost negligible in a neutron diffraction study on $PbCO_3$ ($\mu = 0.04$ cm^{-1}) no correction was applied. A good agreement between symmetry equivalent intensities is stated by $R_{\mathrm{int}} = 0.024$. From merged 757

Table 2. Interatomic distances [Å] in PbCO$_3$ (uncorrected for thermal motion). Standard deviations in units of last digit in parentheses.

PbO$_9$ polyhedron. O–O distances only with O–O < 3.50 Å					
Pb–O1	= 2.5937(13)	1×	O1–O1	= 3.208(1)[a]	2×
	= 2.7653(4)	2×	O1–O2	= 2.225(1)[b]	2×
Pb–O2	= 2.6588(9)	2×		= 3.329(1)	2×
	= 2.6781(9)	2×		= 3.361(1)	2×
	= 2.7158(9)	2×		= 3.414(1)	2×
⟨Pb–O⟩	= 2.692		O2–O2	= 2.221(1)[b]	1×
				= 2.958(1)[a]	2×
				= 3.257(2)	2×
				= 3.362(1)[a]	2×
CO$_3$ group.					
C–O1	= 1.2817(15)	1×	O1–O2	= 2.225(1)	2×
C–O2	= 1.2856(8)	2×	O2–O2	= 2.221(1)	1×

Aplanarity d (distance of C atom from oxygen plane): 0.026(1).

[a] Common edge between two PbO$_9$ polyhedra.

[b] Common edge between PbO$_9$ polyhedron and CO$_3$ group.

independent data, 669 structure factors with $F_o \geq 3\sigma(F_o)$ were used for the structure refinement. The neutron scattering lengths for the Pb, C and O atoms were taken as $b_{\mathrm{Pb}} = 0.94 \cdot 10^{-12}$, $b_{\mathrm{C}} = 0.6648 \cdot 10^{-12}$ and $b_{\mathrm{O}} = 0.5805 \cdot 10^{-12}$ cm (Delapalme, 1985). We found considerable extinction effects, first in an isotropic treatment, which were taken into account finally in anisotropic correction assuming secondary extinction type I with Lorentzian distribution (Becker and Coppens, 1974; $G_{11} = 0.144(9) \cdot 10^{-4}$, $G_{22} = 0.376(35) \cdot 10^{-4}$, $G_{33} = 5.011(44) \cdot 10^{-4}$). It is worth mentioning that the special orientation of the regular shaped sample crystal (a-axis parallel to the rotation axis) does not give differences for the intensities of symmetry equivalent reflections. The strongest extinction correction increased the intensity of the (012) peak by a factor of 1.93. The full-matrix least-squares refinement of 31 variables in space group *Pmcn* led to R-factors of $R(F) = 0.032$ and $R_w(F) = 0.025$ [$w = 1/(\sigma^2(F_o))$]. Final positional and anisotropic displacement parameters are listed in Table 1[1]. The calculations were done using the program PROMETHEUS (Zucker et al., 1983). It should be noted that if instead of the anisotropic extinction

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[1] $F_o - F_c$ lists can be ordered referring to the no. CSD 55214, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany.

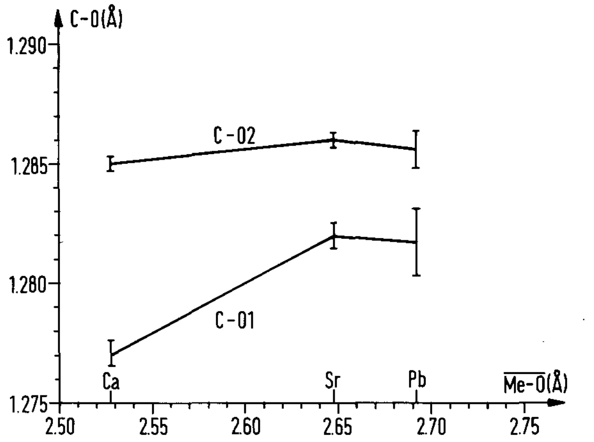

Fig. 1. Variation of the individual C—O bond lengths in aragonite-type carbonates. Abscissa: average Me—O distance ($Ca-O_{av}$ = 2.528 Å, $Sr-O_{av}$ = 2.648 Å, $Pb-O_{av}$ = 2.692 Å).

correction according to Becker and Coppens (1974) only the isotropic extinction correction according to Zachariasen (1967) is applied, the least-squares refinement results in atomic coordinates giving interatomic distances which differ from the ones listed here by up to 0.006 Å [$G_{iso} = 7.3(3) \cdot 10^{-3}$].

Discussion

Our neutron refinement does, of course, not change the general features of the atomic arrangement of cerussite as given e.g. by Sahl (1974), but the present results are considerably more accurate. The new atomic coordinates are within the 1.2σ limits of Sahl's values.

Interatomic distances are presented in Table 2. They are in good agreement with general expectations. As in the previous papers on aragonite-type carbonates they are not corrected for thermal motion.

The PbO_9 polyhedron ($Pb-O$ = 2.594—2.765 Å) is well defined; further oxygen neighbours follow only with $Pb-O > 4.00$ Å. Each PbO_9 polyhedron shares three O—O edges with carbonate groups and six O—O edges with neighbouring PbO_9 polyhedra. The CO_3 groups are slightly aplanar; the distance *d* of the C atom from the plane of the O atoms measures 0.026(1) Å. The direction of the deviation from planarity is the same as in aragonite and strontianite (cf. Zemann, 1981; Jarosch and Heger, 1986, 1988).

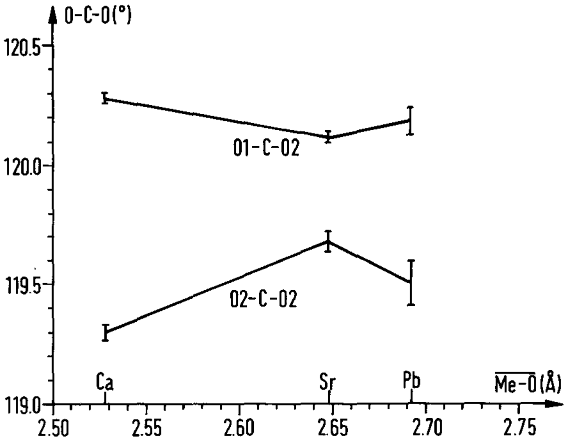

Fig. 2. Variation of O—C—O bond angles in aragonite-type carbonates. Abscissa as in Fig. 1.

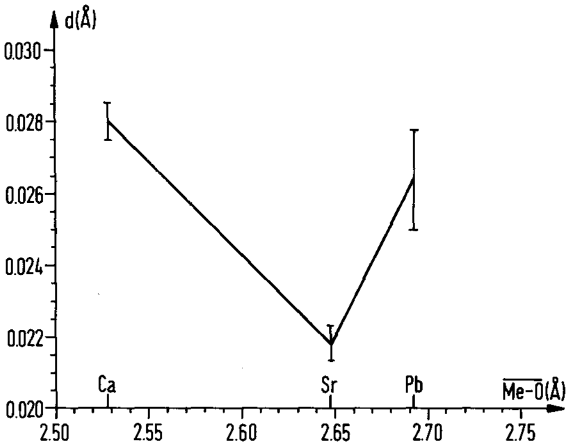

Fig. 3. Variation of the aplanarity of the carbonate group in aragonite-type carbonates. For definition of *d* see text. Abscissa as in Fig. 1.

Comparison with the neutron refinements of aragonite, $CaCO_3$, and strontianite, $SrCO_3$, by Jarosch and Heger (1986, 1988)[2] shows that the shape of the carbonate group in the three isotypic compounds varies only very slightly. Figures 1—3 give the changes of the C—O bond lengths, the

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[2] In the paper of Jarosch and Heger (1988) z(Sr) is erroneously given as 0.75678 instead of 0.24322.

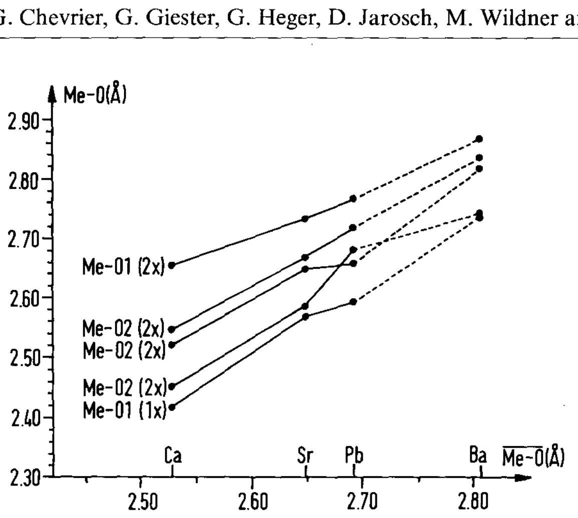

Fig. 4. Variation of the individual Me—O bond lengths in the MeO_9 polyhedron of aragonite-type carbonates. Abscissa as in Fig. 1 ($Ba-O_{av}$ = 2.807 Å).

Table 3. Displacement ellipsoides for $PbCO_3$.

Atom	r.m.s. Amplitude [Å]	Angle [°] with		
		a	*b*	*c*
Pb	0.100	90.0	173.3	83.3
	0.105	90.0	96.8	173.2
	0.107	0.0	90.0	90.0
C	0.093	90.0	91.0	1.0
	0.099	180.0	90.0	90.0
	0.103	90.0	1.0	89.0
O1	0.103	90.0	160.2	70.2
	0.139	90.0	109.8	160.2
	0.144	0.0	90.0	90.0
O2	0.097	153.7	66.3	79.3
	0.133	115.9	137.9	120.5
	0.154	93.8	122.5	32.7

O—C—O bond angles, and the aplanarity as a function of the average Me—O distance. It is seen that the variations are only very minor, but also that the values for $PbCO_3$ do not fully meet the expectations derived from the results for $CaCO_3$ and $SrCO_3$. The X-ray results for $BaCO_3$ (de Villiers, 1971) were not included in Figures 1—3 because the e.s.d.'s within the carbonate group are too large in respect to the details which are discussed.

The changes in the geometry of the MeO_9 polyhedra are considerably larger than in the CO_3 group. For this reason and from the fact that the X-ray investigation on $BaCO_3$ yielded considerably more accurate atomic coordinates for Ba than for C and O, the results for witherite are included in the discussion of the variation of the Me—O bond lengths in the aragonite-type carbonates. Figure 4 presents their variation as a function of the average Me—O distance. It is evident that some of the values for $PbCO_3$ do not exactly correspond to the expectations from the aragonite-type alkaline earth carbonates if the size of a spherosymmetrical Me^{2+} ion is considered to be the decisive parameter. Evidently, the deviations are (as in the case of the carbonate group) the consequence of slightly different chemical bonds in the lead compound, as compared with those in the alkaline earth compounds. Furthermore it is to be noted that in $PbCO_3$ the shortest unshared O—O edge is shorter than the longest shared one by 0.105(3) Å (Table 2), in $SrCO_3$ and $BaCO_3$ the corresponding values are 0.021(2) Å and 0.030(9) Å, respectively. In aragonite the shortest unshared O—O edge in the MeO_9 polyhedron is not *shorter* than the longest shared one, but slightly *longer*, i.e. by 0.013(2) Å. The orientations of the axes of the mean square displacement ellipsoides (Table 3) are similar to those found in aragonite and strontianite (Jarosch and Heger, 1986, 1988). For O1 and O2 the shortest axis again deviates not very strongly from the direction of the corresponding C—O bond.

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