obtained in KCl by Cooper & Rouse. The effect of these anharmonic force constants is much larger in Cs_3CoCl_5 since it is such a relatively soft material with high $\langle u^2 \rangle$ values. It is interesting to note that we obtain large positive values for γ only for those atoms for which both $\langle u^2 \rangle$ is large and there is a short intermolecular contact [Cs(2)–Cl(1) and Cs(2)–Cl(2)]. Moreover, the coefficients for Cs(1) are small, even though its $\langle u^2 \rangle$ is large, which might suggest that it is too small for the 'hole' that it occupies in the lattice. Perhaps the instability of Rb_3CoCl_5 and the non-existence of K_3CoCl_5 may be due to their even smaller cation sizes.

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X-ray Determination of Electron Distributions in Forsterite, Fayalite and Tephroite

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Abstract

Atomic net charges and electron density distributions of the olivine structures forsterite (α-Mg_2SiO_4), fayalite (α-Fe_2SiO_4) and tephroite (α-Mn_2SiO_4) have been determined from accurate single-crystal X-ray data on the respective synthetic crystals. The atomic net charges were obtained from the direct integration of the electron density within the sphere of a newly defined radius, the *effective distribution radius*, around each cation. Such net charges revealed that the tetrahedral Si atom is less ionic than the octahedral cations and the transition-metal Fe and Mn are less ionic than Mg. These charges also showed that the $M(1)$-site cation is less ionic than the $M(2)$-site cation when the cations of the same kind occupy both $M(1)$ and $M(2)$ sites. Radial distributions of valence electrons outside the Ar cores of the transition metals show that the $3d$ electrons have their maximum densities about 0·4 ~ 0·5 Å from the centre of the atom. In three-dimensional difference Fourier maps of forsterite the positive peaks appeared 0·96 Å, on average, from the centre of the Si atom along each of the four Si—O directions. [Crystal data: forsterite: a = 4·7534 (6), b = 10·1902 (15), c = 5·9783 (7) Å, space group *Pbnm*, final R = 0·0209; fayalite: a = 4·8195 (6), b = 10·4788 (17), c = 6·0873 (8) Å, space group *Pbnm*, final R = 0·0255; tephroite: a = 4·9023 (6), b = 10·5964 (16), c = 6·2567 (9) Å, space group *Pbnm*, final R = 0·0310.]

Introduction

We have previously described (Sasaki, Fujino, Takéuchi & Sadanaga, 1980) a procedure for deter-

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Table 1. *Crystal data and data regarding the intensity study*

	Forsterite	Fayalite	Tephroite
Cell dimensions			
a (Å)	4·7534 (6)	4·8195 (6)	4·9023 (6)
b (Å)	10·1902 (15)	10·4788 (17)	10·5964 (16)
c (Å)	5·9783 (7)	6·0873 (8)	6·2567 (9)
V (Å^3)	289·58 (7)	307·42 (8)	325·02 (8)
Cell contents	4[Mg_2SiO_4]	4[Fe_2SiO_4]	4[Mn_2SiO_4]
Space group	*Pbnm*	*Pbnm*	*Pbnm*
ρ_{calc} (Mg m^{-3})	3·226	4·402	4·126
μ(Mo $K\alpha$) (mm^{-1})	1·065	9·859	8·330
Diameter of specimen (mm)	0·26	0·20	0·20
Number of reflections (measured)	2441	2571	2568
Number of reflections (used)	2168	2042	2088
R value	0·0209	0·0255	0·0310
Weighted R value	0·0287	0·0296	0·0356

mining net charges on atoms in the crystalline state. The procedure may be regarded as an improved version of the method used by Kurki-Suonio & Salmo (1971) and, in principle, is applicable to any type of structure. The present paper describes the results of new applications to the structures of the olivines α-Mg_2SiO_4 (forsterite), α-Fe_2SiO_4 (fayalite), and α-Mn_2SiO_4 (tephroite), and discusses, in particular, the electron density distributions about the transition metals in these structures. This paper further provides a new listing of *effective distribution radii*, EDR, which we denoted ER in our previous paper (Sasaki, Fujino, Takéuchi & Sadanaga, 1980), for atoms in some oxides and silicates.

Experimental

Spherically ground crystals were prepared from synthetic crystals and used for the present study; electron microprobe analyses showed that the crystals were chemically pure to a reasonable extent and spatially homogeneous. The cell dimensions obtained from a four-circle Syntex $P2_1$ diffractometer (Mo $K\alpha$ radiation, λ = 0·71069 Å) are given in Table 1. The ω–2θ scan technique was used to measure, on the diffractometer, the graphite-monochromatized Mo $K\alpha$ reflection intensities up to $2\theta = 134°$. In Table 1, we give data regarding the intensity study. The diffraction intensities were corrected for Lorentz and polarization effects, transmission factors, and isotropic-extinction effects (Zachariasen, 1967; Coppens & Hamilton, 1970; Becker & Coppens, 1974). Those intensities greater than $3\sigma(I_o)$ were used for structure refinement.

Refinement of structures and determination of net charges on atoms

For structure refinement, atomic scattering factors of the following form were used:

$$f(s/2) = f_M(s/2) + pf_{m-M}(s/2) + f' + if''; \qquad (1)$$

here, $s = 2\sin\theta/\lambda$, f_M = the scattering factor of the atom in an ionic state M, f_{m-M} = the difference between f's for two ionic states m and M, and p = occupancy factor to be determined. The parameter p was refined simultaneously with the positional and thermal parameters of the atoms. The use of scattering factors of this form was not for the purpose of determining atomic charges but merely for the procedure of structure refinement. In terms of p obtained for an atom, however, we may calculate, apart from the validity of the result, the number of electrons associated with the atom; we previously denoted such a procedure of deriving atomic charges $L1$ (Sasaki, Fujino, Takéuchi & Sadanaga, 1980). The atomic charges thus derived in the present case (Table 4) are obviously less meaningful. The final atomic parameters are listed in Table 2. The interatomic distances and angles calculated using the program *ORFFE* (Busing, Martin & Levy, 1964) are given in Table 3.*

Now, the charges on the atoms were determined, as described elsewhere (Sasaki, Fujino, Takéuchi & Sadanaga, 1980), through two steps. First, the charge on a given cation was determined by counting the number of electrons in the sphere having its center at the atom and a radius, EDR, which we defined in the radial electron density distribution $U(R)$ of the cation. Second, under the constraints that the charges of the cations thus determined were fixed and the total charge

Table 2. *Final atomic coordinates and equivalent isotropic thermal factors* (*Hamilton*, 1959) *with their e.s.d.'s*

	x	y	z	B_{eq} (Å^2)
Forsterite				
M(1)	0·0	0·0	0·0	0·447
M(2)	0·99169 (7)	0·27739 (3)	0·25	0·442
Si	0·42645 (5)	0·09403 (2)	0·25	0·304
O(1)	0·76594 (11)	0·09156 (6)	0·25	0·401
O(2)	0·22164 (12)	0·44705 (5)	0·25	0·403
O(3)	0·27751 (8)	0·16310 (4)	0·03304 (7)	0·435
Fayalite				
M(1)	0·0	0·0	0·0	0·520
M(2)	0·98598 (5)	0·28026 (2)	0·25	0·474
Si	0·43122 (10)	0·09765 (5)	0·25	0·372
O(1)	0·76814 (23)	0·09217 (12)	0·25	0·510
O(2)	0·20895 (25)	0·45365 (11)	0·25	0·526
O(3)	0·28897 (17)	0·16563 (9)	0·03643 (9)	0·583
Tephroite				
M(1)	0·0	0·0	0·0	0·620
M(2)	0·98792 (6)	0·28041 (3)	0·25	0·531
Si	0·42755 (11)	0·09643 (5)	0·25	0·382
O(1)	0·75776 (26)	0·09363 (14)	0·25	0·537
O(2)	0·21088 (28)	0·45369 (13)	0·25	0·542
O(3)	0·28706 (19)	0·16384 (9)	0·04140 (16)	0·579

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* Lists of structure factors and anisotropic thermal parameters, and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35738 (46 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of the crystal was neutral, the charges of the oxygen atoms were determined by least squares using a scattering factor for oxygen atoms of the form (1). This implies that the negative charge of the crystal which should compensate for the total positive charge as determined by the first step was partitioned to individual oxygen atoms by means of the least-squares procedure. For further details, refer to Sasaki, Fujino, Takéuchi & Sadanaga (1980).

Results and discussion

Atomic charges

We give in Table 4 the charges on the atoms which we obtained. The Si atoms have electronic charges between +2·1 and +2·4 and oxygen atoms between −1·1 and −1·5, whereas the octahedral cations have values ranging from +0·8 to +1·8. The ratio of the atomic charge of Si to the formal one (+4) is always smaller than the corresponding ones of octahedral cations except for Fe at the $M(1)$ site of fayalite. Such a tendency is in accordance with the covalency of Si atoms. The atomic charges of the octahedral cations Fe and Mn are all smaller than those of Mg at both $M(1)$ and $M(2)$ sites. This indicates that Mg is more ionic than Fe and Mn as suggested by Tamada (1976) from the electrostatic site energies. Further, it can be seen in Table 4 that the atomic charges of $M(1)$ are smaller than those of $M(2)$ in fayalite and tephroite. This is also consistent with the electrostatic site energies.

Radial electron distributions

Radial electron distributions $U(R)$ of Mg, Mn, Fe, Co and Ni atoms at the $M(1)$ site are illustrated in Fig. 1, in which the effective distribution radius, EDR, is indicated by an arrow for each cation. The values of the EDR for various atoms in olivines, mono-oxides and pyroxenes, which we have examined, are summarized in Table 5 and compared with the ionic radii and crystal radii of Shannon (1976). In spite of the differences in crystal structures, the EDR values of the same kind of atoms are almost identical among various crystal structures. In Table 5 it is apparent that our EDR values are all greater than the corresponding ionic radii of Shannon (1976), and roughly comparable with the crystal radii (Tosi, 1964). A closer examination, however, shows that the values of the EDR of the transition metals Mn, Fe, Co and Ni are greater by 0·18 ~ 0·23 Å than the corresponding crystal radii. On the other hand, the EDR values of Na, Mg and Ca are nearly equal to their crystal radii and that of Li is smaller than its crystal radius. These disagreements between the EDR and Shannon's crystal radii may suggest that the electron clouds of oxygen atoms are not steady but variable and that the mode of variation (or distortion) is different depending upon the species of

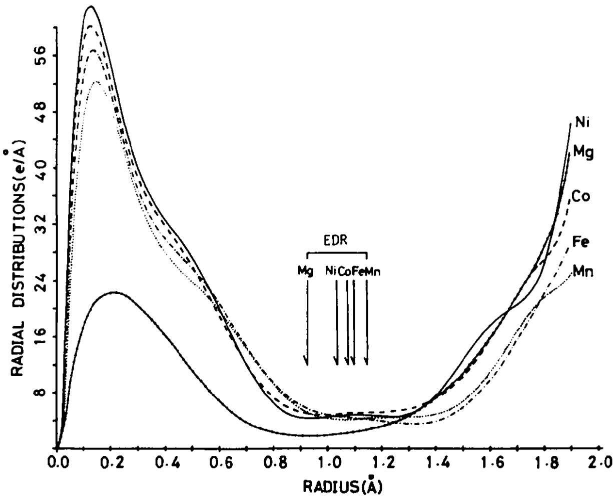

Fig. 1. Radial electron distributions of the Mg, Mn, Fe, Co and Ni atoms at $M(1)$ in the olivine structures. Those of Co and Ni are based on the reflection data provided by Tamada (1980, private communication).

Table 4. *Charges on atoms*

In the pair of lines for each atom, the first gives the value determined from the EDR, and the second that based on f calculation according to the procedure $L1$.

	$[M(1)]$	$[M(2)]$	[Si]	[O(1)]	[O(2)]	[O(3)]
Forsterite						
EDR	1·76 (3)	1·74 (3)	2·11 (3)	−1·52 (7)	−1·29 (7)	−1·40 (7)
$L1$	2·1 (1)	3·1 (1)	1·8 (1)	−1·9 (1)	−1·6 (1)	−1·7 (1)
Fayalite						
EDR	0·85 (8)	1·54 (7)	2·43 (6)	−1·13 (11)	−1·21 (11)	−1·24 (11)
$L1$	1·3 (1)	1·9 (1)	1·9 (2)	−1·2 (1)	−1·3 (1)	−1·3 (1)
Tephroite						
EDR	1·21 (6)	1·49 (6)	2·28 (5)	−1·27 (12)	−1·13 (12)	−1·29 (12)
$L1$	1·3 (1)	2·2 (2)	2·6 (2)	−1·5 (1)	−1·4 (1)	−1·6 (1)

Table 5. *Effective distribution radii, EDR, of cations in various materials as compared with ionic and crystal radii* (*Shannon*, 1976)

Cation	Material	Atomic site	EDR (Å)	Ionic radius (Å)	Crystal radius (Å)	Coordination number of cation
Li	α-Spodumene	$M(2)$	0·83	0·92	1·06	VIII
Na	Jadeite	$M(2)$	1·30	1·18	1·32	VIII
Mg	Periclase		0·92	0·72	0·86	VI
	Forsterite	$M(1)$	0·93			
	Forsterite	$M(2)$	0·94			
	Diopside	$M(1)$	0·91			
	Enstatite	$M(1)$	0·89			
	Enstatite	$M(2)$	0·96			
	(average)		(0·93)			
Ca	Diopside	$M(2)$	1·27	1·12	1·26	VIII
Mn	Manganosite		1·15	0·83	0·97	VI
	Tephroite	$M(1)$	1·15			
	Tephroite	$M(2)$	1·16			
	(average)		(1·15)			
Fe	Fayalite	$M(1)$	1·10	0·78	0·92	VI
	Fayalite	$M(2)$	1·12			
	(average)		(1·11)			
Co	CoO		1·09	0·745	0·885	VI
	Co olivine*	$M(1)$	1·08			
	Co olivine	$M(2)$	1·07			
	(average)		(1·08)			
Ni	Bunsenite		1·08	0·69	0·83	VI
	Ni olivine*	$M(1)$	1·04			
	Ni olivine	$M(2)$	1·05			
	(average)		(1·06)			
Si†	Forsterite		0·96	0·26	0·40	IV
	α-Spodumene		0·96			
	(average)		(0·96)			

* Based on reflection data provided by Tamada (1980, private communication).

† The EDR of Si was derived from the difference Fourier maps.

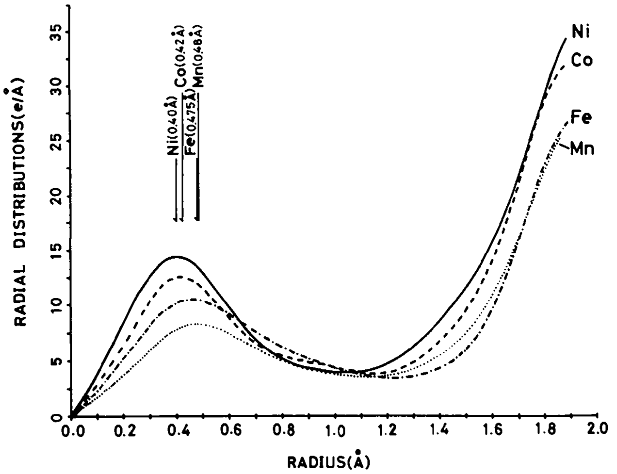

Fig. 2. Radial distributions of valence electrons outside the Ar core of transition metals at $M(1)$ in the olivine structures. Those of Co and Ni atoms are based on the reflection data provided by Tamada (1980, private communication).

neighbouring cations. Such a feature has also been observed for oxygen atoms in a series of NaCl-type mono-oxides (Sasaki, Fujino & Takéuchi, 1979).

To know the radial distributions of $3d$ electrons for each of the transition metals at $M(1)$, we calculated a residual radial electron density distribution, $\Delta U(R)$, by subtracting the theoretical radial electron density of the Ar core from $U(R)$ of the transition metal. The curves of $\Delta U(R)$ (Fig. 2) have maxima at the distances of 0·40 ~ 0·48 Å from the central atoms; the distances increase in the order of Ni, Co, Fe and Mn. These distances agree well with those of the $3d$ electron densities reported for transition metals in γ-spinels (Marumo, Isobe, Saito, Yagi & Akimoto, 1974; Marumo, Isobe & Akimoto, 1977) and NaCl-type mono-oxides (Sasaki, Fujino & Takéuchi, 1979).

Residual electron densities

Since the distributions of $3d$ electrons of the transition metals at the sites having low symmetry [$\bar{1}$ for $M(1)$ and m for $M(2)$ in the olivine type] are of particular interest, the aspherical electron density distributions around the transition metals were studied further by means of difference Fourier syntheses. In Fig. 3, we give composite difference Fourier sections parallel to (100), showing the residual peaks, having absolute heights greater than 0·6 e Å^{-3}, around $M(1)$ and $M(2)$ in fayalite and tephroite. In fayalite a set of four positive peaks is observed at distances of 0·47 ~ 0·53 Å from each of the Fe atoms at $M(1)$ and $M(2)$ (Fig. 3*a*,*b*). There are differences in the mode of arrangement and peak heights between the sets of residual peaks about $M(1)$ and $M(2)$. In the case of tephroite, a set of two positive peaks and two negative peaks appears at distances of 0·48 ~ 0·50 Å from each of the Mn atoms at $M(1)$ and $M(2)$ (Fig. 3*c*,*d*). The arrangement and heights of peaks in one set are, in this case, almost identical with those of the other. The distances of these residual peaks from the central Fe or Mn atoms agree well with those of the peak maxima of the radial distributions $U(R)$ of the $3d$ electrons discussed previously.

In contrast to these cases, no peak maximum with a peak height greater than 0·3 e Å^{-3} was observed around Mg atoms in the difference Fourier maps of forsterite. Therefore, the above residual densities about Fe and Mn are significant and seem to represent aspherical distributions of the $3d$ electrons in the distorted octahedra. Since a formal Mn^{2+} ion has five $3d$ electrons and a spherical electron density according to the crystal-field theory, the above aspherical electron densities of Mn may be related to our result that the charge on Mn does in fact deviate from the formal value of +2. Such an aspherical electron density of Mn has also been found in the case of MnO (Sasaki, Fujino & Takéuchi, 1979). The interpretation of these

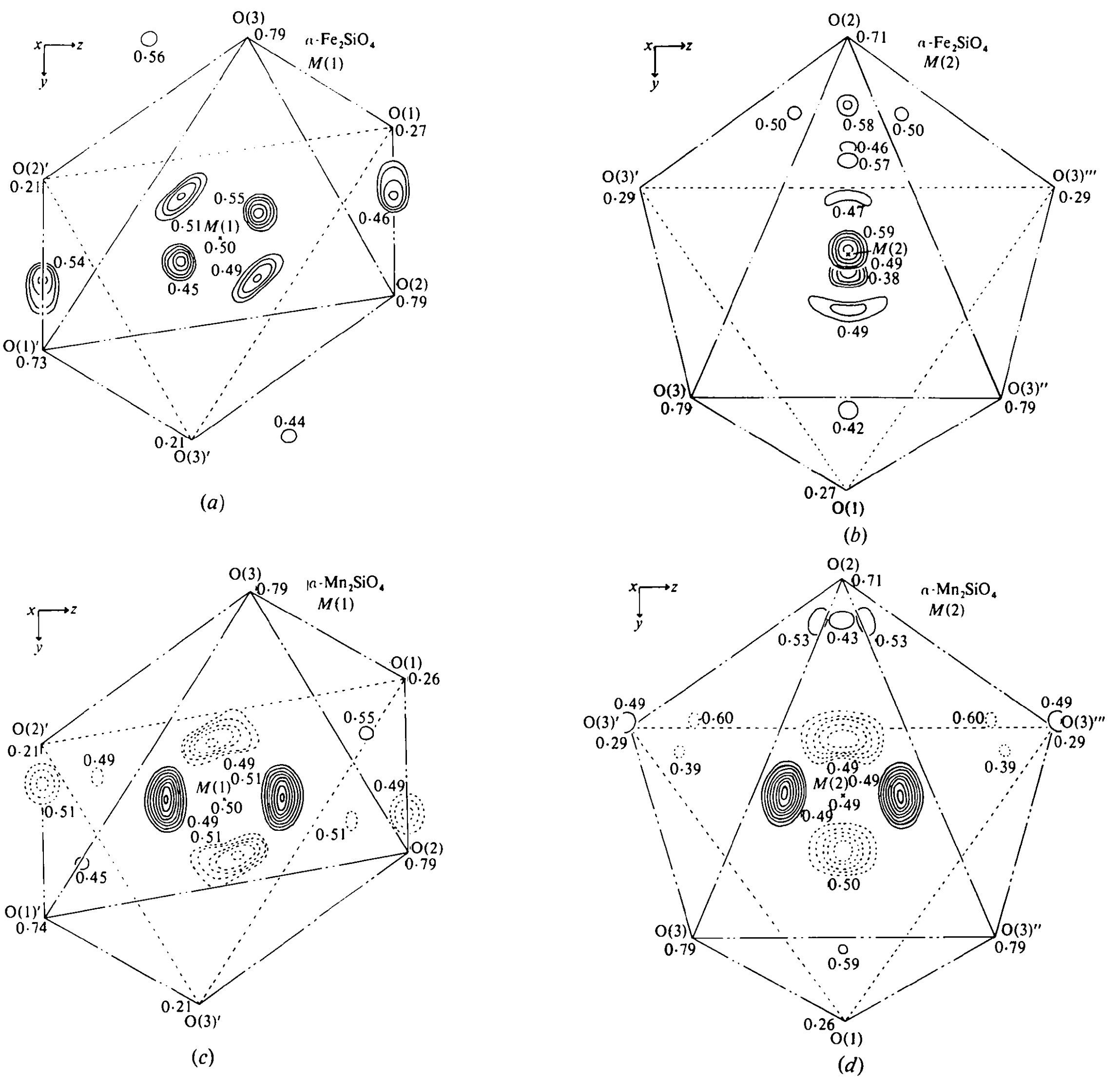

Fig. 3. Composite difference Fourier sections parallel to (100), showing peaks around (*a*) *M*(1) of fayalite, (*b*) *M*(2) of fayalite, (*c*) *M*(1) of tephroite and (*d*) *M*(2) of tephroite; each section passes through a centre of positive or negative peaks. Contours are drawn starting from the absolute value of 0·6 e Å^{-3} with intervals of 0·1 e Å^{-3} for fayalite and 0·2 e Å^{-3} for tephroite, negative contours being broken. Numbers in decimal fractions of the *a* length indicate the heights of atoms or peaks. The octahedron formed by oxygen atoms about each cation site is indicated.

aspherical electron densities of Fe and Mn atoms in the distorted octahedra is reserved for future study.

In the difference Fourier maps of forsterite, the residual positive peaks with peak heights 0·3–0·6 e Å^{-3} appeared along each of the four Si–O directions around the Si atom in a way similar to the cases of α-spodumene and some other silicates (Sasaki, Fujino, Takéuchi & Sadanaga, 1980). The (100) section with $x = 0{\cdot}305$ in Fig. 4 shows such positive peaks between Si and the three basal oxygens in the Si tetrahedron. The distances of these four positive peaks from the central Si atom are in the range from 0·94 to 0·97 Å giving a mean value of 0·96 Å which is close to the mean of the covalent radii of Si and O, $(1{\cdot}17 + 0{\cdot}66)/2 = 0{\cdot}92$ Å (Pauling, 1960).

We are grateful to Dr H. Takei of Tohoku University for placing his synthetic crystals at our disposal. The calculations were performed on a HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo.

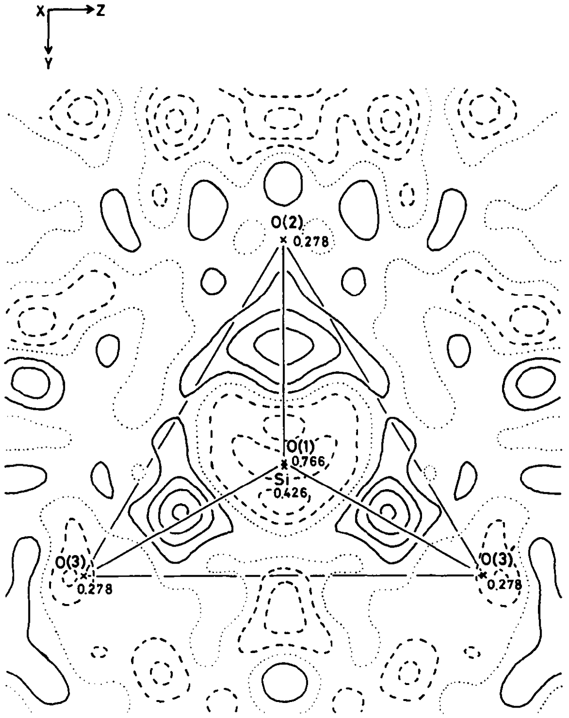

Fig. 4. The section $x = 0{\cdot}305$ of the final difference Fourier synthesis of forsterite, showing the residual peaks around Si. Contours are at intervals of $0{\cdot}1$ e Å^{-3}, negative contours being broken and zero contours dotted. Numbers in decimal fractions of the a length indicate the heights of the atoms. The tetrahedron formed by oxygen atoms about Si is shown.

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Vergleich der Kristallstrukturen von $(NH_4)_3ZnCl_5$ und Ba_3SiS_5

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Abstract

The crystal structure of tribarium tetrathiosilicate(IV) sulphide has been determined by single-crystal X-ray techniques. The crystals are orthorhombic, *Pnma*, with the cell dimensions $a = 12{\cdot}121$ (10), $b = 9{\cdot}527$ (8), $c = 8{\cdot}553$ (8) Å, and $Z = 4$. Full-matrix least-squares refinement of 820 independent observed reflexions gave a conventional R index of 0·044. The crystal structure of triammonium tetrachlorozincate(II) chloride has been reinvestigated [*Pnma*, $a = 8{\cdot}716$ (3), $b = 9{\cdot}887$ (3), $c = 12{\cdot}625$ (7) Å, $Z = 4$]. Full-matrix least-squares refinement of 934 independent observed reflexions gave a final R of 0·044. The structures are described as partly filled combinations of Kagomé 3636 nets of anions. Both structures are derived by symmetry reduction from the Ge_3Rh_5 space group *Pbam*. A family tree of such relationships for a number of known structure types is given. It is shown that Ba_3SiS_5 is a partly filled Sb_3Ca_5 type and $(NH_4)_3ZnCl_5$ a partly filled Bi_3Y_5 type. The Madelung part of the lattice energies is discussed.

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