

informative approach is the study of diffuse scattering from disordered material. Information from ordered states is less informative because the requirements of the periodic structure limit the possible atomic arrangements.

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Rigid-Body Motion in Phosphorus Chalcogenides

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The thermal parameters of P_4S_5 , P_4S_7 , P_4S_{10} and P_4Se_5 have been analysed on the basis of the rigid-body hypothesis, using both Cruickshank's and Shomaker & Trueblood's methods. For these compounds, at least with the data at present available, the fit to the rigid-body model is only moderate, and there is no significant difference in the results of the two methods. Librational corrections to bond lengths have been calculated.

Introduction

Considerable interest has been shown over the last few years in analysing the thermal motion of molecules in crystals on the assumption that they are, to a reasonable approximation, moving as rigid bodies.

In his original paper, Cruickshank (1956) attempted to describe this motion in terms of two symmetric

tensors, T and ω , representing the mean-square translational vibrations of the mass centre and the mean-square angular oscillations (librations) respectively. The chief problem here is the choice of the centre of libration when this is not determined by symmetry, though in many cases a reasonable approximation may be the centre of mass.

Pawley (1963) and others attempted to solve this

problem by regarding the coordinates of the centre of libration as a further three adjustable parameters, although in many cases it was found difficult to obtain satisfactorily refined values.

However, both of these formulations have been shown to be incomplete by an elegant treatment of Schomaker & Trueblood (1968), who showed the need to introduce an additional tensor, *S*, which in general has eight independent components, and represents the average quadratic correlation of translation and libration. These authors show how the motion may most conveniently be pictured as three principal mean-square translations and three screw (helical) librations about three perpendicular non-intersecting axes.

The utility of these calculations lies principally in the librational corrections to bond lengths which may be made once the libration tensor is known.

This work

In the course of developing a program to perform these calculations on the Cambridge University Titan computer, the author has examined published and unpublished data on phosphorus chalcogenides, which, possessing cage-like structures, might be expected to approximate fairly well to the rigid-body model. In order not to interfere with established refinement programs, and in order to facilitate examination of published structures, the program fits the overall tensor components to the refined values of the anisotropic temperature factor components, rather than including them as parameters in the structure refinement [as suggested by Pawley (1964)].

The opportunity has been taken (*a*) to examine generally the applicability of the rigid-body hypothesis to these compounds, which contain elements heavier than most of those dealt with in previous analyses, (*b*) to examine the difference between the parameters obtained from a Cruickshank treatment, using the centre of mass as that of libration, and those from a Schomaker & Trueblood (ST) treatment, and to test whether the eight extra parameters fitted in the latter method produce a significantly better fit to the observed temperature factors, and (*c*) to evaluate the librational corrections to bond lengths.

Tetraphosphorus pentasulphide

This structure was re-refined with anisotropic temperature factors for all atoms by Vos, Olthof, van Bolhuis & Botterweg (1965). The results of the rigid-body analysis are given in Table 1. No estimated standard deviations in the temperature-factor components were given, so all components were given unit weights. The results appear generally reasonable, though the fit to the observed temperature factors is not very good. The estimated standard deviations (e.s.d.'s) show that the *L* tensor is not very well defined, and the *S* tensor even less so. The Cruickshank parameters are all

within 1 e.s.d. of the ST values, and in particular the *T* tensors are very similar. On examining the difference in fit of calculated to observed temperature factors, it is found that the ratio of the generalized *R* factors, R_G , is 1.138. Hamilton's *R* factor ratio test (Hamilton, 1965) shows that this difference is not significant at the 25% level. The librational corrections to bond lengths calculated by both methods are very similar and range from 0.004 to 0.008 Å, compared with the quoted e.s.d. in the bond lengths of 0.011 Å. It is clear that in this molecule there is no significant difference between the results obtained by the two methods.

Table 1. *Tetraphosphorus pentasulphide*

Centre of mass (crystal coordinates): 0.6460 0.1938 0.3924				
Cruickshank calculation about centre of mass				
Tensors w.r.t. original orthogonal axes with e.s.d.'s				
<i>L</i>	3.4 (2.8)	2.0 (2.8)	2.6 (2.9)	
		10.5 (3.7)	-3.0 (2.4)	
			12.6 (4.4)	
<i>T</i>	42 (4)	14 (3)	-18 (3)	
		27 (4)	-2 (3)	
			43 (3)	
Principal r.m.s. amplitudes				
<i>L</i> (deg)	1.35	3.13	3.85	
<i>T</i> (Å)	0.253	0.179	0.122	
Residuals				
Hamilton's $R_G=0.2027$				
R.m.s. deviation=0.0072 Å ²				
Schomaker & Trueblood calculation				
Original origin: centre of mass				
Tensors w.r.t. original orthogonal axes and origin with e.s.d.'s				
<i>L</i>	3.2 (2.8)	1.3 (3.0)	3.5 (3.1)	
		11.2 (3.8)	-4.2 (2.4)	
			12.7 (4.5)	
<i>T</i>	41 (4)	14 (3)	-17 (3)	
		27 (4)	-2 (3)	
			43 (3)	
<i>S</i>	0.06 (0.05)	-0.05 (0.05)	-0.06 (0.06)	
	-0.09 (0.05)	-0.06 (0.06)	-0.09 (0.06)	
	0.02 (0.06)	-0.07 (0.07)	0.00 (0.06)	
Origin (crystal coordinates) which gives symmetric <i>S</i> :				
0.6467 0.2198 0.4032				
Distance of this origin from centre of mass=0.292 Å				
Axis shifts (Å) and screw pitches (Å.deg ⁻¹)				
Axis	Shifts			
1		0.33	0.74	0.057
2	0.01		-0.11	-0.015
3	-0.01	-0.03		0.004
Principal r.m.s. amplitudes				
<i>L</i> (deg)	1.15	3.05	4.06	
<i>T</i> (Å)	0.249	0.178	0.126	
Residuals				
Hamilton's $R_G=0.1781$				
R.m.s. deviation=0.0064 Å ²				

Table 1 (*cont.*)

Librationally corrected bond lengths (Å)		
	Uncorrected	Corrected
P1-P2	2.261	2.270
P2-P3	2.236	2.242
P1-S1	2.129	2.133
P1-S4	2.171	2.177
P2-S2	2.073	2.077
P3-S3	2.082	2.086
P3-S4	2.090	2.096
P3-S5	1.937	1.942
P4-S1	2.102	2.108
P4-S2	2.145	2.153
P4-S3	2.113	2.119

Tetraphosphorus heptasulphide

This structure was re-refined with anisotropic temperature factors for all atoms, again by Vos *et al.* (1965). The results of rigid-body calculations by the two methods are presented in Table 2. The parameters are somewhat better defined than in the pentasulphide, and the fit to the observed temperature factors is better. There is, however, no significant difference between the Cruickshank tensors and the corresponding ST tensors, as indicated by the e.s.d.'s in the latter. The ratio of R_G 's is 1.171, and Hamilton's test shows this to be significant at the 5% level. The librational corrections range from 0.002 to 0.004 Å, that is about half the quoted e.s.d. in the bond lengths. Thus, although the better fit to the observed temperature factors provided by the ST treatment is possibly significant, there is little practical difference in the results.

Table 2. *Tetraphosphorus heptasulphide*

Centre of mass (crystal coordinates): 0.1783 0.3827 0.4000				
Cruickshank calculation about centre of mass				
Tensors w.r.t. original orthogonal axes with e.s.d.'s				
L	7.0	(1.7)	-1.8	(1.4)
			4.2	(1.6)
				3.8
T	34	(2)	0	(2)
			35	(2)
				30
Principal r.m.s. amplitudes				
$L(\text{deg})$	2.83		1.42	2.21
$T(\text{Å})$	0.186		0.162	0.194
Residuals				
Hamilton's $R_G=0.1682$				
R.m.s. deviation=0.0048 Å ²				

Schomaker & Trueblood calculation

Original origin: centre of mass				
Tensors w.r.t. original orthogonal axes and origin with e.s.d.'s				
L	6.2	(1.7)	-2.7	(1.5)
			3.3	(1.6)
				4.2
T	35	(2)	-1	(2)
			35	(2)
				31
S	0.07	(0.03)	0.01	(0.03)
	0.04	(0.03)	-0.11	(0.03)
	-0.04	(0.03)	-0.01	(0.03)

Table 2 (*cont.*)

Origin (crystal coordinates) which gives symmetric S :			
0.1903 0.3726 0.3771			
Distance of this origin from centre of mass=0.261 Å			
Axis shifts (Å) and screw pitches (Å.deg ⁻¹)			
Axis	Shifts		Pitch
1		0.32	-0.002
2	0.79		-0.052
3	-0.16	-0.53	0.014
Principal r.m.s. amplitudes			
$L(\text{deg})$	2.82	0.99	2.20
$T(\text{Å})$	0.155	0.173	0.192
Residuals			
Hamilton's $R_G=0.1436$			
R.m.s. deviation=0.0041 Å ²			

Librationally corrected bond lengths (Å)

	Uncorrected	Corrected
P1-P2	2.327	2.330
P1-S4	2.106	2.109
P1-S7	2.113	2.116
P2-S5	2.101	2.104
P2-S6	2.111	2.114
P3-S1	2.117	2.120
P3-S2	1.915	1.918
P3-S4	2.075	2.078
P3-S5	2.086	2.088
P4-S1	2.110	2.113
P4-S3	1.920	1.923
P4-S6	2.076	2.078
P4-S7	2.078	2.081

Tetraphosphorus decasulphide

This structure was re-refined by Vos *et al.* (1965), but in this case the atoms were permitted only isotropic temperature factors, and hence this molecule would not normally be considered for rigid-body analysis. However, since data were available, it was decided that it would be interesting, for comparative purposes, to see what results would be obtained by rewriting the temperature factors in anisotropic form and proceeding normally. The results are shown in Table 3. It is interesting that the tensors, including L, are at least as well defined as in the pentasulphide. As might be expected the T tensors are very nearly isotropic. There is no significant difference in the tensors calculated by the two methods, while the R_G ratio is 1.057, which is not significant even at the 50% level. The librational corrections are small (0.001 to 0.002 Å) compared with the quoted bond length e.s.d. (0.015 Å), and are therefore not given in detail in the Table.

Table 3. *Tetraphosphorus decasulphide*

Centre of mass (crystal coordinates): 0.1528 0.2579 -0.1840				
Cruickshank calculation about centre of mass				
Tensors w.r.t. original orthogonal axes with e.s.d.'s				
L	2.3	(0.8)	0.4	(0.6)
			2.4	(0.8)
				3.5
T	31	(2)	0	(1)
			31	(2)
				32
S	0.07	(0.03)	0.01	(0.03)
	0.04	(0.03)	-0.11	(0.03)
	-0.04	(0.03)	-0.01	(0.03)

Table 3 (*cont.*)

Principal r.m.s. amplitudes				
<i>L</i> (deg)	1.52	1.41	1.98	
<i>T</i> (Å)	0.176	0.175	0.179	
Residuals				
Hamilton's $R_G=0.1762$				
R.m.s. deviation = 0.0046 Å ²				
Schomaker & Trueblood calculation				
Original origin: centre of mass				
Tensors w.r.t. original orthogonal axes and origin with e.s.d.'s				
	2.7 (0.9)	-0.1 (0.8)	-0.3 (0.8)	
L		2.5 (0.9)	-0.9 (0.8)	
			3.2 (0.9)	
	31 (2)	0 (2)	0 (2)	
T		31 (2)	-1 (2)	
			32 (2)	
	0.01 (0.02)	0.02 (0.02)	-0.03 (0.02)	
S	-0.04 (0.02)	-0.01 (0.02)	0.02 (0.02)	
	0.02 (0.02)	0.00 (0.02)	0.00 (0.02)	
Origin (crystal coordinates) which gives symmetric <i>S</i> :				
0.1930 0.3200 -0.1234				
Distance of this origin from centre of mass = 0.723 Å				
Axis shifts (Å) and screw pitches (Å.deg ⁻¹)				
Axis	Shifts		Pitch	
1		0.23	-0.14	0.005
2	0.21		0.22	0.000
3	-0.10	-0.16		-0.003
Principal r.m.s. amplitudes				
<i>L</i> (deg)	1.64	1.33	1.96	
<i>T</i> (Å)	0.175	0.174	0.177	
Residuals				
Hamilton's $R_G=0.1667$				
R.m.s. deviation = 0.0043 Å ²				

Tetraphosphorus pentaselenide

This is a structure by Penney & Sheldrick (1971); the molecular skeleton is essentially the same as P₄S₅. All atoms were refined anisotropically and standard deviations were estimated for each temperature factor component. It was thus considered a suitable molecule for testing the effect of giving each component the theoretically optimum weight $1/\sigma^2$ in the least-squares procedure. This was in fact done, and the results are presented in Table 4. A calculation with unit weights throughout was also performed; the detailed results, except for the values of the residuals, are not given, but in general the tensor components were found to differ by up to 1 e.s.d. from those derived in the calculation with correct weights. However, the most important feature of the analysis is that in all cases one of the principal mean-square librational amplitudes takes on a physically impossible negative value. If this is significant then it implies that either the molecule deviates considerably from the rigid-body model, or the temperature factors are suffering from a systematic error. The former seems less likely, though it is conceivable that the disparity in atomic mass between phosphorus and selenium could have some unpre-

dictable effects. Pawley (1966) had similar difficulties with negative amplitudes when he was analysing the motion of some polyhedral boron compounds, and he noted that all were cases where only a small proportion of the reflexions within the limiting sphere had been observed, and the accuracy of the temperature factors had presumably suffered in consequence. This is not the case here, but another major source of error in temperature factors, namely absorption, may very well be important. The presence of selenium atoms causes absorption to be considerable (probably greater than in any of the compounds dealt with in published rigid-body calculations), whilst the plate-like habit of the crystals made it difficult to correct for it accurately. It seems highly plausible therefore that absorption is principally responsible for the unsatisfactory result of the calculations. It is nevertheless interesting that this molecule is the only one investigated in this work where the ST treatment gives a really significantly better fit to the observed temperature factors than the Cruickshank method: for the weighted calculation the R_G ratio was 1.569, significant at the 0.5% level, while when unit weights were used the ratio was 1.245, significant at the 2.5% level. The R_G 's were lower for the weighted calculations, as were the parameter e.s.d.'s - this would indicate that weighting by the method adopted improves the results, though of course in the circumstances discussed above, no definite conclusions are possible. For this reason no librational corrections are recorded.

Table 4. *Tetraphosphorus pentaselenide*

Centre of mass (crystal coordinates): 0.8398 0.4192 0.4894				
Except where stated, results are those from calculations where each temperature factor component has been weighted according to their e.s.d.'s, <i>viz.</i> $w=1/\sigma^2$.				
Cruickshank calculation about centre of mass				
Tensors w.r.t. original orthogonal axes with e.s.d.'s				
	5.4 (2.0)	-5.3 (1.7)	1.3 (1.0)	
L		8.7 (2.4)	3.5 (1.3)	
			2.3 (2.3)	
	30 (3)	1 (2)	0 (2)	
T		13 (2)	1 (2)	
			25 (3)	
Principal r.m.s. amplitudes				
<i>L</i> (deg) (imaginary)*		3.61	2.17	
<i>T</i> (Å)	0.159	0.112	0.173	
* Mean-square amplitude = -1.39 deg ²				
Residuals				
Hamilton's $R_G=0.2257$				
R.m.s. deviation = 0.0052 Å ²				
Residuals in calculation using <i>unit weights</i>				
Hamilton's $R_G=0.2327$				
R.m.s. deviation = 0.0050 Å ²				
Schomaker & Trueblood calculation				
Original origin: centre of mass				
Tensors w.r.t. original orthogonal axes and origin with e.s.d.'s				

Table 4 (cont.)

L	6.9 (1.5)	-5.9 (1.4)	1.1 (0.8)
		9.5 (1.9)	3.7 (1.1) 2.6 (1.7)
T	30 (2)	0 (1)	0 (1)
		12 (2)	1 (1) 25 (2)
S	-0.06 (0.02) -0.01 (0.03) -0.04 (0.02)	0.02 (0.02)	-0.05 (0.03)
		-0.03 (0.02)	0.13 (0.03)
		-0.06 (0.02)	0.09 (0.02)

Origin (crystal coordinates) which gives symmetric *S*:
0.9338 0.3624 0.4975

Distance of this origin from centre of mass = 1.361 Å

Axis shifts (Å) and screw pitches (Å.deg⁻¹)

Axis	Shifts	Pitch
1	0.57	-2.80
2	0.17	-0.18
3	-0.48	0.10

Principal r.m.s. amplitudes

L(deg) (imaginary)*	3.83	2.29
T(Å)	0.112	0.170

* Mean-square amplitude = -0.93 deg²

Residuals

Hamilton's $R_G = 0.1441$

R.m.s. deviation = 0.0042 Å²

Residuals in calculation using *unit weights*

Hamilton's $R_G = 0.1869$

R.m.s. deviation = 0.0040 Å²

Conclusions

The overall results are not as good as might have been hoped. Although the fits to the observed temperature factors are not excessively poor, some of the tensors, especially **L**, are not too well-defined. This is probably due as much to inadequate data as to breakdown of the rigid-body hypothesis – in particular it seems clear that better data than are at present available are necessary if the introduction of the **S** tensor is to be worth while for this type of compound. It is likely that absorption by the heavier atoms involved is the main source of error. The accuracy to which bond lengths have been determined is not sufficient to make the librational corrections significant.

Notes on tables

(1) The initially derived tensors are given with respect to the standard orthogonal axes used by the program. If *X*, *Y*, *Z* are ångström coordinates in this system, and *x*, *y*, *z* are fractional coordinates relative to the crystal axes, then

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a \sin \gamma & 0 & c\xi \\ a \cos \gamma & b & c \cos \alpha \\ 0 & 0 & c(\sin^2 \alpha - \xi^2)^{1/2} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

where $\xi = (\cos \beta - \cos \alpha \cos \gamma) / \sin \gamma$ (see Lipson & Cochran, 1966). The units of **L** are (deg)², those of **T** are 10⁻³ Å², and those of **S** are Å.deg.

(2) In the Schomaker & Trueblood calculations, all reductions and conventions are as in those authors' original paper. Therefore the table of axis shifts refers to shifts of the principal axes of **L** away from the origin which makes **S** symmetric. The first column records the shift in the direction of axis 1, the second that in the direction of axis 2, etc. The final root-mean-square (r.m.s.) amplitudes of **T** are those calculated from Schomaker & Trueblood's 'reduced **T**'.

(3) Hamilton's generalized *R* factor, R_G , is defined as

$$R_G = [\sum W(U_{\text{calc}} - U_{\text{obs}})^2 / \sum WU_{\text{obs}}^2]^{1/2}$$

where *U* is a component of the temperature factor in the form

$$\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$$

The r.m.s. deviation is

$$[\langle (U_{\text{obs}} - U_{\text{calc}})^2 \rangle]^{1/2}$$

(4) In the tables of bond lengths, the numbering of atoms follows exactly that adopted in the papers from which the data was taken.

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