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Structure of a Manganese(II) Arsenatotrisilicate, $Mn_4[AsSi_3O_{12}(OH)]$: The Presence of a New Tetrapolyphosphate-Like Anion

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Abstract

A manganese(II) arsenatotrisilicate, $Mn_4^{II}[AsSi_3O_{12}(OH)]$, monoclinic, $P2_1/n$, with $a = 6{\cdot}66\,(1)$, $b = 19{\cdot}92\,(2)$, $c = 7{\cdot}67\,(1)$ Å, $\beta = 95{\cdot}7\,(1)°$, $Z = 4$, $V = 1012{\cdot}6$ Å^3, $D_{obs} = 3{\cdot}84$ (flotation in Clerici solution), $D_{cal} = 3{\cdot}86$ Mg m^{-3}, has recently been found in nature as a new mineral. Computer-controlled four-circle diffractometer data (Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, graphite monochromator) were analysed; $F(000) = 1120$, μ(Mo $K\alpha$) = 8·95 mm^{-1}. The final R index = 0·049 for 1777 independent reflexions. The structure contains an arsenatotrisilicate ion $[AsSi_3O_{12}(OH)]^{8-}$, the conformation of which resembles that of a tetrapolyphosphate, and can be considered to be an extension of the trisilicate ion $[Si_3O_{10}]^{8-}$.

Introduction

An interesting mineral has been recently found in an old manganese mine at Molinello near Chiavari (Liguria), as small orange grains intimately intergrown with rhodochrosite, quartz, parsettensite, *etc.*; its powder diffraction pattern and unit-cell parameters do not match any reported data for either minerals or artificial compounds (Gramaccioli, Griffin & Mottana, 1978). A partial microprobe analysis has shown the mineral to be essentially a manganese silicate, with significant amounts of arsenic; in order to characterize it precisely, an X-ray structure analysis has been considered to be appropriate. For this purpose we have used the only available single crystal, an irregularly shaped squat fragment, the dimensions of which were approximately equal in all directions, measuring about 0·15 mm in diameter. This crystal, from which the preliminary unit-cell data have been derived, was obtained from the matrix after considerable effort (Gramaccioli, Griffin & Mottana, 1978); in view of the danger of loss, no manipulation of it (*e.g.* grinding to a sphere, or breaking it into smaller pieces) was considered to be advisable.

Determination and refinement of the structure

The crystal was mounted on a Syntex $P\bar{1}$ automatic single-crystal diffractometer. The unit-cell dimensions are: $a = 6{\cdot}66\,(1)$, $b = 19{\cdot}92\,(2)$, $c = 7{\cdot}67\,(1)$ Å, $\beta = 95{\cdot}7\,(1)°$; these have been redetermined and refined from 60 reflexions, with 2θ around 50°, using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). These dimensions are in fair agreement with the measurements reported in our previous paper (Gramaccioli, Griffin & Mottana, 1978). The Laue symmetry of the reciprocal lattice is $2/m$, and extinctions are present for $0k0$: $k = 2n + 1$ and $h0l$: $h + l = 2n + 1$. This indicates $P2_1/n$ space-group symmetry.

1777 independent reflexions were measured on the Syntex diffractometer, using the 2θ–θ scan method, and Mo $K\alpha$ radiation with a graphite monochromator. These reflexions are all those available within $2\theta = 50°$; of these, 39 were too weak, *i.e.* their intensities were less than twice their standard deviations, as derived from counting statistics. The reflexion intensities were corrected for Lorentz and polarization factors; furthermore, as soon as the chemical formula could be ascertained from the solution of the structure, thereby deriving a reliable value for $\mu = 8{\cdot}95$ mm^{-1} for Mo $K\alpha$ radiation, an approximate absorption correction was applied, on the assumption that the crystal was spherical. Each reflexion was assigned a variance $\sigma^2(I) = \sigma^2_{c.s.}(I) + (0{\cdot}03S)^2$, where $\sigma^2_{c.s.}$ is the variance as derived from counting statistics, and S is the scan count.

From a three-dimensional Patterson synthesis, the positions of five independent heavier atoms, all initially attributed to manganese, were derived. A first three-dimensional difference Fourier map, obtained by assigning phases consistent with these heavier atoms in the positions derived from the Patterson function,

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showed all the Si and O atoms in the structure; the same synthesis showed that one of the five heavy atoms had an atomic number substantially greater than that of Mn, and consistent with that of As. The chemical formula was then confirmed: the calculated density $D_{\rm cal} = 3{\cdot}86$ Mg m^{-3} (for $Z = 4$) is in good agreement with the observed value $D_{\rm obs} = 3{\cdot}84$ Mg m^{-3}, obtained by flotation in diluted Clerici solution.

Refinement has been carried out by full-matrix least-squares minimization of the quantity $\sum w(|F_o| - |F_c|)^2$. For this purpose, 1738 reflexions were initially considered, *i.e.* those for which $I > 2\sigma(I)$. Final weights were assigned equal to $4|F_o|^2/\sigma^2(|F_o|^2)$; throughout this work, atomic form factors corresponding to the neutral atoms according to Cromer & Waber (1965) have been used, without allowance for anomalous dispersion. Anisotropic temperature factors were initially considered for the As and Mn atoms only; the R index dropped to 5·2% in three cycles. A difference Fourier synthesis was then calculated in order to locate the H atom, but only a minor peak was detected in the proximity of the expected position, whereas several higher peaks were observed in the neighbourhoods of other atoms, some of which revealed considerable anisotropy.

A new series of least-squares refinement was performed, with anisotropic temperature factors including the Si and O atoms; in these calculations, the reflexions with $|F_o| > 150$ were excluded, since, in general, they appeared to be strongly affected by extinction. After three cycles, the R index for all reflexions was 4·9%;* a final difference Fourier synthesis revealed a clear peak of 0·9 e Å^{-3} corresponding to the H atom. A few negative peaks (up to 1·2 e Å^{-3}) still persisted close to the As and Si atoms; the necessity for ionic instead of atomic form factors may be rather superficial, in view of the anomalous-dispersion effects and of the approximations in correcting for absorption. No evidence appeared for partial mutual substitution between Si and As, which would give positive peaks corresponding to the Si atoms. The final positional parameters are given in Table 1.

Table 1. *Fractional atomic coordinates* ($\times 10^5$, *for* H $\times 10^3$)

	x	y	z
As	43066 (11)	30163 (4)	−21252 (10)
Mn(1)	25844 (16)	64836 (6)	−14601 (15)
Mn(2)	−45780 (16)	58376 (5)	54669 (15)
Mn(3)	76253 (16)	50915 (6)	24515 (15)
Mn(4)	5246 (16)	74596 (6)	13942 (15)
Si(1)	23118 (28)	36790 (10)	8072 (26)
Si(2)	26741 (27)	52059 (10)	16158 (25)
Si(3)	4814 (28)	59788 (10)	44013 (26)
O(1)	27074 (75)	23802 (26)	−18296 (70)
O(2)	45977 (83)	31980 (27)	−42138 (69)
O(3)	64941 (75)	28926 (29)	−9053 (71)
O(4)	31652 (72)	36999 (26)	−12036 (66)
O(5)	3333 (76)	32369 (26)	7199 (66)
O(6)	41456 (75)	34321 (26)	21941 (68)
O(7)	17699 (73)	44584 (25)	11549 (70)
O(8)	30120 (74)	55324 (27)	−2563 (65)
O(9)	45704 (73)	51577 (25)	30760 (66)
O(10)	8685 (73)	55831 (27)	25473 (67)
O(11)	4933 (81)	67785 (26)	38415 (72)
O(12)	22133 (74)	58601 (26)	60057 (68)
O(13)	−16437 (78)	56880 (27)	47657 (68)
H	140	710	450

Table 2. *Bond angles* (°) *in the anion*

O(1)–As–O(2)	115·2	O(1)–As–O(3)	110·0
O(1)–As–O(4)	103·1	O(2)–As–O(3)	113·0
O(2)–As–O(4)	108·4	O(3)–As–O(4)	106·2
O(4)–Si(1)–O(5)	109·1	O(4)–Si(1)–O(6)	107·9
O(4)–Si(1)–O(7)	103·1	O(5)–Si(1)–O(6)	115·5
O(5)–Si(1)–O(7)	110·0	O(6)–Si(1)–O(7)	110·4
O(7)–Si(2)–O(8)	104·8	O(7)–Si(2)–O(9)	110·1
O(7)–Si(2)–O(10)	104·0	O(8)–Si(2)–O(9)	118·4
O(8)–Si(2)–O(10)	112·1	O(9)–Si(2)–O(10)	106·4
O(10)–Si(3)–O(11)	103·2	O(10)–Si(3)–O(12)	114·9
O(10)–Si(3)–O(13)	101·2	O(11)–Si(3)–O(12)	108·5
O(11)–Si(3)–O(13)	115·3	O(12)–Si(3)–O(13)	113·3
As–O(4)–Si(1)	123·3	Si(1)–O(7)–Si(2)	145·7
Si(2)–O(10)–Si(3)	140·3	Si(3)–O(11)–H	121

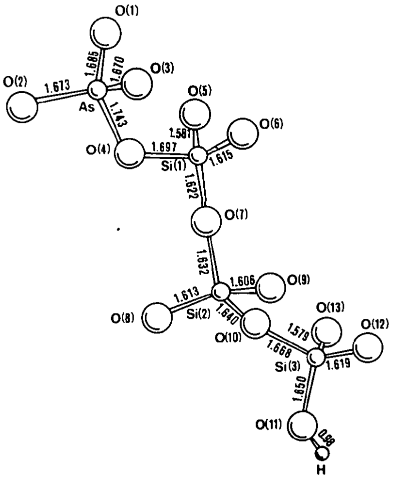

Fig. 1. Conformation of the $[AsSi_3O_{12}(OH)]^{8-}$ ion.

The standard deviation in the $X - O$ (X = Mn, Si, As) bond lengths, as derived from the residuals and the normal-equation matrix in the final least-squares cycle, and from the σ's in the unit-cell parameters, ranges from 0·008 to 0·009 Å; for the O–X–O and X–O–X

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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 34544 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å) *and angles* (°) *around the manganese atoms*

Mn(1)–O(8)$^{(a)*}$	2·115	Mn(1)–O(3)$^{(e)}$	2·235
–O(5)$^{(g)}$	2·151	–O(12)$^{(f)}$	2·300
–O(1)$^{(k)}$	2·213	–O(6)$^{(e)}$	2·309
Average Mn(1)–O	2·220		
O(1)–Mn(1)–O(3)	91·9	O(1)–Mn(1)–O(5)	85·4
O(1)–Mn(1)–O(6)	80·0	O(1)–Mn(1)–O(8)	169·1
O(1)–Mn(1)–O(12)	86·5	O(3)–Mn(1)–O(5)	79·9
O(3)–Mn(1)–O(6)	88·2	O(3)–Mn(1)–O(8)	97·4
O(3)–Mn(1)–O(12)	170·0	O(5)–Mn(1)–O(6)	160·8
O(5)–Mn(1)–O(8)	101·7	O(5)–Mn(1)–O(12)	109·8
O(6)–Mn(1)–O(8)	94·7	O(6)–Mn(1)–O(12)	81·8
O(8)–Mn(1)–O(12)	83·3		
Mn(2)–O(13)$^{(a)}$	2·099	Mn(2)–O′(9)$^{(h)}$	2·276
–O(2)$^{(g)}$	2·148	–O(9)$^{(c)}$	2·305
–O(12)$^{(c)}$	2·217	–O(6)$^{(h)}$	2·306
Average Mn(2)–O	2·225		
O(2)–Mn(2)–O(6)	77·2	O(2)–Mn(2)–O(9)	100·3
O(2)–Mn(2)–O(12)	95·9	O(2)–Mn(2)–O(13)	88·7
O(2)–Mn(2)–O′(9)	177·1	O(6)–Mn(2)–O(9)	172·6
O(6)–Mn(2)–O(12)	83·7	O(6)–Mn(2)–O(13)	104·0
O(6)–Mn(2)–O′(9)	100·0	O(9)–Mn(2)–O(12)	89·7
O(9)–Mn(2)–O(13)	82·8	O(9)–Mn(2)–O′(9)	82·4
O(12)–Mn(2)–O(13)	171·8	O(12)–Mn(2)–O′(9)	83·2
O(13)–Mn(2)–O′(9)	92·6		
Mn(3)–O(8)$^{(e)}$	2·102	Mn(3)–O(10)$^{(d)}$	2·366
–O(9)$^{(a)}$	2·140	–O(4)$^{(e)}$	2·625
–O(13)$^{(d)}$	2·152	–O(7)$^{(e)}$	2·974
–O(12)$^{(f)}$	2·232		
Average Mn(3)–O	2·370		
Average of shorter bonds	2·198		
O(4)–Mn(3)–O(7)	54·9	O(4)–Mn(3)–O(8)	103·4
O(4)–Mn(3)–O(9)	82·2	O(4)–Mn(3)–O(10)	77·4
O(4)–Mn(3)–O(12)	165·9	O(4)–Mn(3)–O(13)	79·4
O(7)–Mn(3)–O(8)	57·9	O(7)–Mn(3)–O(9)	114·2
O(7)–Mn(3)–O(10)	72·4	O(7)–Mn(3)–O(12)	138·2
O(7)–Mn(3)–O(13)	124·1	O(8)–Mn(3)–O(9)	95·4
O(8)–Mn(3)–O(10)	112·4	O(8)–Mn(3)–O(12)	85·3
O(8)–Mn(3)–O(13)	177·1	O(9)–Mn(3)–O(10)	148·5
O(9)–Mn(3)–O(12)	86·0	O(9)–Mn(3)–O(13)	85·6
O(10)–Mn(3)–O(12)	109·8	O(10)–Mn(3)–O(13)	67·3
O(12)–Mn(3)–O(13)	92·1		
Mn(4)–O(5)$^{(g)}$	2·168	Mn(4)–O(2)$^{(k)}$	2·223
–O(3)$^{(e)}$	2·173	–O(1)$^{(g)}$	2·233
–O(6)$^{(l)}$	2·220	–O(11)$^{(a)}$	2·318
Average Mn(4)–O	2·222		
O(1)–Mn(4)–O(2)	93·1	O(1)–Mn(4)–O(3)	169·2
O(1)–Mn(4)–O(5)	91·0	O(1)–Mn(4)–O(6)	81·5
O(1)–Mn(4)–O(11)	82·9	O(2)–Mn(4)–O(3)	92·9
O(2)–Mn(4)–O(5)	82·7	O(2)–Mn(4)–O(6)	77·5
O(2)–Mn(4)–O(11)	173·8	O(3)–Mn(4)–O(5)	80·9
O(3)–Mn(4)–O(6)	108·5	O(3)–Mn(4)–O(11)	91·9
O(5)–Mn(4)–O(6)	158·4	O(5)–Mn(4)–O(11)	102·0
O(6)–Mn(4)–O(11)	97·1		

* Symmetry transformations: (*a*) x,y,z; (*c*) $x-1, y, z$; (*d*) $1+x, y, z$; (*e*) $1-x, 1-y, -z$; (*f*) $1-x, 1-y, 1-z$; (*g*) $-x, 1-y, -z$; (*h*) $-x, 1-y, 1-z$; (*k*) $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$; (*l*) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

bond angles it ranges between 0·35 and 0·40°. Bond lengths and angles are reported in Fig. 1, and Tables 2 and 3.

Discussion

The most interesting characteristic of the structure is the presence of the arsenatotrisilicate ion $[AsSi_3O_{12}(OH)]^{8-}$ comprising four tetrahedra linked together to form a chain fragment. This ion, new to science, is an extension of the trisilicate $[Si_3O_{10}]^{8-}$ ion, which is itself rather rare in natural or synthetic silicates: among the former are ardennite, $Mn_2(Mn,Ca)_2(AlOH)_4[(Mg,Al,Fe)OH]_2(As,V)O_4Si_3O_{10}(SiO_4)_2$ (Donnay & Allmann, 1968), kinoite, $Cu_2Ca_2Si_3O_{10}.2H_2O$ (Laughon, 1971), thalenite, $Y_3(Si_3O_{10})(OH)_2$ (Kornev, Batalieva, Maksimov, Ilyukhin & Belov, 1972), kornerupine, a complex Mg–Al silicate (Moore & Bennett, 1968), and rosenhahnite, $Ca_3Si_3O_8(OH)_2$ (Wan, Ghose & Gibbs, 1977). Of these minerals, ardennite is especially interesting, because it also contains As and Mn; the AsO_4 tetrahedron in ardennite is, however, isolated and not joined to the trisilicate group, as found here. Of all the ions comprising four tetrahedra linked together into an unbranched chain fragment, only the tetrapolyphosphate $[P_4O_{13}]^{6-}$ seems to be known, but no crystal structures of these salts are available in the literature. A curiously 'branched' example of a chromatoarsenate ion, $[AsCr_3O_{13}]^{3-}$, has recently been described (Averbuch-Pouchot, 1978).

In the arsenatotrisilicate ion, the averages of the Si–O (1·627 Å) and As–O bond lengths (1·693 Å) are in good agreement with the average (1·623 Å) given by Smith & Bailey (1963) for metasilicates with no substitution of Al for Si, and with the average value (1·686 Å) given by Ferraris (1970) for the As–O bond length in arsenates. Like the di- and trisilicates, pyro- or triphosphates, di- and trisulphates, dichromates, *etc.*, the 'bridged' Si–O (or As–O) bonds are distinctly longer than the others; here, for instance, the 'bridged' Si–O bond-length average is 1·652 Å, while the 'non-bridged' Si–O bond average is 1·602 Å, two values which are close to the corresponding averages (1·656 and 1·603 Å respectively) found for the trisilicate ion in rosenhahnite (Wan *et al.*, 1977). This is in accord with Cruickshank (1961), who discusses the phenomenon in terms of π-bond formation by $3d$ orbitals; the difference between 'bridged' and 'non-bridged' values is correlated with the values of the X–O–X bond angles, which in this study average 136·4°, and are therefore quite different from 180°. Some of the more recent papers by Gibbs and co-workers using a MO approach may also be helpful: see, for instance, Louisnathan & Gibbs (1972*a*,*b*), Tossell & Gibbs (1976). As for all compounds of this kind, the Si–OH bond (1·650 Å) is

Table 4. *Estimated Pauling bond strength s_i*

For Mn(3), values in parentheses assume coordination number 7, instead of 5; for the other Mn atoms, the coordination number is 6.

'Anions'	'Cations'	s_i	$\sum s_i$
O(1)	Mn(1)	0·333	1·92
	Mn(4)	0·333	
	As	1·25	
O(2)	Mn(2)	0·333	1·92
	Mn(4)	0·333	
	As	1·25	
O(3)	Mn(1)	0·333	1·92
	Mn(4)	0·333	
	As	1·25	
O(4)	Mn(3) long	(0·29)	2·25 (2·54)
	As	1·25	
	Si(1)	1·00	
O(5)	Mn(1)	0·333	1·67
	Mn(4)	0·333	
	Si(1)	1·00	
O(6)	Mn(1)	0·333	2·00
	Mn(2)	0·333	
	Mn(4)	0·333	
	Si(1)	1·00	
O(7)	Mn(3) very long	(0·29)	2·00 (2·29)
	Si(1)	1·00	
	Si(2)	1·00	
O(8)	Mn(1)	0·333	1·73 (1·62)
	Mn(3)	0·40 (0·29)	
	Si(2)	1·00	
O(9)	Mn(2)	0·333	2·07 (1·96)
	Mn(2')	0·333	
	Mn(3)	0·40 (0·29)	
	Si(2)	1·00	
O(10)	Mn(3)	0·40 (0·29)	2·40 (2·29)
	Si(2)	1·00	
	Si(3)	1·00	
O(11)	Mn(4)	0·333	2·33
	Si(3)	1·00	
	H	1·00	
O(12)	Mn(1)	0·333	1·96 (2·07)
	Mn(2)	0·333	
	Mn(3)	0·40 (0·29)	
	Si(3)	1·00	
O(13)	Mn(2)	0·333	1·73 (1·62)
	Mn(3)	0·40 (0·29)	
	Si(3)	1·00	

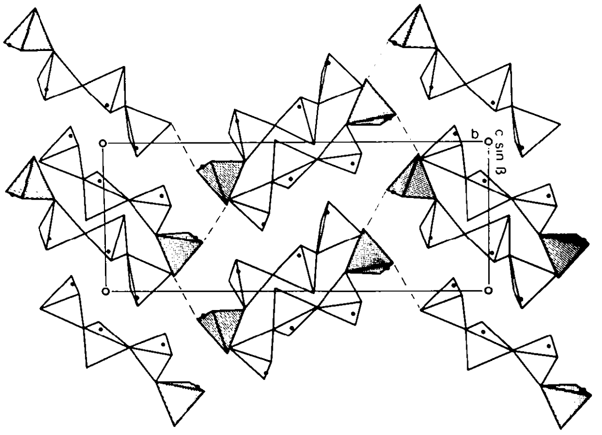

Fig. 2. Packing of the arsenatotrisilicate chain fragment in the crystal, as seen along **a**. The Mn atoms have been indicated by points; shaded tetrahedra correspond to AsO_4. Hydrogen bonds are shown as dashed lines.

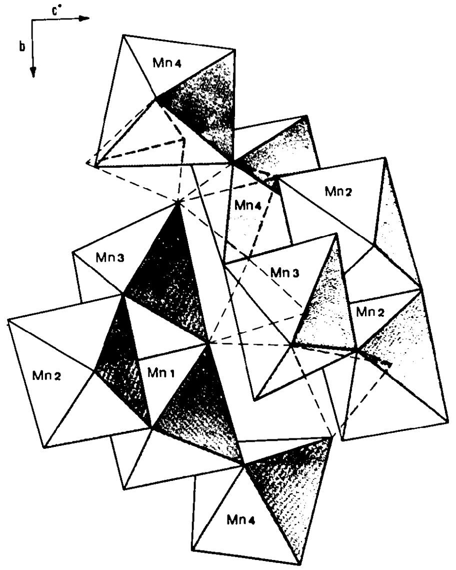

Fig. 3. Coordination polyhedra around Mn atoms, as seen along **a** [the longest distance around Mn(3) is not shown]. An arsenatotrisilicate chain fragment (dashed tetrahedra) is superimposed.

significantly longer than the corresponding Si—O bonds; the hydrogen bond between O(11) and O'(1) (transformed by $\frac{1}{2}-x; \frac{1}{2}+y; \frac{1}{2}-z$) is 2·75 Å.

The variation in bond lengths can also be described in terms of Pauling bond strength (see, for instance, Baur, 1970). For this purpose, estimated bond strengths and their sums with respect to each O atom are reported in Table 4.

Oxygen—metal distances below 3 Å around the Mn atoms are given in Table 3. For Mn(1), Mn(2) and Mn(4) the O atoms are almost octahedrally arranged around the metal, with little distortion: the bond lengths range between 2·099 and 2·318 Å, their average being 2·222 Å, with no significant variation between the three polyhedra, and in close agreement with the average Mn^{2+}—O distance (2·22 Å) reported by Shannon & Prewitt (1969), and with several recent well refined crystal structures of Mn^{2+} compounds. For Mn(3), however, the coordination number is seven (5 + 2): there are, in fact, five 'shorter' Mn—O bonds ranging from 2·102 to 2·366 Å (average 2·198 Å), and two 'longer' bonds on the same side, whose lengths are 2·625 and 2·974 Å respectively (the longest bond is not represented in Fig. 3); a similar 5 + 2 coordination occurs in ardennite (Donnay & Allmann, 1968) for one Mn atom, partly substituted by Ca, where five Mn—O bonds range from 2·189 to 2·305 Å and two are somewhat longer (2·403 and 2·473 Å). The difference between longer and shorter bonds is, however, not so striking as in our case. Fig. 2 is a packing diagram.

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The Nature of the Chemical Bonding in Boron Carbide, $B_{13}C_2$. II. Dynamic Deformation Densities and Valence Densities

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Abstract

The crystal structure of rhombohedral $B_{13}C_2$ is composed of two structural units, the linear C—B—C chain and the B_{12} icosahedron. Based on high-order (HO) refinement results, X–X maps of dynamic deformation densities and valence densities have been calculated for sections in both units. The influence of the scale factor and the local distribution of the variance of difference densities were investigated for the density distribution in the B—C bond of C—B—C, which lies in the hexagonal c axis and shows the largest deviations from the spherical free-atom model. Integrations of residual densities in the C—B—C unit yield experimental evidence for a theoretically postulated charge transfer of one electron towards the B_{12} icosahedron, providing a 10-electron closed-shell configuration for C—B—C. The charge distribution in and around the somewhat distorted B_{12} icosahedron is discussed in terms of a simple covalent-bond model.

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Introduction

In a previous paper (Kirfel, Gupta & Will, 1979; hereafter called part I) the crystal structure of $B_{13}C_2$ was studied by refinements of X-ray diffraction data. Both the conventional spherical free-atom model and the multipole expansion model (Hirshfeld, 1971; Harel & Hirshfeld, 1975) were used. This preceding paper contains the results from the various refinements and first conclusions concerning the bond character in $B_{13}C_2$. As a preliminary result no indication could be found that a charge transfer takes place from the C—B—C chain towards the B_{12} icosahedron. This had been demanded by Longuet-Higgins & Roberts (1955) in a theoretical paper on the bonding features in boron icosahedra. The extreme stability of the refractory borides, including boron carbide, is supposed to be based on such an electron transfer.

In a second part of the analysis we have now studied the dynamic deformation densities and valence den-