SHORT COMMUNICATIONS

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Erratum to *Kinetics of dehydration of single crystals of copper formate tetrahydrate* by Fichte and Flanagan.

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Abstract

An error has been detected in the title paper [Fichte & Flanagan (1971). *Trans. Faraday Soc.* **67**, 1467–1479] concerning the use of X-ray powder data to infer structural information. The nature of the error is discussed and the corrected information given.

In the paper by Fichte & Flanagan (1971), the authors correctly ascribe the strong 6·23 Å line in copper formate tetrahydrate (CFT) to $(001)_{\rm CFT}$, based on the well known argument that in lamellar structures strong, low-angle reflexions correspond to interplanar spacings between layers (Grim, 1953). Besides, the assignment was corroborated by single-crystal data, available at the time. After dehydration into copper formate anhydride (CFA), they assigned the strongest peak in the X-ray diagram (5·24 Å) to the corresponding $(001)_{\rm CFA}$, based on the same qualitative arguments. They thus inferred a 15·9% interplanar contraction in good agreement with the 16·0% they measured in the bulk. As no single-crystal work was attempted at the time, this was as far as they could go.

Recently, a thorough crystallographic report has appeared (Günter, 1980) on the topotactically dehydrated pseudomorph CFA. The powder data presented therein show that the strong 5·24 Å line in fact corresponds to $(110)_{\rm CFA}$, $(001)_{\rm CFA}$ being 3·06 Å and with only a medium intensity. The collapse of $(001)_{\rm CFT}$ planes is thus much more severe (51% shrinkage) than reported by Fichte & Flanagan. Measured values in the bulk, however, are usually very low, due perhaps to some splitting taking place at a submicroscopic level along CFT cleavage planes. Figures as low as a few per cent are not uncommon, even under very careful working conditions. It was certainly an unfortunate coincidence, then, for the authors to have such a misleading match between their measured and expected values.

The reason why a well established, general rule failed to provide the right answer should be attributed to the fact that it was applied too loosely: although CFT is a perfectly suitable (as far as the rule is concerned) layered structure, CFA is not, being distinctly three dimensional in nature. The rule, then, was not applicable from the onset.

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On the aplanarity of the CO_3 group in buetschliite, dipotassium calcium dicarbonate, $K_2Ca(CO_3)_2$: a further refinement of the atomic arrangement.

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Abstract

$M_r = 238{\cdot}3$, rhombohedral, $R\bar{3}m$, $a = 5{\cdot}3822\,(4)$, $c = 18{\cdot}156\,(2)$ Å, $V = 455{\cdot}48$ Å^3, $Z = 3$, $D_x = 2{\cdot}607$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}710688$ Å, $\mu = 2{\cdot}321$ mm^{-1}, $F(000) = 354$, room temperature, $R = 0{\cdot}017$ for 171 observed reflections up to $\sin\theta/\lambda = 0{\cdot}70$ Å^{-1}. The carbonate group is slightly pyramidal with a deviation of the C atom from the plane defined by the three O atoms of $d = 0{\cdot}014\,(2)$ Å. This new value for d agrees with the values found in related compounds.

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Introduction

The crystal structure of buetschliite was determined by Pabst (1974) and refined by Knobloch, Pertlik & Zemann (1980). Although the refinement was very accurate, a relatively large deviation of the carbon atom from the plane defined by the three oxygen atoms of the carbonate group was found [$d = 0{\cdot}038\,(9)$ Å]. Because a two-circle diffractometer had been used for data collection with the rotation axis parallel to the direction of the distance d, this value especially seemed open to discussion. In connection with studies of the aplanarity of zO_3 groups (z = B, N and C; *cf.* Zobetz, 1982; Jarosch & Zemann, 1983; Zemann, 1981) a further refinement seemed to be necessary either to verify or to correct the value of d for buetschliite.

Experimental

Synthetic crystal, dimensions $0{\cdot}05 \times 0{\cdot}05 \times 0{\cdot}15$ mm, STOE four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, cell parameters from 46 reflections up to $2\theta = 41°$, space group D^5_{3d}-$R\bar{3}m$, $Z = 3$; 3 standard reflections, no significant intensity variation; 1790 reflection intensities collected up to $2\theta = 60°$ [θ/ω scan; min. 40 steps, increased for the (α_1, α_2) splitting, step width 0·03°, step time 0·5 to 1·5 s per step], h $\bar{8}$–8, k $\bar{8}$–8, l $\overline{25}$–25, correction for Lorentz and polarization effects, 198 unique reflections, 171 with $F_o \geq 6\sigma(F_o)$, absorption neglected (in addition the crystal was mounted with its longest direction parallel to the φ axis of the diffractometer to keep the absorption effects small), complex scattering factors for K^+, Ca^{2+} and O^{1-} from *International Tables for X-ray Crystallography* (1974), for C^{1+} by interpolation between C^0 and C^{2+} from *International Tables for X-ray Crystallography* (1962). Structural parameters given by Knobloch *et al.* (1980) used as starting parameters. Several cycles of conventional full-matrix least-squares refinement on F with anisotropic temperature parameters gave $R = 0{\cdot}024$ and $R_w = 0{\cdot}016$, $w = 3{\cdot}04/[\sigma(F_o)]^2$. Omission of 27 reflections with $F_o < 6\sigma(F_o)$ reduced the R values to $R = 0{\cdot}017$ and $R_w = 0{\cdot}015$. Max. $\Delta/\sigma = 0{\cdot}0$, max., min. height in final difference Fourier map 1·1, $-0{\cdot}4$ e Å^{-3}.* The atomic coordinates and equivalent isotropic temperature parameters are given in Table 1, some important interatomic distances in Table 2.

Discussion

The carbonate group was found to be slightly pyramidal. The deviation of the C atom from the plane defined by the three O atoms of the CO_3 group was determined to be 0·014 (2) Å–much smaller than that previously reported. The apex of the flat pyramid points towards the same direction as given by Knobloch *et al.* (1980). The crystal structure is built up of alternate layers of K–CO_3–Ca–CO_3. The apex points towards the 'Ca^{2+} atom sheet': as pointed out by Zemann (1981) towards the cations which are smaller and more highly charged where one expects stronger covalent contributions to the chemical bonds between the cations and oxygen atoms.

The new value of d in buetschliite agrees very well with those found in related compounds, *cf.*, for example, $K_2Mg(CO_3)_2$ with $d = 0{\cdot}014$ (3) Å (Hesse & Simons, 1982), eitelite, $Na_2Mg(CO_3)_2$, with $d = 0{\cdot}018$ (5) Å (Knobloch *et al.*, 1980), ankerite, $CaFe(CO_3)_2$, with $d = 0{\cdot}011$ (3) Å (Beran & Zemann, 1977) and dolomite, $CaMg(CO_3)_2$, with $d = 0{\cdot}018$ (1) Å (Effenberger, Kirfel & Will, 1983).

Table 1. *Atomic fractional coordinates and equivalent isotropic temperature parameters* (Å^2), *with e.s.d.'s in parentheses; values of Knobloch et al.* (1980) *in square brackets*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_{i=1}^{3}\beta_{ii}/a_i^{*2}.$$

				B_{eq}
6 K on 6(c)	(0, 0, z)	$z = 0{\cdot}20927$ (3)	[0·20909 (9)]	1·61
3 Ca on 3(a)	(0, 0, 0)			0·95
6 C on 6(c)	(0, 0, z)	$z = 0{\cdot}58831$ (11)	[0·58945 (32)]	0·99
18 O on 18(h)	(x, $\bar{x}$, z)	$x = 0{\cdot}13776$ (10)	[0·13763 (25)]	1·58
		$z = 0{\cdot}58752$ (8)	[0·58736 (18)]	

Table 2. *Interatomic distances* (Å) *with e.s.d.'s in parentheses* (O—O *distances only* <4·0 Å)

K—O	2·825 (1)	(6×)	O—O	2·224 (1)	(3×)⊥c
	2·984 (1)	(3×)		3·158 (1)	(6×)⊥c
				3·428 (2)	(6×)
Ca—O	2·321 (1)	(6×)	O—O	3·158 (1)	(6×)⊥c
				3·403 (2)	(6×)
C—O	1·284 (1)	(3×)	O—O	2·224 (1)	(3×)⊥c

All the interatomic distances and atomic coordination figures agree well with common crystal chemical experience. The equivalent isotropic temperature parameters of buetschliite are somewhat larger than those determined for the isostructural compound $K_2Mg(CO_3)_2$ (Hesse & Simons, 1982). The same tendency was found within calcite-type structures: the thermal motion of magnesite is smaller than that of calcite (Effenberger, Mereiter & Zemann, 1981) because of the shorter atomic radii of the Mg atoms compared with the Ca atoms. A detailed description of the crystal structure is given by Pabst (1974). The structural relationships with eitelite were pointed out by Knobloch *et al.* (1980).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39217 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.