DETERMINATION OF THE CRYSTAL STRUCTURE OF COBALT(II) ORTHOSILICATE

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Received October 18th, 1978

The crystal structure of Co_2SiO_4 (olivine structure type) was solved by Patterson and Fourier synthesis and refined by the full matrix least squares method. A final value of the R factor of 0·057 was obtained from 911 independent reflection intensities. The structure symmetry corresponds to space group *P*nma with lattice parameters $a = 1032{\cdot}8(3)$, $b = 601{\cdot}9(2)$ and $c = 478{\cdot}2(1)$ pm. The unit cell contains four formula units. The Si—O distance in isolated SiO_4 tetrahedra varies from 162·1(3) to 165·9(3) pm. Both cobalt atoms are octahedrally surrounded by oxygen atoms with Co—O distances of 208·0(3)—223·1(2) pm.

In a study of the thermal stability of $CoTeO_4$ (293 – 1 273 K), interaction of the melt with the material of the porcelain crucible resulted in the formation of well-developed purple crystals with composition Co_2SiO_4. As the crystal structure of Co_2SiO_4 has not yet been studied by single crystal methods, these crystals were subjected to X-ray structural analysis.

A microcrystalline powder of cobalt orthosilicate was prepared by Bourgeois[1] by heating a mixture of cobalt(II) oxide, cobalt(II) chloride and silicon(IV) oxide to 1273 K. The lattice parameters and symmetry (*P*nma) of this compound were determined by Gallitelli and Cola[2]. In addition, these authors suggested that the similarity of the X-ray powder patterns of Co_2SiO_4 and olivine $[(Mg, Fe)_2SiO_4]$ indicates that these two compounds are probably isostructural. The crystal structure of olivine was determined earlier by Bragg and Brown[3]. The lattice parameters of Co_2SiO_4 were later found independently by a number of authors[4-7]. Nomura, Santoro, Fang and Newnham[6] investigated the magnetic structure of Co_2SiO_4 and studied its neutron diffraction at 4 and 300 K.

EXPERIMENTAL

The cobalt and silicon contents in the studied material were found by electron microprobe on a Jeol-JXA-50A X-ray microanalyzer. Preliminary values for the dimensions of the unit cell were found from rotation and Weissenberg photographs. Systematic absences of the reflections ($hk0$ where $h = 2n + 1$ and $0kl$ where $k + l = 2n + 1$) in the complete set of diffractometer data correspond to space group *Pnma* or $Pn2_1a$. The former was chosen on the basis of the successful refinement of the structure. The dimensions of the unit cell were refined and reflection intensities measured on a Syntex $P2_1$ four-circle automatic diffractometer. A single crystal with dimensions 0·23 × 0·3 × 0·21 mm was chosen for measurements at laboratory temperature. Graphite-monochromated MoK_α radiation was used. Total of 1314 independent reflections were measured. Only 930 of them were considered as observed, since they fulfilled the condition $I \geqq 3\sigma(I)$, where $\sigma(I) = [\sigma^2_{\text{counter}} + (0{\cdot}04I)^2]^{1/2}$, where quantity σ_{counter} was obtained from the counter statistics. The intensities of the observed reflections were corrected by the Lorentz and polarization factors. Empirical correction to the absorption was carried out using the CAMEL JOCKEY program[8]. Thirteen reflections measured by the ψ scan in 10 degree steps in all equivalent positions were employed to calculate the absorption coefficient. After correction, the highest local R factor decreased from 0·16 to 0·08. The compound density was found pycnometrically at 298 K (under xylene).

Structure Solution and Refinement

The structure was solved by the heavy atom method using the TLS (ref.[9]) program system. The coordinates of the cobalt atoms were found from the Patterson map and the next two Fourier synthesis cycles enabled localization of the silicon and oxygen atoms. The structural parameters were refined by the full-matrix least squares method using the local version of the ORFLS program[10]. The $\sum w(|F_0| - |F_c|)^2$ function was minimized using the weight $w = 1/\sigma^2(F_0)$, where $\sigma(F_0) = (F_0/2I)\,[\sigma^2_{\text{counter}} + (0{\cdot}04I)^2]^{1/2}$. The coefficients of the atomic thermal factor were refined anisotropically. In the final refinement cycle, 13·4 reflections corresponded to one refined parameter and the maximum parameter shift was 0·01 e.s.d. Nineteen of the 930 reflections did not fulfill the condition $0{\cdot}66 < |F_0|/|F_c| < 1{\cdot}5$ and were thus not considered in the refinement. The final values obtained were* $R = \sum ||F_0| - |F_c|| / \sum |F_0| = 0{\cdot}057$ and $R_w = (\sum w||F_0| - |F_c||^2 / \sum w|F_0|^2)^{1/2} = 0{\cdot}064$. The highest maximum found on the final difference Fourier map was $1{\cdot}2e/(100\ \text{pm})^3$ and is located 65 pm away from the Co(1) atom. The tabulated[11] values of the atomic scattering factors for Co, Si and O were used in the calculations.

TABLE I

Basic Crystallographic Data for Co_2SiO_4

$a = 1032{\cdot}8(3)^a$ pm	$\varrho_0 = 4{\cdot}65$ g/cm^3
$b = 601{\cdot}9(2)$ pm	$\varrho_c = 4{\cdot}69$ g/cm^3
$c = 478{\cdot}2(1)$ pm	space group Pnma
$V = 297{\cdot}3(2)\,.\,10^6$ pm^3	$\mu(MoK_\alpha) = 117{\cdot}9$ cm^{-1}
$Z = 4$	$F(000) = 384$

[a] The standard deviation of the last numeral is given in brackets.

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* The values of the observed and calculated structural factors are deposited with the authors and are available on request.

RESULTS AND DISCUSSION

The determination of the crystal structure of Co_2SiO_4 from the three-dimensional data confirmed that this substance is isostructural with olivine and the other members of this group. Basic crystallographic data are given in Table I. The structure consists of isolated SiO_4 tetrahedron, between which the octahedrally coordinated cobalt atoms are located. The mutual orientation of the SiO_4 tetrahedron and CoO_6 octahedron in the structure is depicted in Fig. 1. Fig. 2 depicts projection of the structure in the *xy*-plane. The final fractional atom co-ordinates are given in Table II and the parameters of their anisotropic thermal motion are given in Table III. Table IV gives a survey of the interatomic distances and angles.

TABLE II

Final Fractional Coordinates of the Atoms (. 10^4)

Atom	x	y	z
Co(1)	5 000	5 000	5 000
Co(2)	2 763·8(6)	2 500	—89(1)
Si	949(1)	2 500	4 283(3)
O(1)	915(4)	2 500	7 671(6)
O(2)	4 488(3)	2 500	2 159(6)
O(3)	1 640(2)	336(4)	2 817(4)

TABLE III

Coefficients of the Thermal Factor (. 10^4)

The thermal factor has the form: $T = \exp\left[-(\beta_{11}\,h^2 + \beta_{22}\,k^2 + \beta_{33}\,l^2 + 2\beta_{12}\,hk + 2\beta_{13}\,hl + 2\beta_{23}\,kl)\right]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	17·4(4)	52(1)	26(2)	—3·3(5)	—0·7(6)	—3(1)
Co(2)	14·7(4)	55(1)	35(2)	0	0·5(7)	0
Si	13·7(8)	55(2)	16(3)	0	0·4(13)	0
O(1)	21(2)	59(6)	37(8)	0	4(3)	0
O(2)	14(2)	63(6)	44(7)	0	—0·2(32)	0
O(3)	20(2)	64(4)	46(6)	4(2)	2(2)	—4(4)

The silicate tetrahedron is quite regular in the Co_2SiO_4 structure. In the structures of the other orthosilicates (γ-Ca_2SiO_4 (ref.[12]) Mg_2SiO_4 (ref.[13]), $(Fe, Mg)_2SiO_4$ (ref.[13])), the Si—O distances vary from 158·9 to 172·5 pm and the O—Si—O angles from 102 to 117°. Both cobalt atoms are octahedrally surrounded by oxygen atoms. Compared with the Ca—O distances (228·9 – 253·7 pm) in the CaO_6 octahedra (γ-Ca_2SiO_4), the Co—O distances are shorter. The maximum difference in the corresponding Ca—O and Co—O distances is 35 pm and minimum 18 pm. In contrast, the Mg—O distances (207·0 – 222·0 pm) in the MgO_6 octahedron (Mg_2SiO_4) are almost identical with the Co—O distances. The corresponding Co—O distances are at most

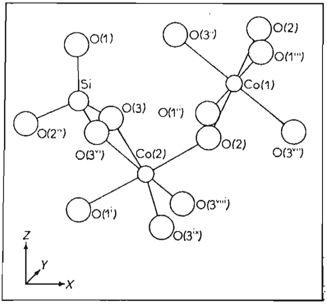

FIG. 1

View of the Mutual Orientation of the SiO_4 Tetrahedron and CoO_6 Octahedron in the Structure

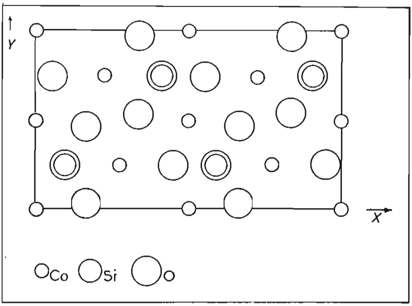

FIG. 2

Projection of the Structure into the *xy*-Plane

TABLE IV

Interatomic Distances, pm and Angles, °

Symmetry code

i: $x, y, z - 1$
ii: $1/2 - x, 1/2 + y, 1/2 + z$
iii: $1/2 + x, y, 1/2 - z$
iv: $x - 1/2, y, 1/2 - z$
v: $1 - x, 1/2 + y, 1 - z$
vi: $x, 1/2 - y, z$
vii: $1/2 + x, 1/2 - y, 1/2 - z$
viii: $1/2 - x, 1/2 + y, z - 1/2$
ix: $1/2 - x, \bar{y}, \bar{z}$

Tetrahedron

Si — O(1)	162·1(3)
Si — O(2^{iv})	165·9(3)
Si — O(3)	164·2(2)
Si — O(3^{vi})	
O(1) — O(2^{iv})	274·0(4)
O(1) — O(3)	276·5(3)
O(1) — O(3^{vi})	
O(2^{iv}) — O(3)	257·6(3)
O(2^{iv}) — O(3^{vi})	
O(3) — O(3^{vi})	260·5(4)

O(1) — Si — O(2^{iv})	113·3(2)
O(1)— Si — O(3)	115·9(1)
O(1) — Si — O(3^{vi})	
O(2^{iv}) — Si — O(3)	102·6(1)
O(2^{iv}) — Si — O(3^{vi})	
O(3) — Si — O(3^{vi})	105·0(1)

Octahedron I

Co(1) — O(1^{iii})	209·7(2)
Co(1) — O(1^{ii})	
Co(1) — O(2)	209·5(2)
Co(1) — O(2^{v})	
Co(1) — O(3^{ii})	217·4(2)
Co(1) — O(3^{vii})	
O(1^{iii}) — O(2)	287·8(4)
O(1^{ii}) — O(2^{v})	
O(2) — O(3^{ii})	340·5(3)
O(2^{v}) — O(3^{vii})	
O(2^{v}) — O(3^{ii})	257·6(3)
O(2) — O(3^{vii})	
O(1^{ii}) — O(3^{vii})	315·1(4)
O(1^{iii}) — O(3^{ii})	
O(1^{ii}) — O(3^{ii})	288·3(3)
O(1^{iii}) — O(3^{vii})	
O(1^{iii}) — O(2^{v})	304·8(1)
O(1^{ii}) — O(2)	

O(2^{v}) — Co(1) — O(1^{ii})	86·7(1)
O(2) — Co(1) — O(1^{iii})	
O(2^{v}) — Co(1) — O(3^{vii})	105·8(1)
O(2) — Co(1) — O(3^{ii})	
O(2^{v}) — Co(1) — O(1^{iii})	93·3(1)
O(2) — Co(1) — O(1^{ii})	
O(2^{v}) — Co(1) — O(3^{ii})	74·2(1)
O(2) — Co(1) — O(3^{vii})	
O(1^{ii}) — Co(1) — O(3^{ii})	84·9(1)
O(1^{iii}) — Co(1) — O(3^{vii})	
O(1^{ii}) — Co(1) — O(3^{vii})	95·1(1)
O(1^{iii}) — Co(1) — O(3^{ii})	

TABLE IV

(*Continued*)

Octahedron II

Co(2) — O(1$^{\mathrm{i}}$)	219·0(4)	O(2) — Co(2) — O(3$^{\mathrm{vi}}$)	97·1(1)
Co(2) — O(2)	208·0(3)	O(2) — Co(2) — O(3)	
Co(2) — O(3)	223·1(2)	O(2) — Co(2) — O(3$^{\mathrm{viii}}$)	89·7(1)
Co(2) — O(3$^{\mathrm{vi}}$)		O(2) — Co(2) — O(3$^{\mathrm{ix}}$)	
Co(2) — O(3$^{\mathrm{viii}}$)	207·3(2)	O(1$^{\mathrm{i}}$) — Co(2) — O(3$^{\mathrm{vi}}$)	81·4(1)
Co(2) — O(3$^{\mathrm{ix}}$)		O(1$^{\mathrm{i}}$) — Co(2) — O(3)	
O(3) — O(3$^{\mathrm{vi}}$)	260·5(4)	O(1$^{\mathrm{i}}$) — Co(2) — O(3$^{\mathrm{ix}}$)	91·3(1)
O(2) — O(3$^{\mathrm{vi}}$)	323·2(4)	O(1$^{\mathrm{i}}$) — Co(2) — O(3$^{\mathrm{viii}}$)	
O(2) — O(3)		O(3$^{\mathrm{vi}}$) — Co(2) — O(3)	71·4(1)
O(1$^{\mathrm{i}}$) — O(3$^{\mathrm{vi}}$)	288·3(3)	O(3) — Co(2) — O(3$^{\mathrm{ix}}$)	88·5(1)
O(1$^{\mathrm{i}}$) — O(3)		O(3$^{\mathrm{viii}}$) — Co(2) — O(3$^{\mathrm{vi}}$)	
O(1$^{\mathrm{i}}$) — O(3$^{\mathrm{viii}}$)	304·9(4)	O(3$^{\mathrm{ix}}$) — Co(2) — O(3$^{\mathrm{viii}}$)	110·9(2)
O(1$^{\mathrm{i}}$) — O(3$^{\mathrm{ix}}$)			
O(2) — O(3$^{\mathrm{viii}}$)	293·0(3)		
O(2) — O(3$^{\mathrm{ix}}$)			
O(3$^{\mathrm{vi}}$) — O(3$^{\mathrm{viii}}$)	300·6(3)		
O(3) — O(3$^{\mathrm{ix}}$)			
O(3$^{\mathrm{viii}}$) — O(3$^{\mathrm{ix}}$)	341·4(4)		

3 pm and at least 0·3 pm longer than the Mg—O distances. Similarly, the O—Co—O angles in the $\mathrm{CoO_6}$ octahedron are very similar to the O—Mg—O angles in the $\mathrm{MgO_6}$ octahedron (71 – 111°), while the O—Ca—O angles in the $\mathrm{CaO_6}$ octahedron vary from 65 to 121°. These phenomena can be explained as resulting from the effect of the size of the central ion ($r_{\mathrm{Ca}^{2+}} = 114$, $r_{\mathrm{Co}^{2+}} = 88{\cdot}5$, $r_{\mathrm{Mg}^{2+}} = 86$ pm) (ref.[14]) on the dislocation of the oxygen atoms in the structure. Atoms O(1), O(2) and O(3) are tetrahedrally coordinated by three cobalt atoms and one silicon atom.

The authors wish to thank Dr J. Sikač for preparing the single crystals of the studied compound and Dr F. Pechar for carrying out the chemical analyses.

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Translated by M. Štulíková.