

the X-ray photographs and Dr M. Wilkens for stimulating discussions.

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Calculation of the Electron Density Distribution in Silicon by the Density-Functional Method. Comparison with X-ray Results

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Abstract

Quantum-chemical density-functional theory (DFT) calculations, using the local-density approximation (LDA), have been performed for hydrogen-bounded silicon clusters to determine the electron density distribution of the Si–Si bond. The density distribution in the bonding region is compared with calculated and X-ray values of the bond in the crystal and found to be in good agreement. Using Hirshfeld's method for charge partitioning, a central Si atom was isolated and used for building a crystal. The corresponding structure factors agree very well ($R \leq 0.14\%$) with experimental ones obtained by the *Pendellösung* method.

Introduction

Silicon has been a subject of intensive research for a few decades now but there are still several properties which are not well understood. Theoretical methods, such as band-structure calculations, do not always seem to reproduce experimental results.

Hohenberg & Kohn (1964) have shown that the ground-state electron density distribution $\rho(\mathbf{r})$ fully characterizes all properties of the many-body system in the ground state. As a corollary, no quantum-mechanical method yielding an inaccurate electron density distribution will give proper energy values, unless compensation of errors occurs. With this in mind we set out to calculate the electron density distribution in silicon. This is all the more interesting because the calculations can be compared with the very accurate structure factors of silicon, obtained by Aldred & Hart (1973) and by Saka & Kato (1986) with the *Pendellösung* method. Spackman (1986) has analyzed various sets of measured structure factors and compared them

with different theories, while Cummings & Hart (1988) have recently reanalyzed the experiments of Aldred & Hart (1973) making some additional corrections.

The work presented in this paper is based on molecular Hartree–Fock–Slater (HFS) LCAO calculations. The present method cannot handle the periodicity of the crystal. To obtain the density distribution of the silicon crystal, we determined $\rho(\mathbf{r})$ in hydrogen-bounded silicon clusters of increasing size. The larger the cluster, the more a central atom is assumed to resemble the atoms in the crystal. By partitioning the charge distribution in the cluster, a central Si atom can be extracted from the cluster and used for building an infinite crystal by applying the proper symmetry operations.

To verify the assumption and to judge the resulting crystalline electron density distribution, structure factors were calculated and compared with the results of *Pendellösung* measurements by Aldred & Hart (1973) and Saka & Kato (1986), with values recommended by Spackman (1986) on the basis of careful analysis of existing data, and with the outcome of Yin & Cohen's (1982) band-structure calculations.

Computational methods

To calculate the electron density distribution $\rho(\mathbf{r})$ in silicon clusters we employed the HFS-LCAO-DVM version of the LDA method. In the Hohenberg–Kohn–Sham formalism (Hohenberg & Kohn, 1964; Kohn & Sham, 1965) the calculation for spin-restricted states consists of self-consistently solving

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad (1)$$

where

$$V_{\text{eff}}(\mathbf{r}) = -\sum_n \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}(\mathbf{r}) \quad (2)$$

(i.e. the sum of the nuclear potential acting on the electrons, the Coulomb potential produced by all the electrons and the exchange-correlation potential).

The ground-state electron density distribution $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \sum_i n_i |\varphi_i(\mathbf{r})|^2 \quad (3)$$

in which n_i is the occupation number of the orbital φ_i . The exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$ is, in the HFS version, approximated by

$$V_{\text{xc}}(\mathbf{r}) = -3\alpha \left[\frac{3}{8\pi} \rho(\mathbf{r}) \right]^{1/3} \quad (4)$$

where α is an adjustable parameter, taken to be 0.7 in the present work.

In the HFS-LCAO-DVM version, as developed by Baerends, Ellis & Ros (1973) and Baerends & Ros (1973), the one-electron orbitals are expanded as a finite set of STO basis functions centered at the atomic nuclei. DVM denotes the discrete variational method as introduced by Ellis & Painter (1970) and Painter & Ellis (1970).

The basis set for silicon clusters consisted of 6s, 5p and 1d Cartesian STO functions on silicon, in addition to a frozen 1s core (see Table 1). To describe the H atoms we used 3s and 1p functions. The angles and distances in the clusters Si_2H_6 (D_{3d} symmetry), $\text{Si}(\text{SiH}_3)_4$ (T_d) and $\text{Si}_2(\text{SiH}_3)_6$ (D_{3d}) were chosen to be the same as in the silicon crystal: all tetrahedral angles and an Si-Si distance of 2.351 Å. To saturate dangling bonds we placed H atoms on the surface of the cluster at a distance of 1.492 Å from the Si atoms, as has been found in Si_2H_6 molecules.

For extracting the most central Si atom or Si-Si bond of a cluster we employed the partitioning scheme proposed by Hirshfeld (1977), which divides the total charge in a sensible way among the different atoms. According to this method one can for each atom define a sharing function

$$W_\alpha(\mathbf{r}) = \frac{\rho_\alpha^{\text{atom}}(\mathbf{r} - \mathbf{R}_\alpha)}{\sum_\beta \rho_\beta^{\text{atom}}(\mathbf{r} - \mathbf{R}_\beta)} \quad (5)$$

where $\rho_\alpha^{\text{atom}}(\mathbf{r} - \mathbf{R}_\alpha)$ denotes the electron density of a free atom centered at the atomic position \mathbf{R}_α in the cluster. The electron density of a Hirshfeld atom can now be defined as

$$\rho_\alpha(\mathbf{r}) = W_\alpha(\mathbf{r})\rho(\mathbf{r}) \quad (6)$$

where $\rho(\mathbf{r})$ is the total electron density of the cluster.

Table 1. Basis sets (Cartesian STO functions) used for the HFS calculations

The 1s on silicon is an additional function for orthogonalization on the frozen 1s core.

	Exponent	
Silicon:	1s	11.90
	2s	5.15
	2s	3.60
	3s	2.95
	3s	1.85
	3s	1.20
	2p	6.85
	2p	3.65
	3p	2.00
	3p	1.20
	3p	0.75
	3d	1.43
Hydrogen:	1s	1.58
	1s	0.92
	1s	0.69
	2p	0.72

To reduce errors which can occur in the numerical integration in the HFS calculation, we used in (6), instead of the total density $\rho(\mathbf{r})$, the deformation density $\Delta\rho(\mathbf{r})$ (i.e. the difference between the molecular density and the superposition of spherically averaged free-atom densities). The density $\Delta\rho_\alpha(\mathbf{r})$ is fitted by a least-squares minimization of the error

$$D = \int \left[\Delta\rho_\alpha(\mathbf{r}) - \sum_i c_i g_i(\mathbf{r}) \right]^2 d\mathbf{r} \quad (7)$$

to a combination of one-center functions $g_i(\mathbf{r})$. Cartesian STO's up to g -type functions were used for the one-center functions $g_i(\mathbf{r})$, obtaining a mean difference between $\Delta\rho_\alpha$ and the fit, lower than 0.01 e Å⁻³ with the largest values close to the nucleus. The structure factors are obtained by applying a Fourier transformation to the fit functions $g_i(\mathbf{r})$ and a summation over all the atoms in the unit cell of the silicon crystal. The resulting structure factors have been added to the structure factors obtained from the Hartree-Fock (non-relativistic) C^3P wavefunction from Clementi (1965). These structure factors for free atoms have been calculated by Dawson & Willis (1967) (see also Cummings & Hart, 1988).

Results and discussion

Deformation density

If the electron density distribution in the central part of an Si cluster remains unchanged when the cluster size is increased, it is assumed to be a representation of the density in the silicon crystal. Consequently, the total charge assigned to an Si atom by Hirshfeld partitioning should be zero. In Fig. 1 the deformation density $\Delta\rho$ along the axis between two neighboring Si atoms is shown for different silicon clusters. For the Si_8H_{18} cluster the two different Si-Si bonds in the cluster are

both given. The less-central Si—Si bond in the Si_8H_{18} cluster is almost equal to the bond in the Si_5H_{12} cluster as is expected. The maximum in $\Delta\rho$ at the midpoint between two Si atoms changes from $0.211 \text{ e } \text{\AA}^{-3}$ in Si_2H_6 to $0.195 \text{ e } \text{\AA}^{-3}$ in Si_5H_{12} and to $0.172 \text{ e } \text{\AA}^{-3}$ in the central bond of the Si_8H_{18} cluster. By adding an extra f function to the basis set of the Si atom these maximum deformation densities are increased slightly by about $0.01 \text{ e } \text{\AA}^{-3}$.

Since these maxima are not the same for different clusters, the clusters do not fully represent the bonds in the crystal. Nevertheless the values are close to the measured values in crystalline silicon: Spackman (1986) reported a value of $0.206 \text{ e } \text{\AA}^{-3}$ and Scheringer (1980) of $0.20 \text{ e } \text{\AA}^{-3}$. The measured value of Price, Maslen & Mair (1978), corrected by Spackman (1986), for the maximum in $\Delta\rho$ is $0.20 \text{ e } \text{\AA}^{-3}$. Saka & Kato (1986) reported a slightly larger value of $0.221 \text{ e } \text{\AA}^{-3}$ which is a direct consequence of their use of the 222 reflection from Fehlmann & Fujimoto (1975). The value reported by Yang & Coppens (1974) of $0.29 \text{ e } \text{\AA}^{-3}$, which has already been questioned several times, is not confirmed by our calculations.

One of the few theoretical calculations of $\Delta\rho(\mathbf{r})$ that has been published is by Wang & Klein (1981). They found a maximum in $\Delta\rho$ of $0.16 \text{ e } \text{\AA}^{-3}$ using a linear combination of Gaussian orbitals (LCO) method, a value which is smaller than the present one and than the experimental values.

While the maximum in $\Delta\rho$ changes with increasing cluster size, the total deformation charge for the central

Si atom decreases from 0.043 e in the Si_5H_{12} cluster to 0.028 e in the Si_8H_{18} cluster.

Possibly, much larger clusters are needed to obtain a fully converged deformation density and to remove density waves in the middle of the cluster. These density waves are the result of introducing a surface. They are observed by changing in the calculations the nuclear charge of the hydrogen atoms or the rather arbitrary, chosen Si—H distance. A nuclear charge on the atoms in the Si_5H_{12} cluster of $q = 0.9$ protons gives a maximum in $\Delta\rho$ of 0.185 compared to $0.195 \text{ e } \text{\AA}^{-3}$ using real H atoms, while with reducing the nuclear charge you would expect this density to increase because the H atoms attract less charge.

In Fig. 2 the deformation density of the Si_8H_{18} cluster is plotted for the plane containing the most central Si—Si bond (the vertical bond on the right-hand side of the figure). This figure shows the density with the nuclei at rest. The areas close to the nuclei contain large positive and negative features. The excess-charge distribution between two neighboring Si atoms is clearly seen to be elliptical in shape, elongated perpendicular to the bond. Experimental deformation density maps confirm this shape as well as the deficit in the region behind the nuclei. In the Si_8H_{18} cluster we find a deficit in density of $-0.094 \text{ e } \text{\AA}^{-3}$, 0.68 \AA behind the Si atoms on the interatomic axis. Saka & Kato (1986) and Spackman (1986) found values of -0.080 and $-0.090 \text{ e } \text{\AA}^{-3}$ for this deficit. The calculated value of

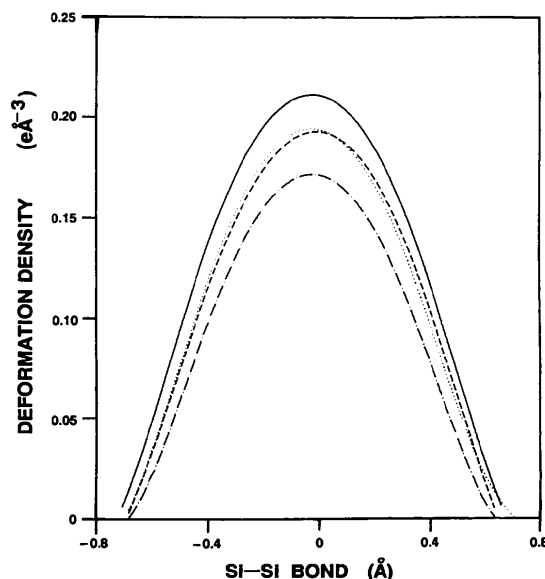


Fig. 1. Static deformation density along the Si—Si bonding, with Si atoms located at -1.175 and 1.175 \AA . Shown: Si_2H_6 (solid line); Si_5H_{12} (dotted line); Si_8H_{18} most central bond (dash-dotted line) and other bond (dashed line).

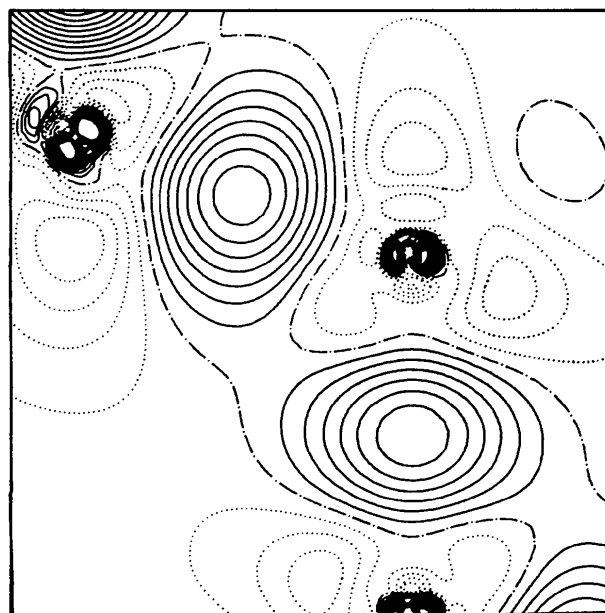


Fig. 2. Static deformation density of the Si_8H_{18} cluster in the plane containing three nearest neighbor Si atoms. The contour interval amounts to $0.025 \text{ e } \text{\AA}^{-3}$. Positive contours (electron excess) are drawn as solid lines, zero contours are dash-dotted and negative contours (electron deficiency) are dotted.

Wang & Klein (1981) of $-0.080 e \text{ \AA}^{-3}$ is also in good agreement with our calculation. The density distribution in the other bond of Fig. 2 is similar to the first one. Since it is closer to the surface of the cluster it is assumed to be slightly inferior in representing a crystalline Si—Si bond.

Structure factors

Structure factors F_{hkl} have been calculated starting from the Si_2H_6 , Si_5H_{12} and Si_8H_{18} clusters. When using the Si_5H_{12} cluster we extracted the central Si atom from the cluster with the help of the Hirshfeld partitioning method. Subsequently, the symmetry operations of the silicon crystal were applied to the atomic deformation density. Structure factors were calculated by adding the Hartree–Fock scattering factors of the isolated atoms to the Fourier transform of the deformation density of the constructed unit cell. For the 800, 844 and 880 reflections which were not reported by Dawson & Willis (1967), we took the scattering factors of Saka & Kato (1986).

For the Si_8H_{18} cluster we employed two methods. The first method (method I) is the same as described above, while in the second one (method II) we only used the most central Si—Si bond of the Si_8H_{18} cluster. For this method we assigned the deformation density of the central bond to all four tetrahedral bonds of the Si atom, before extracting the atom from the cluster. This last method (II) was also used for the Si_2H_6 cluster. In Table 2 the calculated structure factors normalized to single atoms are given based on the Si_8H_{18} cluster (method II). The normalized structure factors are defined as $f_{hkl} = F_{hkl}/Q$, where $Q = 8$ for even-order reflections and $Q = 4(2^{1/2})$ for odd-order reflections. In the second column the calculated f_{hkl} values for $T = 0 \text{ K}$ are listed. These calculated values are compared with the following sets of experimental data. Cummings & Hart (1988) analyzed data sets of Aldred & Hart (1973) and Teworte & Bonse (1984) and report mean values of structure factors. Recently, Saka & Kato (1986) remeasured an extended set of structure factors with increased accuracy ($\sigma \leq 0.1\%$). The values have been corrected for anomalous dispersion and the nucleus Thompson scattering, by Cummings & Hart (1988). In the following the corrected values will be used. Spackman (1986) analyzed combined data sets measured by several authors using both Fourier methods and a rigid pseudo-atom model. His values are corrected for anharmonicity, anomalous dispersion and harmonic thermal motion. His analysis yields a consistent averaged set of structure factors.

In the third, fourth and fifth columns of Table 2 the relative deviations from the theoretical values $\Delta f/f_{\text{calc}}$ ($\Delta f = f_{\text{obs}} - f_{\text{calc}}$), are listed for both sets of experimental data and for Spackman's set. We used $f(\text{mean})$ from Table 3 of Cummings & Hart (1988). We have

Table 2. Calculated normalized structure factors (static) and relative residuals of measured values from Saka & Kato (1986) (S&K), Cummings & Hart (1988) (C&H) and Spackman (1986) (Sp)

Values of $\Delta f/f_{\text{calc}}$ are given in $10^{-2} e$. $\Delta f = f_{\text{obs}} - f_{\text{calc}}$

<i>h k l</i>	f_{calc}	S&K	$\Delta f/f_{\text{calc}}$	
			C&H	Sp
1 1 1	10.6761	0.45	0.49	0.57
2 2 0	8.6571	-0.03	-0.01	0.02
3 1 1	8.0374	-0.19	-0.20	-0.17
4 0 0	7.4636	-0.14	-0.18	-0.20
3 3 1	7.2342	0.20	0.19	0.23
4 2 2	6.7171	-0.05	0.00	0.03
3 3 3	6.4231	-0.02	0.08	0.03
5 1 1	6.4551	-0.18	-0.24	-0.16
4 4 0	6.0575	-0.17	-0.16	-0.11
4 4 4	4.9839	-0.15	-0.06	-0.02
5 5 1	4.8129	-0.02	-0.08	-0.02
6 4 2	4.5533	-0.04	0.07	0.10
8 0 0	4.1839	0.01	-0.14	-0.14
6 6 0	3.8657	-0.05	0.06	0.19
5 5 5	3.7555	0.10	0.17	0.55
8 4 4	3.1433	0.13	-0.20	0.15
8 8 0	2.5350	-0.04	0.01	0.43
R factor (%)		0.14	0.16	0.18

reduced the values in the third and fourth columns to a hypothetical situation in which the atoms are considered to be static, by dividing by the Debye–Waller factor for isotropic harmonic vibrations: $\exp[-B(h^2+k^2+l^2)/4a_0^2]$ (a_0 is the unit-cell dimension). The temperature-dependent factor B is obtained by a least-squares fit of the experimental data with our calculated values.

It can be seen that the relative deviations between the calculated and observed structure factors are small, with the largest value for the 111 reflection. The isotropic B value obtained by the least-squares fit with the measured factors of Saka & Kato (1986) and of Cummings & Hart (1988) is $0.464 (1) \text{ \AA}^2$, which is in excellent agreement with 0.469 \AA^2 of Price, Maslen & Mair (1978), 0.461 \AA^2 of Aldred & Hart (1973) and 0.463 \AA^2 of Spackman (1986).

For a quantitative comparison between our calculations and the experiments, R factors have been calculated. The unweighted R factor is defined as

$$R = \frac{\sum |f_{\text{calc}}| - |f_{\text{obs}}|}{\sum |f_{\text{obs}}|}$$

which is almost equal to the R factor based on F_{hkl} instead of f_{hkl} . At the bottom of Table 2 the R factors corresponding with the sets of experimental data are listed. Table 3 shows the R factors obtained by a least-squares fit of our calculated values of Table 2, with the various data sets listed by Cummings & Hart (1988). Only f factors common to all sets are used. We notice the high quality of Saka & Kato's (1986) data. In the following these data will be used for comparison with the results of our calculations, listed in Table 4.

Table 3. Calculated unweighted (static) R factors ($R \times 100$) for the various sets of structure factors reported in Table 3 of Cummings & Hart (1988)

The values are based on structure factors appearing in all sets.

	R factors
Teworte & Bonse (1984) (Ag)	0.22
Teworte & Bonse (1984) (Mo)	0.20
Saka & Kato (1986)	0.18
Aldred & Hart (1973) (Ag)	0.24
Aldred & Hart (1973) (Mo)	0.27

Table 4. Unweighted R factors ($R \times 100$), comparing different cluster calculations with experimental results of Saka & Kato (1986)

Reference	without $\Delta\rho$	Saka & Kato (1986)
Si ₂ H ₆	method II	0.54
Si ₃ H ₁₂	normal basis	0.11
Si ₃ H ₁₂	extra f function	0.08
Si ₈ H ₁₈	method I	0.07
Si ₈ H ₁₈	method II	0.11
Si ₈ H ₁₈	method II	0.14

In this table the values based on the Si₂H₆ cluster are calculated with method II, while for the Si₃H₁₂ cluster two values are given. The difference between the two values is that for the second an extra f function (Cartesian STO with an exponent of 1.35) was used in the basis set of the Si atom. The Si₈H₁₈ cluster is the basis for the last two rows, calculated with methods I and II respectively. Comparison with a reference value, where f_{calc} is based solely on the Hartree-Fock atoms, shows the improvement in describing the electron density distribution: the discrepancy is reduced by a factor of four or more. Further, it appears that the structure factors obtained for the Si₂H₆ and Si₃H₁₂ clusters are slightly better than those for the Si₈H₁₈ cluster, which is the opposite of what would be expected. The smallest R factor is 0.07%, for the Si₃H₁₂ cluster with an extra f function in the basis set. There is only a small difference in R factors between the two different methods used for calculating the F_{hkl} 's of the Si₈H₁₈ cluster. The differences in the density distribution in the different bonding regions of an Si atom in the Si₈H₁₈ cluster have apparently little influence on the F_{hkl} 's.

Spackman (1986) lists in his paper the R factors corresponding to various theoretical calculations like those from Yin & Cohen (1982) and Stukel & Euwema (1970). Those R factors vary between 0.35 and 1.49%, all much larger than the values we have calculated. Comparison of Yin & Cohen's (1982) data with our values confirmed Spackman's (1986) conclusion that a systematic error occurs in the spherical part of the electron density distribution. Reflections with the same scattering angle, where the same error is made, seem to follow the pattern observed in our calculations.

Table 5. Room temperature values ($T = 293$ K) of the atomic structure factors from the 222, 442 and 622 reflections

		f_{222}	f_{442}	f_{622}
Si ₂ H ₆	method II	0.197	0.0114	0.00074
Si ₃ H ₁₂	normal basis	0.160	0.0084	0.00018
Si ₃ H ₁₂	extra f function	0.167	0.0102	0.00060
Si ₈ H ₁₈	method I	0.152	0.0082	0.00031
Si ₈ H ₁₈	method II	0.143	0.0078	0.00016

Finally, we discuss some forbidden reflections in silicon. The most important of these is the 222 reflection, which strongly contributes to the bonding density [about $0.07 \text{ e } \text{\AA}^{-3}$ to the peak of the dynamic difference density, according to Scheringer (1980)]. The results of our calculations are listed in Table 5. The reported values of $f_{222}(T = 293 \text{ K})$ from different experiments vary from 0.11 to 0.223 e [see Alkire, Yelon & Schneider (1982), Table 2]. The two more recent measurements in this table are from Alkire, Yelon & Schneider (1982) who determined with γ -rays a value of $0.182(1) \text{ e}$ for $f_{222}(T = 293 \text{ K})$, while Fehlmann & Fujimoto (1975) measured a larger value of $0.206(4) \text{ e}$. Saka & Kato (1986) used this larger value in their calculation of the density, resulting in a rather large value for the maximum of the deformation density. Both these values are almost equal to the present value based on the Si₂H₆ cluster and somewhat larger than the values corresponding to the other clusters. This is in agreement with the deviations of the maximum in the deformation density we found for the different clusters. Using method I for the Si₈H₁₈ cluster, $f_{222}(T = 293 \text{ K}) = 0.152 \text{ e}$, larger than with method II. This is probably caused by the asymmetry of the Si atom in this cluster, for which this reflection is very sensitive.

The 442 and 622 reflections are much weaker in silicon. The values we found for the 442 reflection in the Si₈H₁₈ cluster are in excellent agreement with the experimental value of Tischler & Batterman (1984) of $0.0079(4) \text{ e}$. Using the Si₂H₆ cluster gives a somewhat larger value. We found large differences among the clusters for the very weak 622 reflection. The values for the Si₈H₁₈ cluster are smaller than $f_{622}(T = 293 \text{ K}) = 0.00058(25) \text{ e}$ reported by Tischler & Batterman (1984). The Si₂H₆ cluster also gives this reflection the largest value, but within experimental accuracy.

We arrive at the conclusion that HFS-LCAO calculations on silicon clusters yield an excellent representation of the electron density distribution in the silicon crystal as witnessed by:

(i) The maximum deformation density in the bonding region is $0.211 \text{ e } \text{\AA}^{-3}$ calculated in the Si₂H₆ cluster, $0.195 \text{ e } \text{\AA}^{-3}$ in the Si₃H₁₂ cluster and $0.172 \text{ e } \text{\AA}^{-3}$ in the Si₈H₁₈ cluster, all close to the experimental value of $0.21 \text{ e } \text{\AA}^{-3}$. The deficit behind the Si atoms is in good agreement with experimental values (-0.09 versus $-0.08 \text{ e } \text{\AA}^{-3}$).

(ii) The calculated structure factors are in better agreement with experiments than other theoretical calculations as shown by the very small R factors obtained (using no, or only one, fitting parameter) varying between 0.07 and 0.14%, compared with a smallest value of 0.35% in other calculations. The experimental results of Saka & Kato (1986) are seen to be better than the older ones of Aldred & Hart (1973).

(iii) The temperature factor B fitting our calculations to the measurements of Saka & Kato (1986) and with Cummings & Hart (1988) is 0.464 \AA^2 , in excellent agreement with earlier reported values.

The agreement with experiment deteriorates with smaller cluster size, a phenomenon which possibly can only be overcome by using much larger clusters to reduce observed charge density waves inside the cluster.

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Coupling of Ferroelasticity to Ferroelectricity in $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ and the Structure at 295 K

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Abstract

$\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$, $M_r = 905.485$, monoclinic $P2$ but refined in $I2$, $a = 7.3597$ (7), $b = 10.6342$ (15), $c = 7.3618$ (10) \AA , $\beta = 90.77$ (2)°, $V = 576.1$ (2) \AA^3 , $Z = 2$, $D_m = 5.1$ (1) (by flotation), $D_x = 5.219$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71073$ \AA , $\mu = 308.3$ cm^{-1} , $F(000) = 788$, $T = 295$ K, $R = 0.042$ for 1939 symmetry-independent reflections with $F_m^2 > 3\sigma(F_m^2)$. Refinement in $P2$ was not feasible owing to the small number of weak reflections that violated the body-centered condition. Relationships among the atomic coordinates show that

the a and c axes are ferroelastically interchangeable, with the c -axis direction inverted, as the sense of the polar b axis is reversed ferroelectrically. The spontaneous polarization (P_s) is hence structurally coupled directly to the spontaneous strain (e_s). The largest total atomic displacement as P_s is reversed and e_s is reoriented is about 0.73 \AA , by an O,F anion. The largest polar displacement by a W atom within its octahedron of anions that results in zero polarization is about 0.19 \AA , corresponding to a predicted transition temperature of 710 K as compared with a measured temperature of 800 (10) K. Each of the three independent W atoms occupies a distorted octahedron, with average W–O,F distance of 1.90 (5) \AA . The O^{2-} and F^- anions are randomly distributed among the eight

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