Some contacts shorter than the sum of the van der Waals radii (3·90 Å; Wells, 1975) are present between Br atoms of different anions [Br(2)—Br(7^{vii}) 3·78 (2), Br(4)—Br(5^v) 3·88 (1) Å].

Both anions in the title compound seem to be interconnected through the Na(2) atoms into chains parallel to [111]. This is probably the reason for the existence of two kinds of anions. The Na(2) atom is octahedrally coordinated by four Br atoms of both anions and by two H_2O molecules (in *cis* positions). The Na(1) as well as the Na(3) atoms are coordinated by six H_2O molecules. The coordination polyhedra are distorted octahedra. The remaining Na(4) atom is coordinated by four H_2O molecules and by one Br atom in a very irregular polyhedron. The cationic polyhedra are linked into a three-dimensional network through common edges and vertices. Hydrogen bonds do not seem to be important in this structure; there are no contacts between O atoms of different H_2O molecules shorter than 2·80 Å.

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Single-Crystal Refinement of the Structure of Carbon Dioxide

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Abstract. CO_2, $Pa3$, $a_0 = 5·624$ (2) Å. The structure refinement was based on 57 observed reflections of a single crystal at 150 K ($R = 0·041$). The C—O distance is determined as 1·155 (1) Å.

Introduction. The crystal structure of carbon dioxide has been determined by Mark & Pohland (1925, 1926), de Smedt & Keesom (1925) and Krüner (1926) using X-ray powder methods. According to these investigations, CO_2 crystallizes in space group $Pa3$, the C atom occupying position 4(*a*) and the O atoms 8(*c*). In spite of considerable differences in the oxygen *x* parameter in the original papers, it is generally accepted to be $x \simeq 0·11$ (Wyckoff, 1963).

Single crystals of CO_2 were grown from a solution in CH_2SF_4 (Simon, Peters, Lentz & Seppelt, 1980). A miniaturized Bridgman technique was used (Simon,

Deiseroth, Westerbeck & Hillenkötter, 1976) which has proved helpful in numerous cases of low-temperature crystal growth from gases and liquids. In the case of CO_2, a 150/300 K temperature gradient was slowly shifted along the axis of a glass capillary (diameter 0·2 mm) filled with the solution. Several attempts finally led to a single crystal of length *ca* 2 mm. Crystal-growth and intensity measurements were carried out on a Syntex $P2_1$ four-circle diffractometer. The results are based on 71 independent reflections using the *XTL* system [57 reflections with $I > 2\sigma(I)$; originally 281 measured reflections in the range $0 \le h,k,l \le 7$; $7° < 2\theta < 55°$; Mo $K\alpha$, ω scan at 0·5 to 29° min^{-1} with $\Delta\omega = 1·0°$]. No absorption correction was applied.

The final $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0·041$. Refinement including unobserved reflections yielded $R' = 0·065$. Using the general weighting scheme $R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|$, where $w = 1/\sigma^2$, the

Table 1. *Positional and thermal parameters*

B_{ij} (Å^2) are defined by $\exp[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + \cdots + 2B_{23}klb^*c^*)]$.

		x	B_{11}	B_{12}
C	4(a)	0	1·70 (8)	0·20 (13)
O	8(c)	0·1185 (3)	2·30 (6)	−0·32 (6)

corresponding values are $R_w = 0.040$ and $R'_w = 0.042$, respectively.*

Discussion. The structural parameters at 150 K are given in Table 1.

The C—O distance in the CO_2 molecule is determined as 1·155 (1) Å. This value compares well with

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35467 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the results of electron diffraction experiments which led to distances of 1·15 Å (Hassel & Viervoll, 1947) and 1·162 (±1·0) Å (Karle & Karle, 1949, 1950).

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Single-Crystal Structure Analysis of the Spinel Copper Pentaindium Octasulphide

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Abstract. $Cu_{0.5}In_{2.5}S_4$, $M_r = 447.06$, cubic, $F\bar{4}3m$, $a = 10.6858$ (3) Å, $U = 1220.2$ Å^3, $D_c = 4.87$ Mg m^{-3}, $Z = 8$, $F(000) = 1593.9$, μ(Mo $K\alpha$) = 12.25 mm^{-1}. The space group was assigned in a preliminary communication. The present work reports the X-ray single-crystal structural determination of the same compound and a consideration of the anharmonic lattice model found. The structure has been refined to a final R of 0.056 for 242 reflections collected with a four-circle diffractometer (Mo $K\alpha$ radiation).

Introduction. The ideal spinel structure can be viewed as a cubic close-packed array of anions in which one eighth of the tetrahedral and one half of the octahedral interstices are occupied by cations. The general formula of a 1–3 spinel $M_{1/2}^+ M_{5/2}^{3+} X_4^{2-}$ may be written as $M_{1/2-x}^+ M_{1/2+x}^{3+}[M_x^+ M_{2-x}^{3+}]X_4^{2-}$ where the ions in

brackets occupy octahedral sites. Different distributions of cations among the available sites are possible by varying the value of x (the degree of inversion). The two extreme distributions are known as 'normal' for $x = 0$ and 'inverse' for $x = 0.5$. The cationic distribution adopted by a particular spinel depends on the interplay of several forces influencing the total internal energy of the crystal (Blasse, 1964; Gastaldi & Lapiccirella, 1978).

Although the space group $Fd3m$ has usually been assigned to spinels, in the last few years a large body of experimental evidence suggests that in many cases they crystallize with the non-centrosymmetric space group $F\bar{4}3m$ (Thompson & Grimes, 1977; Gastaldi & Scaramuzza, 1979). This lowering of symmetry can arise from a long-range cation ordering within the tetrahedral and/or octahedral sublattice and from a