

tact distances involving the C atoms of the methyl groups.

In Table 2 the displacements of the ligand atoms from the least-squares plane calculated considering only the aromatic part of the molecule are reported. Here the system approaches planarity to a degree (highest displacement 0.022 Å) which was only found in the naphthyridine molecules of the octacoordinated complex $[\text{Fe}(\text{NN})_4](\text{ClO}_4)_2$ (Singh, Clearfield & Bernal, 1971); in all the other 1,8-naphthyridine complexes whose structures have been reported, and even in the free molecule (Clearfield, Sims & Singh, 1972), the displacements are very much higher. Finally it is worth noting that the plane containing the ligand molecule is almost orthogonal to the coordination plane defined by the Cu, Cl and N atoms, the dihedral angle being 87.4°.

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Electron-Density Distributions in Crystals of $\gamma\text{-Fe}_2\text{SiO}_4$ and $\gamma\text{-Co}_2\text{SiO}_4$

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Electron-density distributions in crystals of $\gamma\text{-Fe}_2\text{SiO}_4$ and $\gamma\text{-Co}_2\text{SiO}_4$ have been experimentally determined from single-crystal X-ray diffraction data. Evidence for trigonally deformed distributions of 3d electrons around the transition-metal atoms in the compounds was observed on the final difference Fourier maps. The residual electron-density distribution for $\gamma\text{-Fe}_2\text{SiO}_4$ is significantly different from that for $\gamma\text{-Ni}_2\text{SiO}_4$, in conformity with the difference in the number of 3d electrons. The difference Fourier map of $\gamma\text{-Co}_2\text{SiO}_4$ has an intermediate feature between those of $\gamma\text{-Ni}_2\text{SiO}_4$ and $\gamma\text{-Fe}_2\text{SiO}_4$. Residual electron densities were also observed on the Si–O bonds.

Introduction

Evidence for the aspherical distribution of 3d electrons around the transition-metal atoms in crystals of $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ (Iwata & Saito, 1973) and $\gamma\text{-Ni}_2\text{SiO}_4$ (Marumo, Isobe, Saito, Yagi & Akimoto, 1974) has been obtained by single-crystal X-ray diffraction. The transition-metal atoms are octahedrally coordinated. The two independent Co^{III} atoms in the former crystal are in the low-spin state, and the six 3d electrons occupy the t_{2g} orbitals in the ground state. The distribution of the 3d electrons in the t_{2g} or-

bitals has maxima on the eight threefold rotation axes of the coordination octahedron. Residual densities indicating such an aspherical distribution were clearly observed on the difference Fourier maps of $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$. In the case of $\gamma\text{-Ni}_2\text{SiO}_4$, the Ni^{2+} cation has eight 3d electrons, six of which are in the t_{2g} orbitals, and two in the e_g orbitals in the ground state. Since the sum of the electron-density distributions of three 3d electrons in the t_{2g} and two in the e_g orbitals should be approximately spherical, the electron-density distribution around the Ni^{2+} cation is expected to show an asphericity similar to those observed in $[\text{Co}(\text{NH}_3)_6]-$

[Co(CN)₆]. In fact, eight residual peaks were observed on the body-diagonals with respect to the six Ni—O bonds in the difference Fourier map of γ -Ni₂SiO₄.

It is of interest to examine the electron-density distributions around transition-metal atoms with different numbers of 3d electrons in a similar crystal field. This paper describes the results of an investigation into the electron-density distributions around the Fe²⁺ and Co²⁺ cations in γ -Fe₂SiO₄ and γ -Co₂SiO₄.

Experimental

The specimens used were synthesized from the respective metal orthosilicates of the olivine form with the aid of a tetrahedral-anvil-type high-pressure apparatus. The details are given in a previous report (Yagi, Marumo & Akimoto, 1974). The cell dimension of γ -Fe₂SiO₄ was determined from powder-diffraction data and that of γ -Co₂SiO₄ from ten 2 θ values obtained on a four-circle diffractometer. The crystal data are given in Table 1.

Crystals for intensity measurements were ground into spheres. The sizes and other experimental conditions are given in Table 2. Intensities were collected on a Rigaku automated four-circle diffractometer with Mo K α radiation monochromated with graphite. Background counts were measured at both ends of the scan range. The counting time at each end was varied from 15 to 450 s, according to the peak counts and the scan time. When the peak intensity exceeded 5000 counts s⁻¹, Ni-foil attenuators were inserted to avoid a

counting loss. Scanning was repeated up to 10 times for each reflexion with $\sigma(|F_o|) > 0.0025|F_o|$, where $\sigma(|F_o|)$ is the estimated standard deviation of the observed structure amplitude based on counting statistics. The measurements were carried out over two symmetrically related regions of reciprocal space in each crystal. Reflexions with $|F_o| > 3\sigma(|F_o|)$ were considered to be observed. In the practical calculations, however, only the reflexions in one independent region were adopted. The other sets of reflexions were used to check accidental errors in the data. The intensities were corrected for Lorentz, polarization and absorption factors. Corrections for the secondary-extinction effects were carried out in the course of the structure refinements.

The crystals were known to have normal-spinel structures (Morimoto, Tokonami, Watanabe & Koto, 1974; Yagi *et al.*, 1974). Refinements of the structures were carried out with the full-matrix least-squares program LINUS (Coppens & Hamilton, 1970); isotropic secondary extinctions were assumed. Partial disorders between the transition-metal and Si atoms were taken into account, and the populations were included in the variables to be refined (with the constraint of electrical neutrality). The population obtained [0.024(4)] for Fe²⁺ ions at the tetrahedral site suggested the presence of partial disorder between Fe and Si atoms in γ -Fe₂SiO₄, while the corresponding value of 0.014(5) for Co²⁺ cations indicated that the structure of γ -Co₂SiO₄ is practically of the ideal normal-spinel

Table 1. Crystal data of γ -Fe₂SiO₄ and γ -Co₂SiO₄

	γ -Fe ₂ SiO ₄	γ -Co ₂ SiO ₄
Space group	<i>Fd3m</i>	<i>Fd3m</i>
<i>a</i> (Å)	8.234 (1)	8.140 (1)
<i>Z</i>	8	8
<i>D_x</i> (g cm ⁻³)	4.85	5.17
μ (Mo K α) (cm ⁻¹)	108.62	130.02

Table 2. Experimental conditions

	γ -Fe ₂ SiO ₄	γ -Co ₂ SiO ₄
Diameter of specimen	0.090 mm	0.075 mm
Radiation	Mo K α	Mo K α
Monochromator	Graphite	Graphite
2 θ _{max}	135°	135°
Scan technique	ω -2 θ	ω -2 θ
Scan speed	2° min ⁻¹	2° min ⁻¹
Scan width	1.5° + 1.0° tan θ	1.4° + 1.0° tan θ
Maximum number of repetitions	10	10
Criterion to terminate repetition	$\sigma(F)/ F \leq 0.0025$	$\sigma(F)/ F \leq 0.0025$
Number of observed reflexions	217	202

Table 3. The final parameters and *R* values for γ -Fe₂SiO₄ and γ -Co₂SiO₄

The values of the positional and thermal parameters are multiplied by 10⁵ and those of populations by 10³. The temperature factors are in the form:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

	Intermediate-spinel model	Normal-spinel model	
	γ -Fe ₂ SiO ₄	γ -Co ₂ SiO ₄	γ -Co ₂ SiO ₄
Tetrahedral sites			
Population	{ Si 976 Fe 24 (4)	Si 986 Co 14 (5)	Si 1000 —
<i>x</i> (= <i>y</i> = <i>z</i>)	0	0	0
β_{11} (= β_{22} = β_{33})	137 (4)	122 (5)	111 (3)
β_{12} (= β_{13} = β_{23})	0	0	0
Octahedral sites			
Population	{ Fe 988 Si 12	Co 993 Si 7	Co 1000 —
<i>x</i> (= <i>y</i> = <i>z</i>)	62500	62500	62500
β_{11} (= β_{22} = β_{33})	169 (1)	151 (1)	152 (1)
β_{12} (= β_{13} = β_{23})	-3 (1)	-8 (1)	-8 (1)
Oxygen sites			
<i>x</i> (= <i>y</i> = <i>z</i>)	36588 (7)	36728 (8)	36727 (8)
β_{11} (= β_{22} = β_{33})	172 (3)	154 (3)	153 (3)
β_{12} (= β_{13} = β_{23})	-14 (3)	-10 (4)	-10 (4)
<i>G</i> ($\times 10^7$)	31 (3)	102 (5)	103 (5)
<i>R</i>	0.0138	0.0150	0.0154
<i>R_w</i>	0.0135	0.0149	0.0152

type. Therefore, the structure of $\gamma\text{-Co}_2\text{SiO}_4$ was also refined on the ordered model.

The final atomic parameters are given in Table 3, together with the conventional and weighted R values. The atomic scattering factors and dispersion correction factors for the Fe^{2+} , Co^{2+} and Si^{4+} ions were taken from *International Tables for X-ray Crystallography* (1968). The scattering factors used for O^{2-} ions were those given by Tokonami (1965). The dispersion correction was ignored for O^{2-} ions. Unit weight was given to all the observed reflexions in the least-squares calculations.*

Results and discussion

All the atomic parameters are in good agreement with those reported previously (Morimoto *et al.*, 1974; Yagi *et al.*, 1974). The electron-density distributions were examined by synthesizing difference Fourier maps. For $\gamma\text{-Co}_2\text{SiO}_4$, the synthesis was carried out with the final parameters obtained on the assumption of an ideal normal-spinel structure, whereas that for $\gamma\text{-Fe}_2\text{SiO}_4$ was performed with parameters based on the

partial-disorder model. Sections of the maps of both crystals through the plane $y = x$ are shown in Figs. 1 and 2. The transition-metal, Si and O atoms appear on these sections. In contrast to $\gamma\text{-Ni}_2\text{SiO}_4$ (Marumo *et al.*, 1974), where eight peaks were observed around the Ni^{2+} ion in three dimensions, only two large peaks exist around the Fe^{2+} ion, as seen in Fig. 1. These peaks are on the threefold rotation axis running through the cation site. The distance is about 0.046 \AA from the Fe^{2+} ion and the peak height is about $1.2 e \text{ \AA}^{-3}$.

The Fe^{2+} ion is known to be in the high-spin state in $\gamma\text{-Fe}_2\text{SiO}_4$ with six $3d$ electrons. The cation is octahedrally surrounded by six O^{2-} anions, but the exact symmetry of the coordination polyhedron is not cubic but trigonal, because of the flattening of the polyhedron along the direction of the threefold rotation axis. Therefore, the triply degenerate t_{2g} level is split into one singlet and one twofold degenerate level. From the shape of the coordination octahedron, the singlet level is presumed to be lower than the twofold degenerate level. Accordingly five out of the six $3d$ electrons occupy each of the five $3d$ orbitals, and the remaining one occupies the singlet level in the ground state. The observed peaks seem to originate in this trigonally deformed distribution of $3d$ electrons.

In the difference Fourier map of $\gamma\text{-Co}_2\text{SiO}_4$, eight peaks are observed around the Co^{2+} ion, as in the case of $\gamma\text{-Ni}_2\text{SiO}_4$, four being on the section given in Fig. 2. However, the peaks on the threefold rotation axis ($1.0 e \text{ \AA}^{-3}$ in height) are much larger than the remaining six

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32093 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

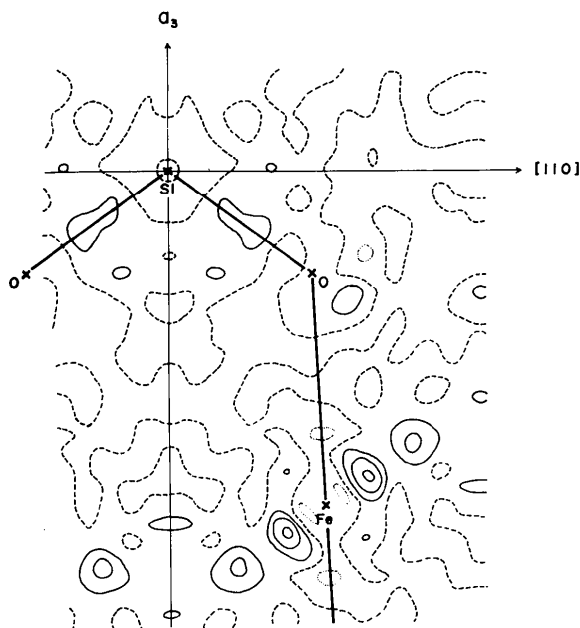


Fig. 1. The section of the difference Fourier map of $\gamma\text{-Fe}_2\text{SiO}_4$ through the plane $y = x$. Contours are at intervals of $0.4 e \text{ \AA}^{-3}$. Zero contours are in broken lines, and negative contours dotted.

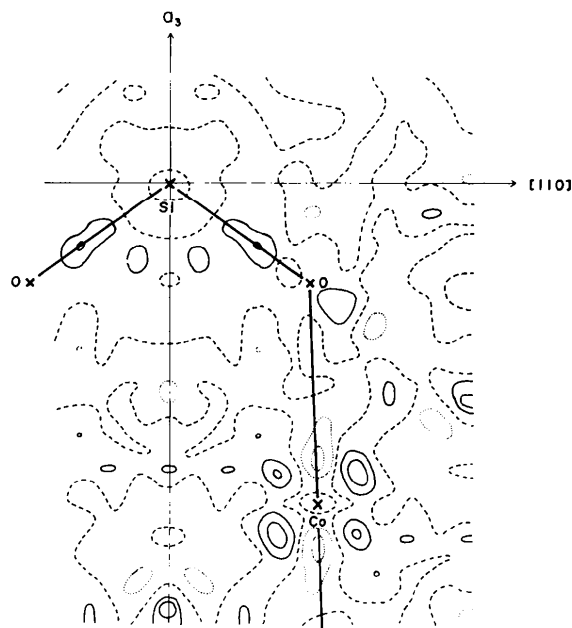


Fig. 2. The section of the difference Fourier map of $\gamma\text{-Co}_2\text{SiO}_4$ through the plane $y = x$. Contours are at intervals of $0.4 e \text{ \AA}^{-3}$. Zero contours are in broken lines, and negative contours dotted.

(0.8 e Å⁻³), giving a feature just intermediate between those in the difference Fourier maps of γ -Fe₂SiO₄ and γ -Ni₂SiO₄. This trend in the density distributions of 3d electrons is parallel to the degree of flattening of the coordination octahedra. Namely, the Fe²⁺ ion, which only gives a pair of residual densities on the threefold rotation axis, has the most flattened coordination octahedron among those around the three kinds of cations. The distances of the peaks from the Co²⁺ site are also about 0.46 Å.

Residual densities are observed on the Si—O bonds in both γ -Fe₂SiO₄ and γ -Co₂SiO₄. A common feature is that the positive regions are guitar-shaped with double maxima.

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The Crystal Structure and Absolute Configuration of Condelphine Hydroiodide

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Condelphine, a C₁₉ diterpene alkaloid isolated from *Delphinium denudatum*, has been investigated by an X-ray crystal structure determination of its hydroiodide derivative, C₂₅H₃₉NO₆·HI. The crystals are triclinic, *P*1, *a* = 9.3404 (9), *b* = 17.442 (2), *c* = 9.0953 (8) Å, α = 94.891 (9), β = 118.891 (7), γ = 86.594 (9)°. The unit cell contains two independent molecules, related by approximate *I*-centering. The structure has been refined to *R* = 0.100, *R*_w = 0.111, based on 3828 observed reflections. The absolute configuration is established as 1*S*,4*S*,5*R*,7*S*,8*S*,9*R*,10*R*,11*S*,13*R*,14*S*,16*S*,17*R*, by examination of Friedel pairs of reflections. The alkaloid is a member of the aconitine family, and bears 1 α -hydroxy, 8 β -hydroxy, 14 α -acetyl, 16 β -methoxy and *N*-ethyl substituents. Intramolecular hydrogen bonding between the protonated N atom and the 1 α -hydroxy group stabilizes ring *A* in a boat form. The two independent molecules have no significant contacts with each other. Because condelphine has been correlated with isotalatzidine and talatzidine, this work confirms the molecular structure and establishes the absolute configuration of the latter two alkaloids as well.

Introduction

The alkaloids of the C₁₉ diterpene family are based on a skeleton which is heavily substituted with oxygenated groups. The structures of these alkaloids have generally been elucidated on the basis of chemical correlations, supported by crystallographic and spectral studies. Condelphine (I) is a member of this family which has been isolated from both *Delphinium denudatum*

