

The Pseudo-Symmetric Structure of Pb(SPh)₂

A. DAVID RAE,^{a*} DONALD C. CRAIG,^b IAN G. DANCE,^b MARCIA L. SCUDDER,^b PHILIP A. W. DEAN,^{c†} MARY ANN KMETIC,^c NICHOLAS C. PAYNE^c AND JAGADESE J. VITTAL^c

^aResearch School of Chemistry, Australian National University, Canberra, ACT 0200, Australia, ^bSchool of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia, and ^cDepartment of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7. E-mail: rae@rsc.anu.edu.au

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Abstract

The crystal structure of Pb(SC₆H₅)₂ is pseudo-*C*-centred orthorhombic, $a = 54.06(1)$, $b = 11.468(1)$, $c = 7.4387(8)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $Z = 16$, and may be described as a partial ordering of a 1:1 disordered parent structure of symmetry *Pm*cn, $Z = 4$ ($\mathbf{a}' = \mathbf{a}/2$, $\mathbf{b}' = \mathbf{b}/2$, $\mathbf{c}' = \mathbf{c}$), in which the mirror imposes a 1:1 disorder on two-dimensionally polymeric layers perpendicular to \mathbf{a}^* . An ideally ordered structure has monoclinic space group *C*112₁/*d* (*P*2₁/*c* using an alternative axis system \mathbf{b} , \mathbf{c} , $[\mathbf{a} + \mathbf{b}]/2$), but may also be described as two inversion-related substructures of *C*mc2₁ pseudo-symmetry, where the *b*-glide planes of one substructure coincide with the mirror planes of the other and *vice versa*. Moving one substructure by $\mathbf{b}/2$ relative to the other creates a different orientation of the structure. The crystal studied showed a partial disorder of each substructure relative to origins $\mathbf{b}/2$ apart [0.964(4):0.036 for one substructure and 0.584(3):0.416 for the other]. This lowers the symmetry of the average structure to *C*112₁ with intensities realistically described as $K^2[(1 - \delta)|F(hkl)|^2 + \delta|F(\bar{h}k\bar{l})|^2]$, where K^2 for h odd, k odd reflections is 0.444(7) of the value for h even, k even reflections, δ is 0.325(5) and $F(hkl)$ is the structure factor for an ideally ordered structure. Final values for R of 0.046 and 0.090 were obtained for the 844 h even, k even and 687 h odd, k odd reflections with $I(\mathbf{h}) > 3\sigma(I(\mathbf{h}))$ used in refinement. A bond-valence interpretation of the bonding within the polymeric layer structure is given.

1. Introduction

Few structural data are available for simple lead(II) thiolates, Pb(SR)₂. The structures of Pb[(SCH₂)₂] (Dean, Vittal & Payne, 1985) and Pb(SC₆H₄Me-4)₂ (Krebs, Brommelhaus, Kersting & Nieuhaus, 1992) show them to be non-molecular. Such non-molecularity is, presumably, responsible for the poor solubility of the simple thiolates in non-coordinating solvents. This in turn has

led to difficulty in obtaining them in a form suitable for single-crystal X-ray diffraction studies. The addition of SR⁻ solubilizes Pb(SR)₂ to form Pb(SR)₃⁻ (Arsenault & Dean, 1983) and this enhanced solubility can lead to crystallization at Pb(SR)₂/SR⁻ > 1 (Dean *et al.*, 1985; Krebs *et al.*, 1992). This method was used to obtain crystals of Pb(SPh)₂ (1) that could be used for single-crystal X-ray structural analysis.

Structure elucidation and refinement were complicated by the fact that layers of polymeric Pb(SPh)₂ show disorder with alternative origins $\mathbf{b}/2$ apart. A 1:1 disorder relative to these origins corresponds to a structure of *Pm*cn symmetry, $Z = 4$, for a cell $\mathbf{a}' = \mathbf{a}/2$, $\mathbf{b}' = \mathbf{b}/2$, $\mathbf{c}' = \mathbf{c}$. The actual *C*-centred structure may then be described as an occupancy modulation of this *Pm*cn parent structure with an associated modulation vector, $\mathbf{a}^* + \mathbf{b}^*$. A doubly degenerate irreducible representation is necessarily associated with this modulation vector and the resulting average structure has a space-group symmetry that depends upon the disorder parameters.

2. Experimental

2.1. Crystalline Pb(SPh)₂

The literature method (Shaw & Woods, 1971) was used to synthesize yellow microcrystalline Pb(SC₆H₅)₂ (1) from reagent-grade lead acetate (M and B) and benzenethiol (Aldrich). Crystals were produced by allowing a mixture of the microcrystalline material (0.25 g, 0.59 mmol), PhSH (0.12 ml, 0.11 g, 1.0 mmol) and NaOMe [produced *in situ* from Na (0.012 g, 0.53 mmol)] in MeOH [10 ml, deoxygenated with N₂(g)] to stand at 313 K for 60 h. After this time the yellow supernatant liquid was removed using a pipette and the yellow plates were washed with three 5 ml portions of MeOH and dried under a flow of N₂(g). Similar results were obtained using EtOH as the solvent. Although the crystals obtained in this way were far from ideal for single-crystal X-ray diffractometry, they were the best that were obtained from many attempts in which the solvent, Pb(SPh)₂/SPh⁻ ratio and temperature were varied.

† Visiting Fellow, School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia (1993–1994).

Table 1. *Experimental details*

Crystal data	
Chemical formula	C ₁₂ H ₁₀ PbS ₂
Chemical formula weight	425.5
Cell setting (ordered)*	Monoclinic
Space group (ordered)†	C112 ₁ /d
<i>a</i> (Å)	54.06 (1)
<i>b</i> (Å)	11.468 (1)
<i>c</i> (Å)	7.4387 (8)
γ (°)	90.0
<i>V</i> (Å ³)	4611 (1)
<i>Z</i>	16
<i>D_s</i> (Mg m ⁻³)	2.45
Radiation type	Mo <i>K</i> α
Wavelength (Å)	0.71073
No. of reflections for cell parameters	21
θ range (°)	15–20
μ (mm ⁻¹)	15.06
Temperature (K)	294
Crystal form	Thin plates
Crystal size (mm)	0.41 × 0.18 × 0.03
Crystal colour	Yellow
Data collection	
Diffractometer	CAD-4
Data collection method	$\theta/2\theta$ scans
Absorption correction	de Meulenaer & Tompa (1965)
<i>T</i> _{min}	0.08
<i>T</i> _{max}	0.48
No. of measured reflections	2338 (includes absences)
No. of independent reflections	2228
No. of observed reflections	1531
Criterion for observed reflections	<i>I</i> > 3 σ (<i>I</i>)
<i>R</i> _{int}	Unmerged
θ _{max} (°)	25
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 64 0 → <i>k</i> → 13 0 → <i>l</i> → 8
No. of standard reflections	1
Frequency of standard reflections	2000 s
Refinement	
Refinement on	See text
<i>R</i>	0.057
<i>wR</i>	0.078
<i>S</i>	2.56
No. of reflections used in refinement	1531
No. of parameters used	54
H-atom treatment	Part of rigid body phenyl
Weighting scheme	$w = 1/\sigma^2(F_o)$
(Δ/σ) _{max}	0.12
$\Delta\rho$ _{max} (e Å ⁻³)	4.5
$\Delta\rho$ _{min} (e Å ⁻³)	-3.5
Extinction method	None
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)

* The observed structure is pseudo-*C*-centred orthorhombic; disordering lowers the symmetry (see text). † Non-standard setting of *P*2₁/*c*.

2.2. Data collection

A crystal of dimensions 0.03 × 0.41 × 0.18 mm was mounted on a silica fibre with cyanoacrylate glue. Reflection data to $2\theta_{\max} = 50^\circ$ were measured at 294 K with an Enraf–Nonius CAD-4 diffractometer in the $\theta/2\theta$ scan mode using graphite-monochromated Mo *K* α radiation ($\lambda = 0.7107 \text{ \AA}$). Cell dimensions were determined from 21 reflections with $\theta > 15^\circ$. 1531 reflections with $I(\mathbf{h}) > 3\sigma(I(\mathbf{h}))$ were considered observed out of the 2228 unique reflections of one octant. The reflection

weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. There was no crystal decomposition.

3. Structure solution and refinement

An approximate structure solution obtained using space group *Cmc*2₁ correctly located the relative positions of the 16 Pb atoms per cell, half lying on the mirror planes and half lying on *b*-glides half way between the mirror planes. The asymmetric unit contains Pb on two special positions and one general position. It was subsequently shown that the structure consists of polymeric layers perpendicular to **a***, four layers per unit cell repeat **a**. The positions of the Pb atoms within individual layers implied that these heavy atoms only contributed to the *h* even, *k* even reflections. Consequently, the Pb atoms could be described using a smaller unit cell of **a'** = **a**/2, **b'** = **b**/2, **c'** = **c** with now four Pb atoms per unit cell. The maximum space-group symmetry consistent with the Pb atoms was *Pm**cn* (number 62), with the asymmetric unit containing a Pb on a mirror plane. An origin shift is required to locate the origin at a centre of inversion. A map of *Pm**cn* symmetry obtained using only *h* even, *k* even reflections has an implicit 1:1 disorder, which is manifest as a 1:1 disorder across the mirror planes. Ordering the structure then involves replacing a mirror perpendicular to **a*** by a *b*-glide in the larger cell. Unfortunately, in *Cmc*2₁ only half the disordered layers can be so ordered. Nevertheless, structure determination was continued using this space group.

Phasing of *h* odd, *k* odd reflections was initiated by an ordering of S atoms adjacent to what then became the *b*-glide plane of *Cmc*2₁. For a fixed set of symmetry elements a distinction between possible Pb positions **b**/4 apart had to be made. Meaningful refinement is only possible for one of the two options, see Appendix 1. Refinement and subsequent electron-density maps showed that in the region of the *b*-glide plane a chemically sensible polymeric layer perpendicular to **a*** could be determined. An inversion-related layer with a mirror-imposed 1:1 disordering occurred in the region of the mirror plane. Additional peaks suggested a partial disorder in the layers in the region of the *b*-glide. It was therefore necessary to consider the implications of various orderings of individual layers over origins **b**/2 apart, see Appendix 1.

It was assumed that a substructure composed of a single ordered layer per unit cell maintains *Pbc*2₁ symmetry. An ordered structure consistent with *C*-centring has *C*112₁/*d* symmetry. The asymmetric unit of *C*112₁/*d* is the equivalent position *x*, *y*, *z* and the pseudo-equivalent position (i) $x, \frac{3}{4} - y, \frac{1}{2} + z$. The 2₁ screw operation $\frac{1}{4} - x, \frac{1}{4} - y, \frac{1}{2} + z$ then creates the pseudo-equivalent position (ii) $\frac{1}{4} - x, \frac{1}{2} + y, z$. These four operations create an ordered layer of the structure at $x = \frac{1}{8}$. *C*-centring and inversion through the origin are the additional genera-

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Pb	0.12125 (2)	0.45092 (6)	0.08844 (9)	0.029
S1	0.1529 (1)	0.4227 (4)	-0.2125 (6)	0.027
S2	0.1047 (1)	0.2320 (4)	0.0133 (8)	0.038
C11	0.1773 (2)	0.3226 (10)	-0.1657 (18)	0.028
C12	0.1737 (2)	0.2150 (11)	-0.0819 (17)	0.032
C13	0.1940 (3)	0.1441 (10)	-0.0427 (18)	0.035
C14	0.2179 (2)	0.1809 (12)	-0.0874 (20)	0.036
C15	0.2214 (2)	0.2885 (13)	-0.1713 (20)	0.036
C16	0.2011 (2)	0.3594 (9)	-0.2104 (19)	0.032
C21	0.0738 (2)	0.2452 (12)	-0.0635 (21)	0.039
C22	0.0652 (2)	0.3424 (10)	-0.1579 (22)	0.040
C23	0.0405 (2)	0.3482 (10)	-0.2124 (23)	0.043
C24	0.0244 (2)	0.2569 (13)	-0.1725 (25)	0.045
C25	0.0329 (2)	0.1597 (11)	-0.0780 (25)	0.043
C26	0.0576 (3)	0.1538 (10)	-0.0235 (22)	0.040
Pb ^b	0.12125 (2)	0.29908 (6)	0.58844 (9)	0.029
S1 ^b	0.1529 (1)	0.3273 (4)	0.2875 (6)	0.027
S2 ^b	0.1047 (1)	0.5180 (4)	0.5133 (8)	0.038
C11 ^b	0.1773 (2)	0.4274 (10)	0.3343 (18)	0.028
C12 ^b	0.1737 (2)	0.5350 (11)	0.4181 (17)	0.032
C13 ^b	0.1940 (3)	0.6059 (10)	0.4573 (18)	0.035
C14 ^b	0.2179 (2)	0.5691 (12)	0.4126 (20)	0.036
C15 ^b	0.2214 (2)	0.4615 (13)	0.3287 (20)	0.036
C16 ^b	0.2011 (2)	0.3906 (9)	0.2896 (19)	0.032
C21 ^b	0.0738 (2)	0.5048 (12)	0.4365 (21)	0.039
C22 ^b	0.0652 (2)	0.4076 (10)	0.3421 (22)	0.040
C23 ^b	0.0405 (2)	0.4018 (10)	0.2876 (23)	0.043
C24 ^b	0.0244 (2)	0.4931 (13)	0.3275 (25)	0.045
C25 ^b	0.0329 (2)	0.5903 (11)	0.4120 (25)	0.043
C26 ^b	0.0576 (3)	0.5962 (10)	0.4765 (22)	0.040

Half of the asymmetric units of space group $C112_1/d$ is obtained from the other half applying the pseudo-symmetrical operation: (i) $x, \frac{3}{4} - y, \frac{1}{2} - z$.

tors required to create an ordered structure with layers perpendicular to \mathbf{a}^* at fractional coordinates $x = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}, \frac{7}{8}$. However, the symmetry of the average structure can be as low as $C112_1$ because of stacking faults that distribute individual layers relative to origins $\mathbf{b}/2$ apart and destroy the d -glide absence condition, see Appendix 1. Space group $Cmc2_1$ is the special case where a 1:1 disorder exists for half the layers.

Modelling the disorder is detailed in Appendix 2. Intensities may be realistically described as $K^2[(1 - \delta)|F(hkl)|^2 + \delta|F(\bar{h}k\bar{l})|^2]$, where K^2 for h even, k odd reflections is 0.444 (7) of the value for h even, k even reflections and $F(hkl)$ is the structure factor for an ideally ordered structure. For layers constrained to have local $Pbc2_1$ symmetry, the h even, k even intensities have orthorhombic diffraction symmetry and only the weaker h odd, k odd intensities are modified by the disorder. The diffraction pattern shows reasonably well shaped h odd, k odd reflections (some diffuseness along \mathbf{a}^* does occur) and this implies that the stacking faults occur only occasionally. The refinement indicated an average structure that approaches $Cmc2_1$ symmetry with $\delta:(1 - \delta) = 0.325(5):0.675$, see Appendix 2. Any lowering of the local $Pbc2_1$ symmetry of a layer should result in the c -glide absence condition not strictly holding. However, all $h0l$, l odd reflections had $I(\mathbf{h}) < 2\sigma(I(\mathbf{h}))$. The absence condition $hk0$, $h + k \neq 4n$, h even, k even, corresponds to

Table 3. Selected geometric parameters ($\text{\AA}, ^\circ$) for (1)

Pb—S1	2.837 (5)	Pb—S2 ^b	3.519 (5)
Pb—S2	2.723 (5)	S1—C11	1.780 (10)
Pb—S1 ^b	2.671 (5)	S2—C21	1.776 (10)
Pb—S2 ^b	3.373 (6)		
S1—Pb—S2	86.0 (2)	S1 ^b —Pb—S2 ^b	109.7 (1)
S1—Pb—S1 ^b	89.4 (1)	S2 ^b —Pb—S2 ^b	92.2 (1)
S1—Pb—S2 ^b	157.7 (1)	Pb—S1—C11	111.4 (5)
S1—Pb—S2 ^b	75.9 (1)	Pb—S2—C21	107.3 (5)
S2—Pb—S1 ^b	80.5 (2)	S1—C11—C12	123.8 (7)
S2—Pb—S2 ^b	108.4 (2)	S1—C11—C16	116.1 (7)
S2—Pb—S2 ^b	158.9 (2)	S2—C21—C22	122.8 (8)
S1 ^b —Pb—S2 ^b	76.8 (1)	S2—C21—C26	117.2 (8)

Symmetry codes: (i) $x, \frac{3}{4} - y, \frac{1}{2} + z$; (ii) $\frac{1}{4} - x, \frac{1}{2} + y, z$.

the n -glide absence condition for $Pm\bar{c}n$. The extension of the condition $h + k \neq 4n$ to the h odd, k odd reflections corresponds to the diamond glide condition of an ordered structure. However, this absence condition no longer holds when disorder occurs, only one of $F(hk0)$ and $F(\bar{h}k0)$ being a diamond glide absence for an h odd, k odd reflection.

The fractional coordinates in Table 2 are presented in terms of an ordered $C112_1/d$ structure. The structure and atom-numbering scheme are shown in Fig. 1. Atomic parameters, bond lengths and bond angles are given in Tables 2 and 3, respectively. The S and Pb atoms were unconstrained. H atoms were included in geometrically sensible positions each cycle. The phenyl rings were refined as identical planar groups of local $mm2$ symmetry, the position and orientation of each group being refined. Each SPh moiety was refined using a 12-parameter TL thermal parameter model centred on the S atom (Rae, 1975). The Pb atom was refined anisotropically.

Final values of $R = \sum_h w_h |\Delta F_h| / \sum_h w_h |F_h|$ obtained for the 844 h even, k even and 687 h odd, k odd reflections with $I(\mathbf{h}) > 3\sigma(I(\mathbf{h}))$ used in refinement were 0.046 and 0.090 (0.057 overall). Values for $wR = [\sum_h w_h |\Delta F_h|^2 / \sum_h w_h |F_h|^2]^{1/2}$ were 0.057 and 0.117 (0.078 overall). 54 independent parameters were used in refinement.† Atomic scattering factors and anomalous dispersion parameters were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Structure solution was by *MULTAN80* (Main, 1980) and refinement used *RAELS92* (Rae, 1992). *ORTEPII* (Johnson, 1976) running on a Macintosh IIcx was used for the structural diagrams.

4. Results and discussion

In the structure of Pb(SPh)_2 (1) the pseudo-symmetry relationship between atoms within a layer was con-

† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: BR0034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

strained to be exact. Therefore, it is sufficient to describe the environment of a single $\text{Pb}(\text{SPh})_2$ unit. The Pb atom has strong primary bonds to three sulfur atoms, S1, S2 and S1^i , and more weakly to two other sulfur atoms, S2^i and S2^{ii} (Fig. 1). S1 acts as a bidentate bridge, linking *c*-glide-related $\text{Pb}(\text{SPh})_2$ units into strongly bonded chains parallel to *c*. The S2 atoms also bridges adjacent Pb atoms along *c*, but in this case, one Pb—S2 bond is a primary bond and the other is a weaker secondary bond. A second weak Pb—S2 bond links *b*-glide-related

chains into layers perpendicular to \mathbf{a}^* (Fig. 2). There are no $\text{Pb} \cdots \text{S}$ interactions between adjacent layers, each layer having a hydrocarbon coating. A stacking fault of the layers has been satisfactorily accounted for by the model used.

The layer structure of (1) bears a strong resemblance to that of $\text{Pb}(\text{SC}_6\text{H}_4\text{Me-4})_2$ (2) (Krebs *et al.*, 1992), which was reported after the start of our own work. Indeed, both structures may be regarded as being derived from the ordering of 1:1 disordered parent structures

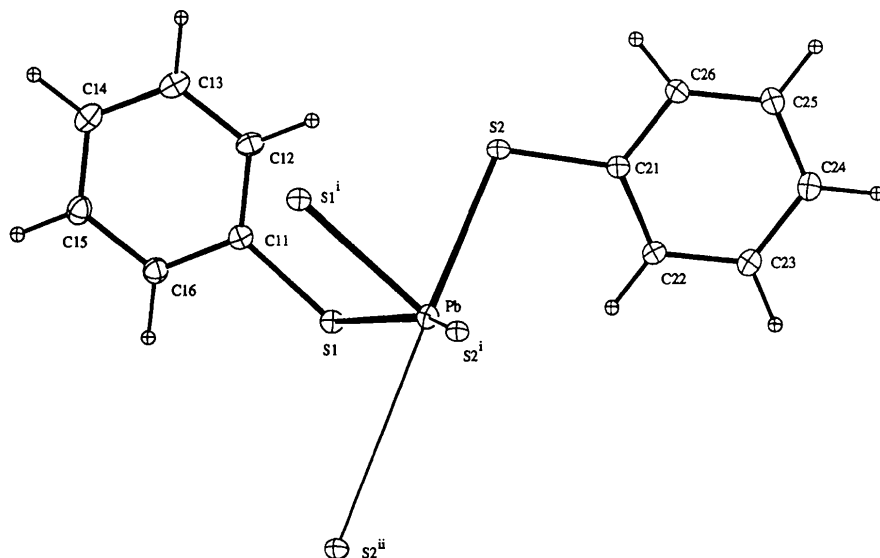


Fig. 1. A view of the environment of the Pb atom of $\text{Pb}(\text{SC}_6\text{H}_5)_2$ showing the labelling scheme. Equivalent positions: (i) $x, \frac{3}{4} - y, \frac{1}{2} + z$; (ii) $\frac{1}{4} - x, \frac{1}{2} + y, z$.

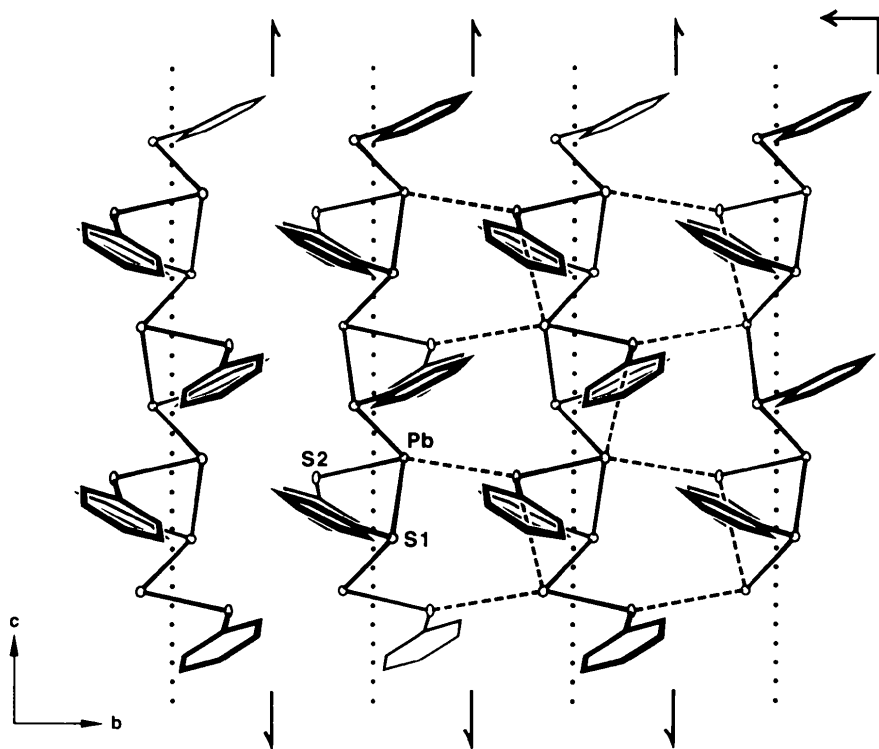


Fig. 2. A projection down \mathbf{a} of a layer of the $\text{Pb}(\text{SC}_6\text{H}_5)_2$ structure. Crystallographic screw axes parallel to *c* relate adjacent chains that contain a pseudo-*c*-glide. The long secondary $\text{Pb} \cdots \text{S}$ bonds are omitted on the left side of the diagram to reveal the S—C bonds.

of $Pm\bar{c}n$ in which the mirror creates disordered layers perpendicular to \mathbf{a}^* . This is elaborated in Appendix 1. A projection down \mathbf{a} of a layer of the structure of (2) is shown in Fig. 3. A major difference between the two structures is in the orientations of the aryl rings on the surface of the layer of inorganic material. Whereas the Ph rings C11–C16 and C21–C26 are almost superimposed in the projection of (1) down \mathbf{a} (Fig. 2), this is not so for the *p*-tolyl rings of (2) (Fig. 3). In (1) the pseudo-mirror ensures that the orientations of the Ph groups are nearly identical on both faces of a single layer, as seen in a projection down \mathbf{c} (Fig. 4). The presence of the Me groups in (2) leads to the two surfaces of a layer being dissimilar, with one surface (surface 1) having the substituents approximately perpendicular to it, the other (surface 2) having them oriented obliquely (Fig. 5). The packing of the layers in (2) is such that surface 1 abuts surface 1, while surface 2 abuts surface 2.

The primary kernel $PbS1S1'S2$ of (1) is pyramidal and can be thought of as being of VSEPR type AX_3E (Gillespie, 1972). A stereochemically active lone pair may then occupy the large vacant space opposite $S1'$. The formation of such PbS_3 kernels is common to several lead thiolates (Hitchcock, Lappert, Samways & Weinberg, 1983; Dance, Guerny, Rae, Scudder & Baker, 1986; Krebs *et al.*, 1992) and the same kernel occurs in $[Pb(SPh)_3]^-$ (Christou, Folting & Huffman, 1984; Dean, Vittal & Payne, 1984). However, when steric considerations permit secondary weak $Pb \cdots S$ bonding also occurs (Dean *et al.*, 1985; Dance *et al.*, 1986; Krebs *et al.*, 1992).

Within the $PbS1S1'S2$ kernel of (1), the bond distances fall in the range 2.671 (5)–2.837 (5) Å. This may be compared with the range 2.650 (3)–2.874 (3) Å in (2). The secondary $Pb \cdots S2'$ and $Pb \cdots S2''$ distances of (1) are 3.373 (6) and 3.519 (5) Å, respectively, compared with 3.292 (4) and 3.689 (4) Å in (2). The sum of the van

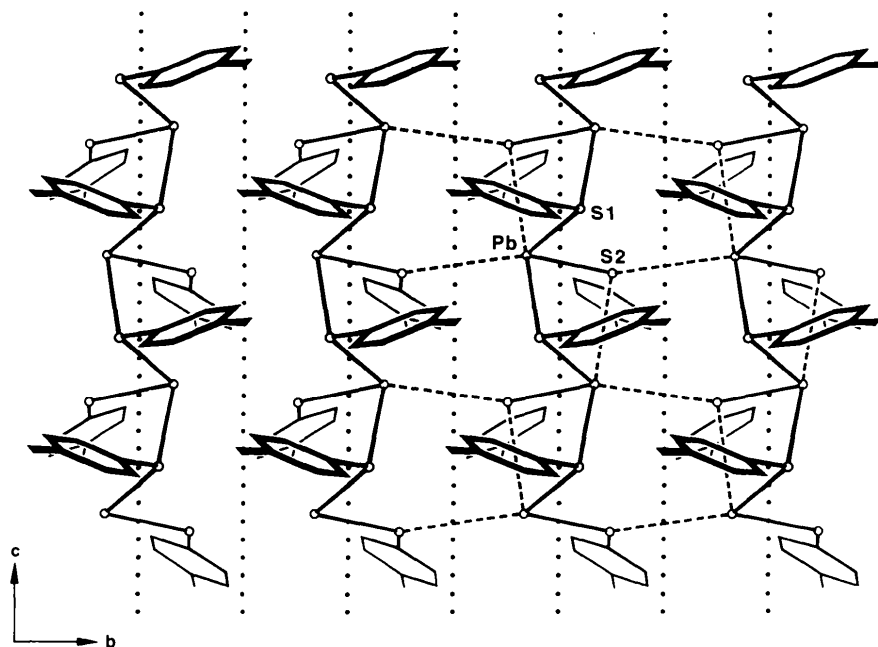


Fig. 3. A projection down \mathbf{a} of a layer of the $Pb(SC_6H_4Me-4)_2$ structure. Crystallographic c -glides relate adjacent chains that also contain a c -glide. The long secondary $Pb \cdots S$ bonds are omitted on the left side of the diagram to reveal the $S-C$ bonds.

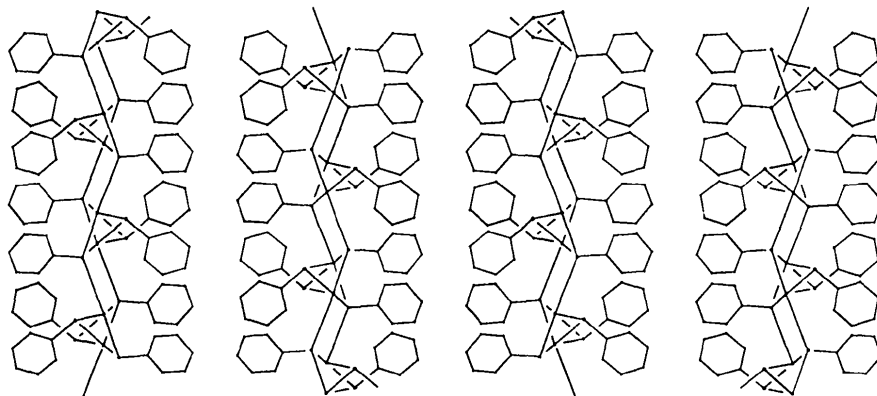


Fig. 4. A projection down \mathbf{c} of the $Pb(SC_6H_5)_2$ structure. Note the pseudo-mirror symmetry relating the phenyl rings on opposite sides of a layer. Layers 1 and 3 are related by a mirror plane which is not a symmetry element of layer 2.

der Waals radii is 3.8 Å (Bondi, 1964). Brown (1978, 1981) has proposed a bond-valence model that allows for a continuum of the distances between a metal and its bonded atoms. In this model the total bond valence is $V_i = \sum_j \exp[(r_o - r_{ij})/0.37]$ (Brown & Altermatt, 1985). Using recent values of r_o (Bresle & O'Keeffe, 1991) the total bond valences calculated for Pb in (1) and (2) are 1.97 and 2.06, respectively, both acceptable values for Pb^{II}. It is relevant to note that the two longer bonds Pb···S2ⁱ and Pb···S2ⁱⁱ together contribute 0.18 to the value in both (1) and (2).

The S—Pb—S angles in the PbS1S1ⁱS2 kernel of (1) are 86.0 (2), 89.4 (1) and 80.5 (2)°. Bond angles that are well below the tetrahedral angle are a common feature of structures of the VSEPR type AX₃E when the central atom is a heavy *ns*² atom such as Pb^{II} or Bi^{III} etc. We present separately a more detailed discussion of the layered structures of (1) and (2) in relation to the structures of monolayers of thiolates on metal surfaces (Dean, Kmetc, Payne, Vittal, Rae, Craig, Dance & Scudder, 1997).

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APPENDIX A

A1. Implications of the diffraction pattern pseudo-symmetry

The reflections can be subdivided into two subsets, those with *h* even, *k* even and those with *h* odd, *k* odd. The average intensity for the first subset was much greater than that for the second subset. Reflections $F(hkl)$ of subset (1) are the Fourier transform of the apparent electron density $\frac{1}{2}[\rho(\mathbf{r}) + \rho(\mathbf{r} + \mathbf{b}/2)]$ and reflections of subset (2) are the Fourier transform of the apparent electron density $\frac{1}{2}[\rho(\mathbf{r}) - \rho(\mathbf{r} + \mathbf{b}/2)]$, where the true electron density $\rho(\mathbf{r})$ has the periodicity of the *C*-centred unit cell. One sees that reflections in subset (1) are not modified if parts of the structure are displaced by $\mathbf{b}/2$.

Thus, the structure, *i.e.* $\rho(\mathbf{r})$, can be thought of as an ordering (or partial ordering) of a 1:1 disordered parent structure corresponding to $\frac{1}{2}[\rho(\mathbf{r}) + \rho(\mathbf{r} + \mathbf{b}/2)]$, with occupancy waves, *i.e.* $\frac{1}{2}[\rho(\mathbf{r}) - \rho(\mathbf{r} + \mathbf{b}/2)]$, associated with the modulation wavevector $\mathbf{q} = \mathbf{a}^* + \mathbf{b}^*$.

Absence conditions were consistent with the symmetry of the parent structure $\frac{1}{2}[\rho(\mathbf{r}) + \rho(\mathbf{r} + \mathbf{b}/2)]$ being *Pm**cn* and that of the *C*-centred structure $\rho(\mathbf{r})$ being *Cmc*2₁, a subgroup of *Pm**cn*. However, the combination of parent structure and modulation wavevector identifies this structure as being describable as a commensurately modulated structure with a doubly degenerate irreducible representation associated with the modulation vector. Such structures commonly have refinement problems (Rae, 1996).

A2. Possible structures as occupancy modulations of the disordered parent structure

The parent structure has *Pm**cn* symmetry and can be separated into two symmetry-related substructures of *Pmc*2₁ symmetry. The odd layers perpendicular to \mathbf{a}^* belong to one substructure, the interleaving even layers to the other. The mirror causes 1:1 disorder.

Let us first consider an ordering of the disordered layers that does not change the volume of the unit cell, since this allows the known crystal structure of Pb(SC₆H₄CH₃-4)₂ (2), $a' = 31.929$, $b' = 5.966$, $c' = 7.178$ Å, $\beta' = 94.60^\circ$, *P*2₁/*c*, *Z* = 4 (Krebs *et al.*, 1992), to be related to the structure of (1) studied here. Such an ordering allows either (1) space group *P*112₁/*n* or *P*2₁2₁2₁ with substructure symmetry lowered to *P*112₁ or (2) space group *P*12₁/*c*1 or *Pmc*2₁ with substructure symmetry lowered to *P*1*c*1. Two of these options allow distortion of the orthorhombic cell to form a monoclinic cell and two do not. Twinning and disorder are prevented from occurring in the structure of (2), because the methyl groups at the interface between adjacent layers destroy the pseudo-mirror perpendicular to \mathbf{a}'^* that holds well for the phenyl rings in individual layers.

We note that the transformations $x = x'/2$, $y = \frac{3}{4} - y'/2$, $z = \frac{1}{2} + z'$ can be used to show that the listed coordinates of Pb, S1, S2, C11 and C21 in (2) correspond to our atom positions for (1), *i.e.* step 1: change to equivalent

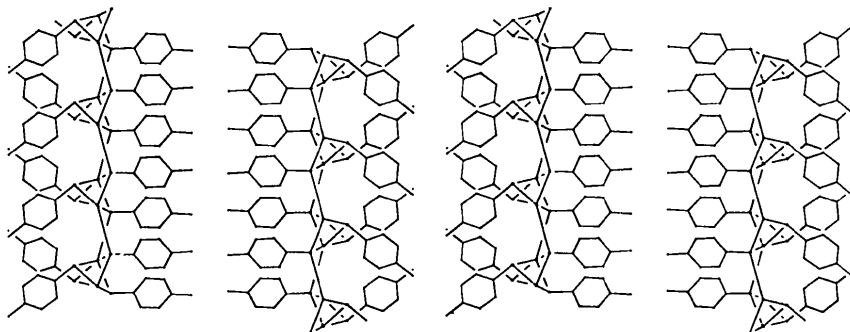


Fig. 5. A projection down *c* of the Pb(SC₆H₄Me-4)₂ structure. Note that the presence of methyl groups leads to the two surfaces of a layer being distinctly different.

Table 4. *Equivalent positions and pseudo-equivalent positions*

Equivalent positions of disordered structure in $Pm\bar{c}n$

For cell $\mathbf{a}' = \mathbf{a}/2$, $\mathbf{b}' = \mathbf{b}/2$, $\mathbf{c}' = \mathbf{c}$, $Z = 4$.

Layer at $x' = \frac{1}{4}$.

x', y', z' ;	$\frac{1}{2} - x', \frac{1}{2} - y', \frac{1}{2} + z'$;	$x', \frac{1}{2} - y', \frac{1}{2} + z'$;	$\frac{1}{2} - x', y', z'$.
$-x', -y', -z'$;	$\frac{1}{2} + x', \frac{1}{2} + y', \frac{1}{2} - z'$;	$-x', \frac{1}{2} + y', \frac{1}{2} - z'$;	$\frac{1}{2} + x', -y', -z'$.

Equivalent and pseudo-equivalent positions of ordered structure in $C112_1/d$

For cell $\mathbf{a}, \mathbf{b}, \mathbf{c}$, $Z = 16$.

Layer at $x = \frac{1}{8}$.

x, y, z ;	$\frac{1}{4} - x, \frac{1}{4} - y, \frac{1}{2} + z$;	$x, \frac{3}{4} - y, \frac{1}{2} + z$;	$\frac{1}{4} - x, \frac{1}{2} + y, z$.
$\frac{1}{2} - x, \frac{1}{2} - y, -z$;	$\frac{1}{4} + x, \frac{1}{4} + y, \frac{1}{2} - z$;	$\frac{1}{2} - x, \frac{3}{4} + y, \frac{1}{2} - z$;	$\frac{1}{4} + x, -y, -z$.
$\frac{1}{2} + x, \frac{1}{2} + y, z$;	$\frac{3}{4} - x, \frac{3}{4} - y, \frac{1}{2} + z$;	$\frac{1}{2} + x, \frac{1}{4} - y, \frac{1}{2} + z$;	$\frac{3}{4} - x, y, z$.
$-x, -y, -z$;	$\frac{3}{4} + x, \frac{3}{4} + y, \frac{1}{2} - z$;	$-x, \frac{1}{4} + y, \frac{1}{2} - z$;	$\frac{3}{4} + x, \frac{1}{2} - y, -z$.

Half of the equivalent positions of $Pm\bar{c}n$ have been selected by choosing between equivalent positions $\mathbf{b}' = \mathbf{b}/2$ apart.

Any layer in isolation creates a substructure with symmetry $Pbc2_1$.

Layers ($x = \frac{1}{8}, \frac{5}{8}$) in isolation create a substructure with symmetry $Cmc2_1$.

Layers ($x = \frac{3}{8}, \frac{7}{8}$) describe substructure symmetry $Cmc2_1$, but with an inequivalent origin.

The first two positions of each layer are true equivalent positions of $C112_1/d$.

The remaining two positions are pseudo-symmetry positions.

Operation by a pseudo-equivalent position of one $Cmc2_1$ substructure translates the other substructure by $\mathbf{b}/2$. This creates a different orientation of the same structure.

position $x'' = x'$, $y'' = \frac{3}{2} - y'$, $z'' = \frac{1}{2} + z'$, of $P2_1/c$; step 2: change axial lengths so that $x = x'/2$, $y = y'/2$, $z = z'$ for the cell $\mathbf{a} = 2\mathbf{a}'$, $\mathbf{b} = 2\mathbf{b}'$, $\mathbf{c} = \mathbf{c}'$.

We can now look at the C -centred possibilities arising for our structure as a result of occupancy modulation waves corresponding to the modulation wavevector $\mathbf{q} = \mathbf{a}^* + \mathbf{b}^*$. There are two possible two-dimensional irreducible representations associated with this wavevector (Bradley & Cracknell, 1972) and each has a corresponding space group of $C112_1$ symmetry formed by using only those symmetry elements that have characters $+2$. Half the screw axes parallel to \mathbf{c} of $Pm\bar{c}n$ have character $+2$, while the other half have character -2 . The two irreducible representations differ only in the selection of the half that has the $+2$ character. There is a $\mathbf{b}/4 = \mathbf{b}'/2$ translation between the two sets of screw axes. We assume that the mirror of a disordered layer is replaced by a b -glide, giving two substructures of $Cmc2_1$ symmetry, in each of which C -centring relates layers of $Pbc2_1$ symmetry. Shorter Pb—S bonds link $\text{Pb}(\text{SC}_6\text{H}_5)_2$ moieties in chains parallel to \mathbf{c} . One irreducible representation has individual chains propagated by a screw axis, while the other has the chains propagated by a c -glide as in our final structure, see Fig. 2.

The second option for forming a layer of $Pbc2_1$ symmetry can be created from the first option by translating the asymmetric unit by $\pm\mathbf{b}/4$ relative to fixed symmetry elements. This is equivalent to moving the origin of the $Pm\bar{c}n$ parent structure by $\mathbf{b}'/2$ to an equivalent origin. There is no difference in the calculated intensities of the h even, k even reflections for the two models. However, the wrong choice gave a value for R_1 of 0.59 for the h odd, k odd reflections (compared with our final value

of 0.09) and allowed the correct model to be clearly distinguished. The correct model has a c -glide relating atoms within a chain parallel to \mathbf{c} . The structure of (2) also has a c -glide relating atoms within a chain parallel to \mathbf{c} . However, for (2) adjacent chains in a layer are related by an implied c -glide, whereas for (1) adjacent chains are related by a 2_1 screw axis, see Fig. 2.

A3. Equivalent positions and pseudo-equivalent positions

Table 4 describes the eight equivalent positions and eight pseudo-equivalent positions of an ordered structure. The action on the whole structure of a symmetry operation leaves the structure unchanged. However, the action of a pseudo-symmetry operation on the whole structure leaves one $Cmc2_1$ substructure unchanged, but translates the other by $\mathbf{b}/2$.

Four ordered C -centred structures are possible from the packing of four geometrically identical layers in a cell, but two are related to the other two by a translation of $\mathbf{b}/2$. Either the generator $\frac{1}{4} + x, \frac{1}{4} + y, \frac{1}{2} - z$ or the generator $x - \frac{1}{4}, \frac{1}{4} + y, \frac{1}{2} - z$ may be used together with the space group $C112_1$ to create the true symmetry elements and this gives mirror-related versions of the same $C112_1/d$ structure $\{P2_1/c$ for axes \mathbf{b}, \mathbf{c} , $[\mathbf{a} + \mathbf{b}]/2$ or axes \mathbf{b}, \mathbf{c} , $[-\mathbf{a} + \mathbf{b}]/2\}$. The two options have different d -glide absence conditions for $hk0$ reflections. Either reflections with $h + k \neq 4n$ are absent or reflections with $h - k \neq 4n$ are absent.

A pseudo-symmetry operation creates an alternative origin for one of the two $Cmc2_1$ substructures. This operation becomes a real symmetry operation if there

is a 1:1 disorder with respect to the two origins for this substructure. A symmetry element that relates one substructure to the other only remains a symmetry element of a disordered structure if the disorders in the individual substructures are appropriately matched. If h odd, k odd reflections are observed, then, depending on the disorder, we can have $C112_1$, one of two orientations of $C112_1/d$ or one of two settings of $Cmc2_1$. If these reflections are not observed then $Pm\bar{c}n$ is appropriate. If the substructure symmetry is lowered from $Cmc2_1$ to $C112_1$, then $P112_1/n$ is also possible.

APPENDIX B

B1. Calculating intensities for a disordered stacking of ordered layers

There are four components of a faulted structure and the average per unit cell gives rise to a structure factor that may be constructed using pseudo-equivalent reflections $F_1(hkl)$ and $F_1(\bar{h}kl)$ of an ideally ordered $C112_1/d$ prototype. Layers at $x = \frac{1}{8}$ and $\frac{5}{8}$ are $(p_1 + p_3):(p_2 + p_4)$ disordered and layers at $x = \frac{3}{8}$ and $\frac{7}{8}$ are $(p_1 + p_4):(p_2 + p_3)$ disordered, where p_1 is the population associated with the reference structure, p_2 is the population associated with both substructures being translated by $\mathbf{b}/2$, p_3 is the population associated with only the second substructure being translated by $\mathbf{b}/2$ and p_4 is the population associated with only the first substructure being translated by $\mathbf{b}/2$. However, only two degrees of freedom are associated with p_1, p_2, p_3 and p_4 . The pseudo-translation $x, \frac{1}{2} + y, z$ creates the population p_2 and the pseudo- b -glides $\frac{3}{4} - x, \frac{1}{2} + y, z$ and $\frac{3}{4} - x, \frac{1}{2} + y, z$ create the populations p_3 and p_4 , respectively.

Consequently,

$$F(hkl) = p_1 F_1(hkl) + p_2 F_2(hkl) + p_3 F_3(hkl) + p_4 F_4(hkl),$$

where

$$\sum_i p_i = 1,$$

$$F_2(hkl) = (-1)^k F_1(hkl),$$

$$F_3(hkl) = i^h F_1(\bar{h}kl), \text{ and}$$

$$F_4(hkl) = (-i)^h F_1(\bar{h}kl).$$

Thus,

$$F(hkl) = [p_1 + (-1)^h p_2] F_1(hkl) + i^h [p_3 + (-1)^h p_4] F_1(\bar{h}kl).$$

When h is even

$$F_1(\bar{h}kl) = i^h F_1(hkl),$$

so that

$$F(hkl) = F_1(hkl).$$

When h is odd

$$F(hkl) = (p_1 - p_2) F_1(hkl) + i^h (p_3 - p_4) F_1(\bar{h}kl)$$

and

$$F(\bar{h}kl) = (p_1 - p_2) F_1(\bar{h}kl) - i^h (p_3 - p_4) F_1(hkl).$$

This can be reexpressed as

$$|F(hkl)|^2 = K^2 [(1 - \delta) |F_1(hkl)|^2 + \delta |F_1(\bar{h}kl)|^2] + \varepsilon,$$

where

$$K^2 = [(1 - p) + (-1)^h p]^2,$$

$$(1 - 2p)^2 = [(p_1 - p_2)^2 + (p_3 - p_4)^2] \text{ and}$$

$$(1 - 2\delta) = [(p_1 - p_2)^2 - (p_3 - p_4)^2] / (1 - 2p)^2.$$

The term ε is zero if $F_1(hkl) * F_1(\bar{h}kl)$ contains no imaginary component. The reference structure has a centre of inversion at the origin and so ε is zero in the absence of anomalous dispersion. We see that it is not necessary to enlarge the atom list to account for disorder.

It is simply necessary to combine the contribution of pseudo-symmetry-related reflections. The determination of $(p_1 - p_2)$ and $(p_3 - p_4)$ allow the evaluation of $p_1 + p_3 = [1 + (p_1 - p_2) + (p_3 - p_4)]/2, p_1 + p_4$ etc.

If ε is assumed to be zero, the disorder can be refined using two scale constants and a twinning parameter, δ . This was done using the program *RAELS92* (Rae, 1992). It is seen that averaging over separate mosaic blocks will also give an answer describable in this way and so is indistinguishable. A more recent modification of this program allows evaluation of the populations directly, bearing in mind the degrees of freedom restrictions, i.e. making p_2 zero and $p_1 + p_3 + p_4 = 1$. Twinning correlates with the above model and may be ignored.

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