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Variation in $d(T\text{—O})$, $d(T\cdots T)$ and $\angle TOT$ in Silica and Silicate Minerals, Phosphates and Aluminates

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Abstract

The interdependences between tetrahedral $d(T\text{—O})$ bond lengths, nonbonded $d(T\cdots T)$ separations and TOT angles (T = Al, Si, P) are examined by regression analysis. The dependence between $d(T\cdots T)$ and $\angle TOT$ improves in the sequence P, Si and Al while the $d(T\text{—O})$ on $\angle TOT$ dependence deteriorates. A continuous range of $d(\text{Si}\cdots\text{Si})$ values observed for silicates, siloxanes and silicides between bonded and proposed nonbonded separations suggests that a 'hard-sphere' nonbonded radius for Si may not be realized in solids.

Introduction

In the last ten years there have been several studies devoted to understanding variations in Si—O bond length, $d(\text{Si—O})$, nonbonded Si$\cdots$Si separations, $d(\text{Si}\cdots\text{Si})$, and SiOSi angles, $\angle$SiOSi, in the silica polymorphs. However, the small variation in $d(\text{Si—O})$

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and the paucity of accurate data for these minerals have made it difficult to establish an unequivocal correlation between d(Si–O) and ∠SiOSi (Brown, Gibbs & Ribbe, 1969; Baur, 1971; Taylor, 1972; Gibbs, Hamil, Louisnathan, Bartell & Yow, 1972; Gibbs, Prewitt & Baldwin, 1977; Baur, 1977). The near constancy of ∠SiOSi in low quartz and low cristobalite (144°) and silica glass (147°) along with the suggestion that the variance in d(Si···Si) is small have led O'Keeffe & Hyde (1976) and Glidewell (1977) to assert that angle variation may be limited by Si···Si nonbonded contacts. Furthermore, in a combined analysis of silica minerals and silicates exhibiting a wide range of angles, O'Keeffe & Hyde (1978) observed that d(Si–O) correlates with ∠SiOSi for angles less than 145° but that it is independent of angle when ∠SiOSi is greater than 145°. On the other hand, semi-empirical molecular orbital (MO) calculations predict that the d(Si–O) on −sec ∠SiOSi correlation should obtain over the entire range of observed angles with shorter bonds involving wider ∠SiOSi (Gibbs *et al.*, 1972; Tossell & Gibbs, 1978; Meagher, Tossell & Gibbs, 1978).

Recently, Konnert & Appleman (1978) published the results of a careful structure analysis of low tridymite that provides 320 individual Si–O distances with e.s.d.'s of 0·005 Å. These data and accurate data obtained for low quartz (Le Page & Donnay, 1976), low cristobalite (Dollase, 1965) and coesite (Gibbs *et al.*, 1977) constitute an excellent data set with which to test these concepts. Moreover, because the bond-number sum to each O in the silica polymorphs is exactly 2·0, these minerals are ideally suited for studying d(Si–O), d(Si···Si) and ∠SiOSi interdependence to gain further insight into the role played by Si···Si nonbonded interactions. Similar interdependence will be examined for the silicates in general as well as for aluminates and phosphates.

Silica polymorphs and silicates

To learn whether the Si–O bond lengths in the four silica polymorphs correlate linearly with −sec ∠SiOSi, a linear-regression equation was fitted to the data in Fig. 1 and the null hypothesis, H_0, tested that the slope, b, of the line might be zero. Since the statistics obtained in the regression analysis (Table 1) show that the hypothesis can be rejected only at the 99·9% level, we conclude that a correlation obtains between d(Si–O) and −sec ∠SiOSi for the silica minerals. A regression analysis was also calculated to learn whether d(Si–O) is independent of ∠SiOSi for angles wider than 145°. The resulting line is statistically identical to that calculated for all the data and to that calculated for data involving ∠SiOSi less than 145° (Table 1). Moreover, the H_0 that the slope is zero can be rejected for both smaller data sets at the 99·9% level. We conclude, therefore, despite the small range of bond lengths exhibited by the silica polymorphs, that d(Si–O)

Table 1. *Linear-regression analysis*

b is the slope and a the intercept of the regression equation; N is the number of data in the sample and r the correlation coefficient; $|t|$, Student's statistic $= b/\hat{\sigma}(b)$ where $\hat{\sigma}(b)$ is the e.s.d. of b.

Dependent variable	Independent variable	N	b	a	r	$\lvert t\rvert$
Silica polymorphs						
d(Si–O)	−sec∠SiOSi (137° ≤ ∠SiOSi ≤ 180°)	332	0·068	1·526	0·74	20·0
d(Si–O)	−sec∠SiOSi (∠SiOSi ≥ 145°)	220	0·070	1·524	0·66	13·0
d(Si–O)	−sec∠SiOSi (∠SiOSi < 145°)	112	0·069	1·525	0·39	5·9
log 2⟨d(Si–O)⟩	logsin($\frac{1}{2}$∠SiOSi) (137° ≤ ∠SiOSi ≤ 180°)	161	−0·212	0·504	0·84	13·0
log d(Si···Si)	logsin($\frac{1}{2}$∠SiOSi) (137° ≤ ∠SiOSi ≤ 180°)	161	0·808	0·503	0·98	55·0
⟨d(Si–O)⟩	d(Si···Si)	161	−0·121	1·982	0·74	14·0
Silicates						
d(Si–O)	−sec∠SiOSi (120° ≤ ∠SiOSi ≤ 180°)	174	0·080	1·530	0·73	14·0
d(Si–O)	−sec∠SiOSi (∠SiOSi ≥ 145°)	62	0·058	1·554	0·28	2·2
d(Si–O)	−sec∠SiOSi (∠SiOSi < 145°)	112	0·084	1·525	0·68	9·0
log 2⟨d(Si–O)⟩	logsin($\frac{1}{2}$∠SiOSi)	87	−0·312	0·507	0·79	9·0
log d(Si···Si)	logsin($\frac{1}{2}$∠SiOSi)	87	−0·809	0·510	0·93	23·0
⟨d(Si–O)⟩	d(Si···Si)	87	−0·118	2·000	0·42	4·0
Phosphates and aluminates						
log 2⟨d(P–O)⟩	logsin($\frac{1}{2}$∠POP)	76	−0·341	0·493	0·85	14·0
log d(P···P)	logsin($\frac{1}{2}$∠POP)	76	0·723	0·495	0·95	25·0
⟨d(P–O)⟩	d(P···P)	76	−0·202	2·202	0·65	7·0
log 2⟨d(Al–O)⟩	logsin($\frac{1}{2}$∠AlOAl)	8	−0·010	0·546	0·14	0·4
log d(Al···Al)	logsin($\frac{1}{2}$∠AlOAl)	8	−1·040	0·549	0·98	12·0
⟨d(Al–O)⟩	d(Al···Al)	8	0·000	1·757	0·00	0·0

correlates linearly with −sec ∠SiOSi over the entire range of observed angles with shorter bonds involving wider ∠SiOSi.

Similar regression analyses completed for 174 *d*(Si—O) data from 56 carefully refined silicates (other than silica polymorphs) show that the *d*(Si—O) *vs* −sec ∠SiOSi correlation is highly significant for all the data and for the data with angles less than 145°. However, as discovered by O'Keeffe & Hyde (1978), the correlation for data with ∠SiOSi wider than 145° is much more poorly developed (Table 1). Nevertheless H_0 for these data can only be rejected at the 95% confidence level.

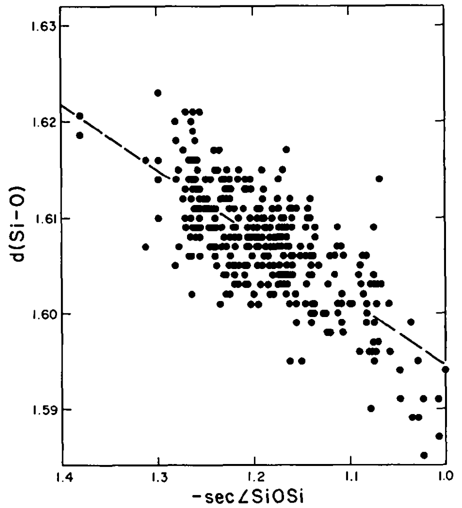

Fig. 1. Si—O bond length, *d*(Si—O), *vs* −sec ∠SiOSi plot for the silica polymorphs low tridymite (Konnert & Appleman, 1978), low quartz (Le Page & Donnay, 1976) and coesite (Gibbs *et al.*, 1977). The e.s.d.'s of *d*(Si—O) are 0·005 Å or less. The estimated regression line (dashed) fit to these data is statistically identical to that calculated in a similar regression analysis of the coesite data [see Fig. 3(*b*) of Gibbs *et al.* (1977)].

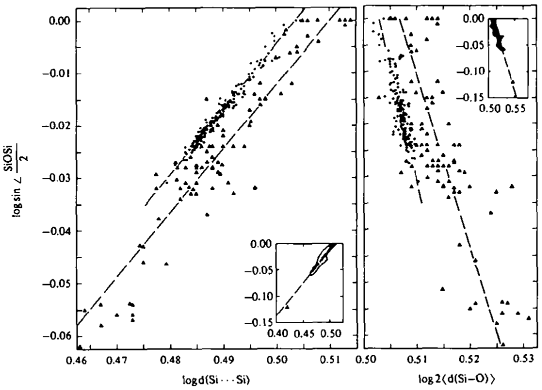

Fig. 2. Scatter diagrams of log sin ($\frac{1}{2}$∠SiOSi) *vs* log *d*(Si···Si) and log 2⟨*d*(Si—O)⟩ for the silica polymorphs (plotted as solid circles) and for the silicates (plotted as solid triangles). The data for stishovite (plotted as triangles in the insets) fall close to the extrapolated line for the silicate data (outlined by shaped regions).

As shorter Si—O bonds tend to involve wider angles, we may expect, as observed by Brown, Gibbs & Ribbe (1969) and Baur (1978), that the size of a silicate tetrahedron will also depend on ∠SiOSi with larger tetrahedra tending to involve narrower angles. In addition, Baur (1978) has shown that the size of a silicate tetrahedron may depend on the number of bridging O atoms, NC, and their mean coordination numbers, CNM. Nevertheless, despite the variation of NC and CNM in the silicates and their invariance in the silica polymorphs, the slopes of the regression lines [*d*(Si—O) *vs* −sec ∠SiOSi] calculated for these two mineral groups are statistically identical (Table 1).

From a study of Si···Si separations in the silica polymorphs, Glidewell (1977) has concluded, despite the wide range in SiOSi angle (137 to 180°), that the variance in *d*(Si···Si) is very small. If true, then the average length, ⟨*d*(Si—O)⟩, of the two bonds comprising the sides of a SiOSi angle can be approximated by the linear equation

$$\log 2\langle d(\text{Si—O})\rangle = \log d(\text{Si}\cdots\text{Si}) - \log\sin(\tfrac{1}{2}\angle\text{SiOSi}). \qquad (1)$$

If we adopt the Si···Si separation of 3·19 Å involved in the straight angle in coesite (Gibbs *et al.*, 1977), equation (1) becomes

$$\log 2\langle d(\text{Si—O})\rangle = 0{\cdot}504 + b\log\sin(\tfrac{1}{2}\angle\text{SiOSi}),$$

where the slope *b* equals −1·0. A regression analysis of log 2⟨*d*(Si—O)⟩ *vs* log sin ($\frac{1}{2}$∠SiOSi) for the silica polymorphs (Fig. 2) indicates that a well developed correlation (r = 0·84) obtains with an intercept of 0·503 and a slope of −0·212. The intercept is close to the expected value but the slope is significantly less than −1·0, indicating that the variance in *d*(Si···Si) is appreciably larger than that in *d*(Si—O). A frequency distribution of *d*(Si—O) and *d*(Si···Si) for the silica polymorphs (Fig. 3) confirms this indication and shows

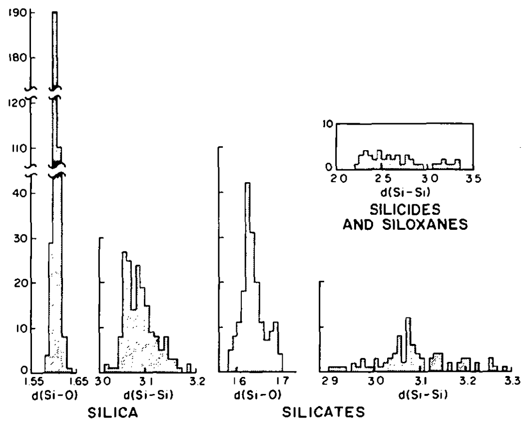

Fig. 3. Frequency distributions of *d*(Si—O) for silica polymorphs and silicates and *d*(Si···Si) for silica polymorphs, silicates, silicides and siloxanes.

that the range in $d(\text{Si}\cdots\text{Si})$ from 3·02 to 3·19 Å is about four times that (1·58 to 1·62 Å) in $d(\text{Si—O})$. Similar results apply to the silicates in general, despite a significantly larger range in the observed bond lengths from 1·58 to 1·70 Å (Fig. 3).

On the other hand, if we assume that the variance in $\langle d(\text{Si—O})\rangle$ is relatively small, then the Si···Si separation involved in a SiOSi linkage can be approximated by the linear equation

$$\log d(\text{Si}\cdots\text{Si}) = \log 2\langle d(\text{Si—O})\rangle + b \log \sin(\tfrac{1}{2}\angle\text{SiOSi}), \qquad (2)$$

where $b = +1\cdot0$. Because the correlation between $\log d(\text{Si}\cdots\text{Si})$ and $\log\sin(\frac{1}{2}\angle\text{SiOSi})$ (Fig. 2) is very well developed ($r = 0\cdot98$) and because the slope (0·81) of the regression equation is close to the expected slope, it is clear that $d(\text{Si}\cdots\text{Si})$ varies in a regular way with angle, with longer Si···Si separations involving wider ∠SiOSi. Moreover, because $d(\text{Si—O})$ also varies in a regular way with shorter bonds involving wider angles, the data suggest, as asserted by O'Keeffe & Hyde (1978) and Tossell & Gibbs (1978), that SiOSi angles result as a compromise of Si—O and Si···Si interactions.

When equations (1) and (2) were fitted to the silicate data plotted in Fig. 2, the slopes of the resulting lines were found to be statistically identical to those calculated for the silica polymorphs (Table 1). This result indicates that the dependence of $d(\text{Si}\cdots\text{Si})$ and $d(\text{Si—O})$ on ∠SiOSi is nearly the same for silicate and silica minerals alike. On the other hand, the intercepts of the lines are significantly larger than those fitted to the silica data, indicating, for a given SiOSi angle, that $d(\text{Si—O})$ and $d(\text{Si}\cdots\text{Si})$ values are about 0·02 Å larger, on the average, than corresponding values recorded for the silica polymorphs.

If nonbonded Si···Si contacts control the lower limit of the SiOSi angle (O'Keeffe & Hyde, 1976; Glidewell, 1977; Baur, 1977), then one might expect the trends in Fig. 2 to depart from the straight line at some lower limit of $\log d(\text{Si}\cdots\text{Si})$. However, the linearity of the data appears to obtain to a $\log d(\text{Si}\cdots\text{Si})$ value of 0·463 which corresponds to a $d(\text{Si}\cdots\text{Si})$ of 2·904 Å, a value significantly less than the proposed lower limit (3·0–3·1 Å). Moreover, although O'Keeffe & Hyde (1978) have suggested that the concept of nonbonded Si···Si contacts should not be applied to situations in which Si atoms are bonded to more than one common oxygen, it is interesting to note that the data for stishovite [$d(\text{Si}\cdots\text{Si}) = 2\cdot66$ Å; Baur & Khan, 1971] fall close to the extrapolated line for the silicate data (Fig. 2, insets). This result is consistent with the observations of Bürgi (1975), who has argued that nonbonded interactions change continuously into bonded interactions without showing a sharp break. In fact, $d(\text{Si}\cdots\text{Si})$ values observed in 42 silicides and siloxanes span the entire range of distances between 2·2 Å (silicon metal) and 3·3 Å (Fig. 3, inset), suggesting that the concept of a particular 'hard-sphere' nonbonded radius for silicon may not be realized in solids.

Phosphates and aluminates

The results of regression analyses completed for the phosphate and aluminate data plotted in Figs. 4 and 5, respectively, are given in Table 1. The correlations between $\log d(\text{P}\cdots\text{P})$ *vs* $\log\sin(\frac{1}{2}\text{POP})$ and $\log d(\text{Al}\cdots\text{Al})$ *vs* $\log\sin(\frac{1}{2}\text{AlOAl})$ are well developed ($r \sim 0\cdot95$). Both of these results are consistent with the trends observed for the silicates in suggesting that the variance in $d(T\cdots T)$ is appreciably larger than that in $d(T\text{—O})$. The correlation between $\log 2\langle d(\text{P—O})\rangle$ and $\log\sin(\frac{1}{2}\text{POP})$ is also well developed ($r = 0\cdot85$), with shorter bonds involving wider angles. On the other hand, the correlation between $\log 2\langle d(\text{Al—O})\rangle$ and $\log\sin(\frac{1}{2}\text{AlOAl})$ is indicated to be nonexistent. However, because of the paucity of data, the regression results for the aluminates must be accepted with reservation.

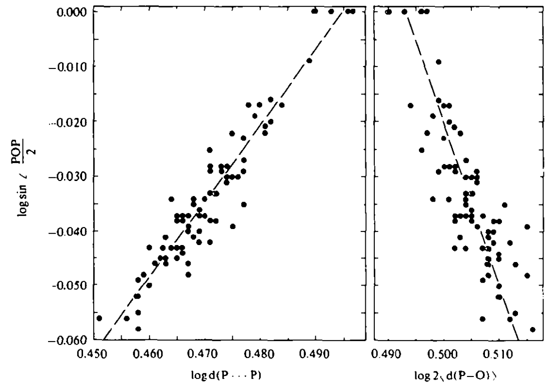

Fig. 4. Scatter diagrams of $\log\sin(\frac{1}{2}\angle\text{POP})$ *vs* $\log d(\text{P}\cdots\text{P})$ and $\log 2\langle d(\text{P—O})\rangle$ for phosphates.

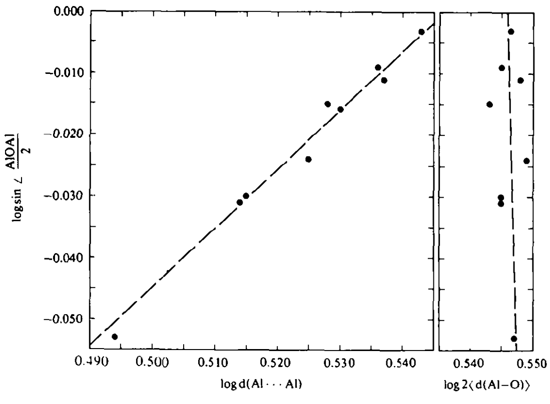

Fig. 5. Scatter diagrams of $\log\sin(\frac{1}{2}\angle\text{AlOAl})$ *vs* $\log d(\text{Al}\cdots\text{Al})$ and $\log 2\langle d(\text{Al—O})\rangle$ for aluminates.

In a comparative study of O···O nonbonded repulsions in third-row tetrahedral oxyanions, McDonald & Cruickshank (1967) have concluded from scatter diagrams of ⟨*d*(*T*—O)⟩ *vs* *d*(O···O) that O···O nonbonded repulsions become progressively more important in the sequence of ions SiO$_4^{4-}$, PO$_4^{3-}$, and SO$_4^{2-}$. To gain further insight into *T*···*T* nonbonded repulsions in *TOT* linkages in the aluminates, silicates and phosphates studied here, a similar set of scatter diagrams of ⟨*d*(*T*—O)⟩ *vs* *d*(*T*···*T*) were prepared (Fig. 6). On the one hand, if *T*···*T* nonbonded repulsions require *d*(*T*···*T*) to be constant, then data points would lie on vertical lines characteristic of the ion. On the other hand, if *T*···*T* nonbonded repulsions are negligible, then the data for an ion would lie on a horizontal line. This latter situation appears to be realized by the aluminate data. Regression lines fitted to the data for the aluminates, the silica polymorphs, the silicates and phosphates (Table 1) show that the slopes increase in the sequence from 0·0 for the aluminates, —0·12 for the silicates and silica polymorphs and —0·20 for the phosphates. Although this result suggests that *T*···*T* nonbonded interactions become progressively more important in the sequence AlO$_4^{5-}$ to PO$_4^{3-}$, it also conforms with semi-empirical MO theory (Tossell & Gibbs, 1977) which predicts that the *d*(*T*—O) on —sec ∠*TOT* dependence should improve in the same sequence. However, it is possible that the improved dependence of ⟨*d*(*T*—O)⟩ on nonbonded *T*···*T* and O···O interactions is merely a function of the decrease in the size of the tetrahedral ion (Hill, Gibbs, Craig, Ross & Williams, 1978).

Conclusions

(1) The Si—O bond lengths in accurately refined silica polymorphs correlate with —sec ∠SiOSi, with shorter bonds involving wider ∠SiOSi. This correlation continues to hold for bond-length data involving angles wider than 145° where proposed Si···Si contacts are not realized.

(2) The dependence of *d*(Si—O) on ∠SiOSi for the silica polymorphs and the silicate minerals is statistically identical. However, for a given ∠SiOSi, Si—O bond lengths in silicates are, on the average, ~0·02 Å longer than those in the silica polymorphs. Hence, the cations other than silicon in silicates have the effect of lengthening Si—O bonds for a given ∠SiOSi but they do not appear to affect the *d*(Si—O) on ∠SiOSi dependence significantly.

(3) Nonbonded Si···Si separations vary in a regular way with SiOSi angle below accepted Si···Si nonbonded contacts. In fact, *d*(Si···Si) values recorded in the range between nonbonded and bonded separations indicate that Si···Si nonbonded interactions change continuously into bonded ones instead of showing a sharp discontinuity.

(4) Nonbonded *T*···*T* interactions like O···O interactions appear to become progressively more important in the series of ions AlO$_4^{5-}$, SiO$_4^{4-}$ and PO$_4^{3-}$.

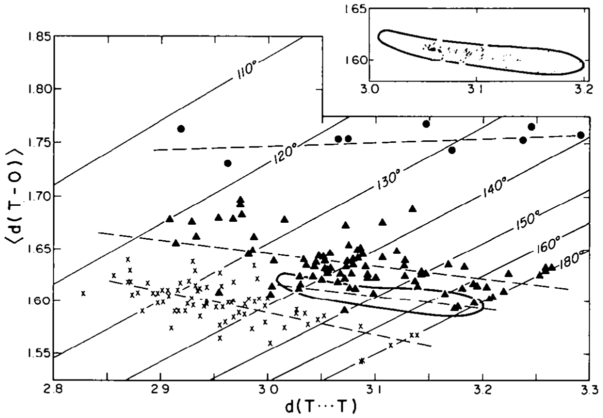

Fig. 6. Scatter diagram of ⟨*d*(*T*—O)⟩, the mean bond length to the bridging O atom in a *TOT* linkage, *vs* *d*(*T*···*T*) for aluminates (plotted as large solid circles), silicates (solid triangles), and phosphates (crosses). The data for the silica polymorphs have been plotted as small solid circles in the inset and occur within the outlined area below the regression line for the silicates.

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Redetermination of the Crystal Structure of $Cr_{12}P_7$

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Abstract

Crystals of $Cr_{12}P_7$ are hexagonal, space group $P6_3/m$, with $a = 8{\cdot}981$ (2) and $c = 3{\cdot}313$ (2) Å. The material is isotypic with Th_7S_{12}. All atoms lie on mirror planes. Chromium atoms are coordinated by either five phosphorus atoms in a distorted square pyramidal arrangement, or by four in a distorted tetrahedral arrangement. One phosphorus atom is disordered between two positions, and half of the chromium atoms exhibit disorder coupled to that of the phosphorus atoms. The average Cr—P distance in the part of the structure least affected by disorder is 2·392 Å. Extra reflections in the $hk0$ layer require a sevenfold larger superlattice with $\mathbf{A} = 2\mathbf{a} - \mathbf{b}$, $\mathbf{B} = \mathbf{a} + 3\mathbf{b}$, $\mathbf{C} = \mathbf{c}$.

Introduction

Several workers have reported structural data for the chromium phosphide of stoichiometry $Cr_{1.7}P$, but certain features have remained ambiguous. Lundström (Aronsson, Lundström & Rundqvist, 1965) indexed the diffraction pattern from powder samples on a hexagonal cell, and reported $a = 15{\cdot}552$, $c = 3{\cdot}319$ Å for a chromium-rich preparation, $a = 15{\cdot}536$, $c = 3{\cdot}313$ Å for a phosphorus-rich preparation. Later Lundström (1969) suggested that the compound has the anti-Th_7S_{12} structure (Zachariasen, 1949); this description presumably implies a smaller cell with $a = 15{\cdot}55/\sqrt{3} = 8{\cdot}98$ Å, space group $P6_3/m$, and disorder at least among some phosphorus atoms – all in analogy with Th_7S_{12}. Baurecht, Boller & Nowotny (1971) carried out a single-crystal photographic study leading to $a = 8{\cdot}977$, $c = 3{\cdot}316$ Å and a structure in space group $P\bar{6}$ that is essentially the anti-Th_7S_{12} type except that no disorder is present.

The availability of good single crystals prompted us to attempt to clarify the details and improve the accuracy of the structure by use of diffractometer data. In the course of this study the existence of a superlattice became evident.

Experimental

Shiny dark-brown plate-like crystals of composition $Cr_{1.7}P$ were grown by chemical vapor transport by Dr R. Madar in the laboratory of Professor A. Wold. Dr Madar also measured the density of the crystals by the method of Archimedes.

Preliminary photographic study confirmed the cell dimensions reported by Baurecht *et al.* (1971). However, systematic absences were noted for reflections $00l$ with l odd, reflections that they had not examined. The Laue symmetry was evidently $6/m$, so the possible space groups are $P6_3/m$ and $P6_3$; the former was shown to be correct by the structure determination. Furthermore, photographs showed a few weak superlattice reflections, all with $l = 0$ and conforming to $6/m$ symmetry. Baurecht *et al.* (1971) had looked for superlattice reflections [in an attempt to explain Lundström's original cell (Aronsson *et al.*, 1965)], but failed to find any from their crystals.

A crystal of approximate dimensions 0·04 × 0·13 × 0·44 mm was cut from a larger plate, mounted along c (the long axis of the specimen), and selected for intensity measurements on the basis of freedom from twinning and reasonably narrow mosaic spread (0·14°). Twelve reflections, scattered through reciprocal space, were carefully centered, and their angle settings were used to refine the cell dimensions by least-squares fitting. The crystal data are summarized below.

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