Acta Cryst. (1972). A**28**, 445

Constrained Refinement Techniques applied to the Structure of Ammonium Hydrogen Sulphate above the Ferroelectric Transition

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(*Received* 15 *March* 1972)

The structure of ammonium hydrogen sulphate (AHS) in its room-temperature, non-ferroelectric phase – as determined from X-ray and neutron data – has been published [Nelmes, R. J. (1971). *Acta Cryst.* B**27**, 272]. The asymmetric unit contains two sulphate groups, *S*1 and *S*2. The thermal parameters as published showed unusually high values for oxygen atoms in just *one* of these groups – namely *S*1. The closely similar results subsequently obtained for the isomorphous salt rubidium hydrogen sulphate [Ashmore, P. (1970). Private communication] suggested the appearance of these high values to be significant. The techniques of constrained least-squares refinement and significance testing have now been applied to the analysis of this and other features of the AHS structure. The advantages and remaining limitations of these techniques and the methods of applying them are explained and illustrated. The principal conclusion reached is that *S*1 is disordered equally between two sites. It is also shown that the inclusion of the HSO_4^- hydrogen atoms is significant; that the sulphate groups $SO_3.O(H)^{2-}$ are distorted from a regular trigonal shape, principally by displacement of the O(H) atom – the oxygen to which the hydrogen is closer in the sulphate-linking O–H···O bonds; and that in thermal motion the sulphate groups can be treated as rigid bodies. The disorder of *S*1 is of considerable interest with regard to the transition to a ferroelectric phase at −3 °C.

1. Introduction

The structure of ammonium hydrogen sulphate (AHS), NH_4HSO_4, has been determined in its room-temperature non-ferroelectric phase from X-ray and neutron data by Nelmes (1971). In this phase AHS is monoclinic with space group $P2_1/c$; but as before (Nelmes, 1971) it is convenient to adopt the pseudo-orthorhombic unit cell ($a=24{\cdot}66\pm0{\cdot}02$, $b=4{\cdot}60\pm0{\cdot}01$, $c=14{\cdot}82\pm0{\cdot}02$ Å, and $\beta=89{\cdot}87\pm0{\cdot}01°$) of space group $B2_1/a$. This cell contains sixteen formula units, with two in each asymmetric unit. The published structural parameters (Table 2 of Nelmes, 1971) show anomalously high values for some thermal parameters of *S*1, *one* of the two symmetrically inequivalent sulphate groups (see Table 1). This effect was thought to be not demonstrably significant.

Table 1. *The thermal parameters of the unconstrained ordered model*

Temperature factor
$=\exp[-2\pi^2(U_{11}(ha^*)^2+2U_{12}(ha^*kb^*)+\ldots)]$.
U_{ij} are given in units of $10^{-3}\times$ Å^2.
$\underset{i\neq j}{U_{ij}}$ are omitted.

	U_{11}	U_{22}	U_{33}		U_{11}	U_{22}	U_{33}
S(1)	32	23	39	S(2)	26	22	26
O(1)	41	58	49	O(5)	35	56	41
O(2)	42	118	64	O(6)	37	39	35
O(3)	125	34	108	O(7)	49	25	44
O(4)	91	41	38	O(8)	44	26	42
N(1)	29	39	38	N(2)	36	47	31

More recently the structure of the equivalent phase of rubidium hydrogen sulphate (RHS), an isomorphous salt (Pepinsky & Vedam, 1960), has been independently determined by Ashmore (1970). This structure has parameters closely similar to AHS, including the appearance of high thermal parameters in the *S*1 group. Though the accuracy of the *absolute* values of the thermal parameters of AHS remains uncertain, the comparison with RHS strongly suggests the appearance of these *relatively* large values to be significant.

The present paper is concerned with the investigation of this and other aspects of the structure of AHS. The analysis employs the techniques of constrained least-squares refinement and significance testing. The value of this approach is explained and demonstrated.

2. Method

If the number of parameters used in constructing a structural model is increased from *n* to *N* then in general an improved least-squares fit will be obtained – as judged from any of the conventional indices. If only the model with *N* parameters is refined then *in principle*, because of correlation and non-linearity, it is not possible to determine whether it is significantly better than would be a model with *n* parameters. For example, if each of the atoms in AHS is refined with three positional parameters there can be, strictly, no rigorous test of the hypothesis that all the sulphate group S–O bonds are the same length – though in practice physically meaningful conclusions may often be reached. To obtain a more rigorous test a refinement must also be performed with these S–O bond lengths constrained to be equal. Then statistical analysis can be applied to determine the level of significance of the improved fit obtained with the increased degrees of freedom of the unconstrained (free) model.

If the constrained model is found not to be a significantly poorer description its parameters are more precise and, in any case, more accurate than the corresponding values obtained by combining parameters from the free model refinement (see an example in § 5).

The grounds for using this approach and the practical techniques of constrained least-squares refinement are fully explained in the review by Pawley (1972).

The statistical test used to compare two models is the R-value ratio test proposed by Hamilton (1965). For each model the value of R_w is computed, where

$$R_w=\sum_{i=1}^{M} w_i(F_i^o-F_i^c)^2\ .$$

The summation is over all M reflexions used in the refinement, w_i is the weight applied to the ith observation, and F_i^o and F_i^c are, respectively, the observed and calculated values of the ith structure amplitude. M, w_i and F_i^o must be the same for both models. $\mathscr{R}$, the ratio $[R_w\ (\text{constrained})/R_w\ (\text{free})]^{1/2}$, is distributed as $[\{(N-n)/(M-N)\}\,.\,F+1]^{1/2}$ where F is F-distributed with N–n and M–N degrees of freedom (Hamilton, 1965). Pawley (1970) has investigated an approximation for the F-distribution which gives sufficiently accurate values for the $\mathscr{R}$ distribution in the range of degrees of freedom usually encountered in crystallographic problems. The use of this method is illustrated in § 4 and there are other examples in Pawley (1972).

In applying the R-value ratio test the number of degrees of freedom applicable is not well defined with non-linear least-squares observational equations, and strictly the test requires that the hypothesis under test be linear. The former difficulty is probably not serious in practice (where observations greatly outnumber parameters); the effect of the latter remains to be investigated (see § 4 of Hamilton, 1965). These and other unassessed or imponderable effects arising from such factors as the essential non-linearity of the least-squares procedures and inadequacies of the data set do remain. They probably are, and will be assumed to be, negligible where strong indications are obtained (see § 4). But statistical and physical significance cannot be equated: some caution must be exercised.

Nevertheless, as a procedure for testing hypotheses about the results of crystal structure analysis, the techniques of constrained refinement and significance testing comprise a method of more power and rigour than do arguments based on the parameters and standard deviations derived from one (free) refinement. The problems caused by correlation and non-linearity of the observational equations in the latter procedure are largely removed in the former (see § 5 for an example). The need for correct weights, $[1/\sigma^2(F_i^o)]$, and a data set free from systematic error can be relaxed to the degree that both sets of parameters compensate equally for these errors.

The data set used for the refinements discussed below is the same as that used for the final refinement in Nelmes (1971) except that the 'accidentally absent' reflexions are omitted. They are omitted because of the problem of obtaining a correct weighting scheme for them (see Nelmes, 1971). The data set thus comprises 3248 independent observations – with their weights unchanged.

The labelling of atoms follows Nelmes (1971). The same atomic scattering curves are used and the ammonium groups continue to be treated as units, denoted N(1) and N(2). The two symmetrically independent sulphate groups are here denoted $S1$ and $S2$. $S1$ comprises atoms S(1), O(1), O(2), O(3) and O(4); $S2$ comprises S(2), O(5), O(6), O(7) and O(8).

The full-matrix least-squares program used for the constrained refinement was written by Dr G. S. Pawley of this Department. The program uses an orthogonal Ångstrom coordinate system (see § 3 of Pawley, 1972) with axes X, Y and Z such that X is parallel to $\mathbf{a}$, Y is parallel to $\mathbf{b}^*$ and Z is parallel to $\mathbf{a}\wedge\mathbf{b}^*$. This coordinate system is used throughout the paper.

3. Models and constraints

The first constraint introduced was to treat the sulphate groups as being rigid with regard to thermal motion. Each group then requires twenty thermal parameters – six each to determine the mean-square translational and librational tensors, **T** and **L**, and eight for the screw rotation tensor **S** (see Pawley, 1972, and Schomaker & Trueblood, 1968). This will be called the TLS model. In the refinement program the origin for the **T**, **L** and **S** tensors is set at the position obtained by taking an average over the coordinates of the atoms in the group considered. For a sulphate group the origin is thus close to the sulphur atom. The reader is referred to § 10 of Pawley (1972) for the relationship between the **T**, **L** and **S** parameters and the more customary individual atom anisotropic temperature factors.

The free refinement of Nelmes (1971) yielded the thermal parameters listed in Table 1. The anomalously high values in $S1$ are evident. With the TLS constraint applied the **T** and **L** parameters refined to the values given in Table 2. $\mathbf{T}_1$ and $\mathbf{T}_2$ do not differ markedly: $\mathbf{L}_1$ and $\mathbf{L}_2$ do. If the small values of L_{23} and L_{12} are ignored, $\mathbf{L}_1$ has eigenvalues $L'_{11}=0{\cdot}011$, $L'_{22}=0{\cdot}018$ and $L'_{33}=0{\cdot}048$ radian^2 referred to eigenvectors close to [201], [010] and [$\bar{1}$02] – in terms of unit vectors along X, Y and Z. The anomalous thermal behaviour of $S1$ can thus be described as a pronounced libration of the group about a direction close to [$\bar{1}$02].

Combining the principal **T** and **L** amplitudes for $S2$ (the screw tensor makes relatively small contributions) the oxygen atoms have a mean-square thermal motion of $\sim0{\cdot}05$ Å^2, which is a physically reasonable ('normal') magnitude at room-temperature [compare for example the study of $(NH_4)_2SO_4$ by Schlemper & Hamilton, 1966]. For $S1$ the value is $\sim0{\cdot}13$ Å^2. These figures agree with the free refinement (see Table 1). It is readily shown that if the mean-square motion for an atom, in direction **i**, is in excess of the 'normal' value by Δ then an approximately equivalent description is given by two 'half atoms' – with 'normal' thermal motion – separated along **i** by $2\Delta^{1/2}$. Here $\Delta \sim 0{\cdot}08$ Å^2, so that the separation is 0·55 Å.

Table 2. *Thermal parameters for model* 2

The subscripts on **T** and **L** refer to $S1$ and $S2$. T_{11} is the mean-square translational motion along the X axis (in $10^{-3} \times$ Å^2), L_{11} is the mean-square librational motion about the X axis (in $10^{-3} \times$ radian^2), *etc.*, referred to an origin as defined in the text (§3). Least-squares errors are of the order of 0·6 units on T_{33} ($\mathbf{T}_1$), T_{12} ($\mathbf{T}_1$), L_{33} ($\mathbf{L}_1$) and L_{12} ($\mathbf{L}_1$), and 0·3 units otherwise.

	$\mathbf{T}_1$	$\mathbf{T}_2$		$\mathbf{L}_1$	$\mathbf{L}_2$
T_{11}	33	25	L_{11}	19	9
T_{22}	23	22	L_{22}	18	11
T_{33}	39	26	L_{33}	42	11
T_{23}	−3	2	L_{23}	1	1
T_{31}	6	−2	L_{31}	−15	4
T_{12}	−3	−3	L_{12}	1	3

This suggested an alternative model in which the $S1$ group is disordered between two sites. To obtain initial coordinates the oxygen atoms of $S1$ were each separated into two 'half atoms' by rotation of the group in opposite senses (+ and −) about [$\bar{1}$02] to give sites $\sim$0·55 Å apart and equally displaced from the ordered model coordinates (Nelmes, 1971). The ordered model is denoted O, and the disordered, D. In the latter $S1$ is replaced by $S1_D$ comprising $S1^+$ [S(1)$^+$, O(1)$^+$, O(2)$^+$, O(3)$^+$ and O(4)$^+$] and $S1^-$ [S(1)$^-$, O(1)$^-$, O(2)$^-$, O(3)$^-$ and O(4)$^-$].

The occupancies of $S1^+$ and $S1^-$ may not be equal. A parameter α was introduced such that the occupancy of $S1^+$ is α, and that of $S1^-$ is $1-\alpha$.

If the TLS constraint is applied the ordered model requires two sets of constrained thermal parameters, TLS_1 for $S1$ and TLS_2 for $S2$. The disorder model requires TLS_1^+ for $S1^+$ and TLS_1^- for $S1^-$. The constraint $\mathrm{TLS}_1^+ = \mathrm{TLS}_1^-$ was to be tested.

To determine whether or not the SO_4^{2-} groups are significantly distorted, models were refined with these groups constrained to a regular shape – accepting that earlier results had established the S–O(H) bonds to be significantly longer than the S–O bonds, where O(H) denotes the oxygen to which the hydrogen atom is closer in the hydrogen bonds linking sulphate groups along **b** (see Nelmes, 1971). The constraint applied was as follows: the three oxygens other than O(H) form an equilateral triangle of variable size; the sulphur and O(H) atoms lie on a line which is perpendicular to this triangle and passes through its centroid; and the distances of the sulphur and O(H) atoms from the plane of the triangle are separately variable. This constraint is designated F (full shape). Applied to the various groups it is denoted F_1 for $S1$, F_2 for $S2$, F_1^+ for $S1^+$ and F_1^- for $S1^-$. In some models the constraint was relaxed to the extent that the O(H) atom positions were refined independently, each with the usual three positional parameters. So in this case the shape constraint (designated P – partial shape) applied only to the basal oxygen triangle and the sulphur atom (the SO_3 group). The symbols for such a constraint applied to the various groups are distinguished as above (*e.g.* P_1^+ for $S1^+$). The groups were constrained to have the same dimensions (*e.g.* $F_1 = F_2$ and $P_1^+ = P_1^- = P_2$), allowed to vary their dimensions independently (*e.g.* F_1^+, F_1^-, F_2) or partly constrained (*e.g.* $P_1^+ = P_1^-$, P_2).

The orientation of each group was defined by constructing an axial system, x, y and z, in the SO_4^{2-} ion (see Pawley, 1972, §8). Taking the centroid of the basal oxygen triangle, C, to define the origin, **x** was set along CO_B, where O_B is one of the basal oxygens [O(3)$^+$, O(3)$^-$ or O(8)], **z** along CS – the direction of C to the sulphur, and **y** along $\mathbf{z} \wedge \mathbf{x}$. In refinement the *shape* is varied using the lengths CO_B,CS and, unless omitted, COH [C to O(H)]; the *position* of each group is determined by the variable coordinates X_c, Y_c and Z_c of C; and the *orientation* is given by three variable Euler angles, φ, θ and ψ (Pawley, 1972, §8; Goldstein, 1962). These three angles define the rotations of the group axes x, y and z with respect to the crystal axes X, Y and Z that are necessary to bring the atoms of the group into the correct relative orientation with respect to the crystal axes. Starting with the SO_4^{2-} group positioned such that x, y and z are parallel to X, Y and Z respectively, the group is first rotated (in a left-handed sense) by φ about Z, then by θ about X, and finally by ψ about Z. In each group the positions of all the atoms are thus fully defined by nine parameters – three each for shape (CO_B, CS and COH), position X_c, Y_c and Z_c) and orientation (φ, θ and ψ). In models where O(H) is freed from the shape constraint the shape is defined by two parameters (CO_B and CS), and three extra parameters are required to locate each O(H).

In most of the models the refinement did not include the HSO_4^- hydrogen atoms. The significance of their inclusion in the structural model – given the experimental data – was tested.

Throughout all refinements the ammonium groups N(1) and N(2) were treated as single units (see Nelmes, 1971) each with three positional and six thermal parameters.

4. Refinements and significance tests

Table 3 summarizes the models of AHS refined in this present study. First is given the number by which the model is referred to in the text. Hereafter 'model n' will be designated Mn, *e.g.* $M9$. Then follow the details of the model using symbols explained in §3. The occupancy α is refined (R) or fixed at 0·5. H under the column headed H signifies the inclusion of the HSO_4^- hydrogen atoms. NP is the number of parameters required to describe the model. R_w is defined in the text (§2). Where α is refined its value and standard deviation ($\times 10^2$ in brackets) are given.

The conclusions to be derived from Table 3 are presented as a series of hypotheses. Each hypothesis is tested using the value of $\mathcal{R}$ calculated as the square-root of the ratio of the R_w values for the two models concerned (see §2). The level of significance of $\mathcal{R}$ is found from Table 4 for which the $\mathscr{R}$-distribution points were obtained by the method due to Pawley (1970).

(i) *Disorder*

Hypothesis 1: $S1$ is disordered.

Compare $M1$ and $M21$ which give $\mathscr{R}=(333/208)^{1/2}=1{\cdot}265$. Table 4 shows that the hypothesis can be accepted at the 0·001 significance level.

It is convenient to establish this hypothesis concerning disorder first; but the comparison involves the assumptions that $\alpha=0{\cdot}5$, and that the (as yet) untested inclusion of hydrogen is permissible. It is shown later that α is not significantly different from 0·5, and it is argued below that, with one exception, interaction of the constraints (of which the exclusion of hydrogen may be considered one) is negligible.

(ii) *α and the TLS constraint for $S1_D$*

Hypothesis 2: $\alpha=0{\cdot}5$.

Hypothesis 3: $\mathrm{TLS}_1^+\neq\mathrm{TLS}_1^-$.

These two hypotheses cannot be tested separately as they are clearly correlated. This is illustrated in Table 5 where the principal **T** and **L** parameters for $M8$ and $M16$ are given. $\mathbf{T}_1^+$ and $\mathbf{L}_1^+$ are the **T** and **L** tensors for $S1^+$; $\mathbf{T}_1^-$ and $\mathbf{L}_1^-$ refer to $S1^-$. As expected, a decrease in α corresponds to an overall increase of the thermal parameters of $S1^-$ relative to those of $S1^+$.

Sub-hypothesis 2*a*: If $\alpha=0{\cdot}5$ then $\mathrm{TLS}_1^+\neq\mathrm{TLS}_1^-$.

Compare $M6$ and $M9$. $\mathscr{R}=1{\cdot}185$, and the hypothesis can be accepted at the 0·001 level. It is then evident from $M9$ and $M10$ that $\alpha=0{\cdot}5$. This conclusion is supported by comparisons $M11/M12$, $M16/M17$ and $M18/M19$.

Thus hypotheses 2 and 3 are accepted at the 0·001 level.

Here it is worth comparing the thermal parameters for the ordered model ($M2$) and disordered model ($M16$) given in Tables 2 and 5 respectively. Within error the parameters of $S2$ are the same for both. Those of $S1^+$ and $S1^-$ (particularly the libration parameters) remain significantly higher than those of $S2$ – which is physically reasonable. The effect of introducing the disorder model is seen in reducing L_{33} (of $\mathbf{L}_1^+$ and $\mathbf{L}_1^-$) to the same order of magnitude as L_{11} and L_{22}.

(iii) *Shape constraints*

Hypothesis 4: The sulphate groups all have a regular shape of the same dimensions ($F_1^+=F_1^-=F_2$).

Compare $M9$ and $M16$. $\mathscr{R}=1{\cdot}342$, and the hypothesis can be rejected at the 0·001 level.

Sub-hypothesis 4*a*: If the groups all have a regular shape of the same dimensions ($P_1^+=P_1^-=P_2$) the O(H) atoms must be free.

Compare $M9$ and $M11$. $\mathscr{R}=1{\cdot}266$, and the hypothesis is accepted at the 0·001 level.

Table 3. *Refined models*

Symbols used are explained in the text.

To assist any readers wishing to derive the listed values of NP for themselves the following example is given. In $M9$ there are two ammonium groups requiring three positional and six thermal parameters each (18 in all); and there are three sulphate groups which are independent with regard to (i) thermal motion (20 TLS parameters × 3 = 60 in all), (ii) position (3 parameters × 3 = 9) and (iii) orientation (3 parameters × 3 = 9), but are all the same shape (3 parameters only). There is one scale factor. Hence NP = 18 + 60 + 9 + 9 + 3 + 1 = 100. Another example is afforded by studying Table 7 in relation to $M14$.

	Model and constraints								
			Shape						
M	O/D	TLS	F/P	O(H)	α	H	NP	$R_w\times10^{-2}$	α
1	O					H	119	333	
2	O	TLS_1, TLS_2				H	99	352	
3	O	TLS_1, TLS_2	$F_1 = F_2$				74	782	
4	O	TLS_1, TLS_2	$P_1 = P_2$	Free			79	465	
5	O	TLS_1, TLS_2					89	385	
6	D	$\mathrm{TLS}_1^+=\mathrm{TLS}_1^-$, TLS_2	$F_1^+=F_1^-=F_2$		0·5		80	619	
7	D	$\mathrm{TLS}_1^+=\mathrm{TLS}_1^-$, TLS_2	$F_1^+=F_1^-=F_2$		R		81	546	0·65 (1)
8	D	$\mathrm{TLS}_1^+=\mathrm{TLS}_1^-$, TLS_2			R		105	296	0·68 (1)
9	D	TLS_1^+, TLS_1^-, TLS_2	$F_1^+=F_1^-=F_2$		0·5		100	441	
10	D	TLS_1^+, TLS_1^-, TLS_2	$F_1^+=F_1^-=F_2$		R		101	441	0·50 (2)
11	D	TLS_1^+, TLS_1^-, TLS_2	$P_1^+=P_1^-=P_2$	Free	0·5		108	275	
12	D	TLS_1^+, TLS_1^-, TLS_2	$P_1^+=P_1^-=P_2$	Free	R		109	275	0·47 (2)
13	D	TLS_1^+, TLS_1^-, TLS_2	F_1^+, F_1^-, F_2		0·5		106	426	
14	D	TLS_1^+, TLS_1^-, TLS_2	$P_1^+=P_1^-$, P_2	Free	0·5		110	266	
15	D	TLS_1^+, TLS_1^-, TLS_2	P_1^+, P_1^-, P_2	Free	0·5		112	262	
16	D	TLS_1^+, TLS_1^-, TLS_2			0·5		124	245	
17	D	TLS_1^+, TLS_1^-, TLS_2			R		125	245	0·47 (3)
18	D				0·5		154	231	
19	D				R		155	231	0·48 (3)
20	D	TLS_1^+, TLS_1^-, TLS_2			0·5	H	139	220	
21	D				0·5	H	169	208	

Sub-hypothesis 4*b*: If the groups all have a regular shape but of differing dimensions ($P_{\bar{1}}^{+}$, $P_{\bar{1}}^{-}$, P_2) the O(H) atoms must be free.

Compare *M*13 and *M*15. $\mathscr{R}$ = 1·275, and the hypothesis is accepted at the 0·001 level.

It is clear that the full constraint *F* cannot be applied: the O(H) atoms, at least, must be free. Now the validity of the partial constraint *P* is examined.

Sub-hypothesis 4*c*: The shape of the SO_3 group in *S*2 is different from the shape of the SO_3 groups in $S1^+$ and $S1^-$ ($P_{\bar{1}}^{+}=P_{\bar{1}}^{-}$, P_2).

Compare *M*11 and *M*14. $\mathscr{R}$ = 1·017, and the hypothesis is accepted at the 0·001 level.

Sub-hypothesis 4*d*: The SO_3 groups of *S*2, $S1^+$ and $S1^-$ differ in dimensions ($P_{\bar{1}}^{+}$, $P_{\bar{1}}^{-}$, P_2).

Compare *M*14 and *M*15. $\mathscr{R}$ = 1·008 and the hypothesis is accepted at the 0·001 level.

Sub-hypothesis 4*e*: No regular shape constraint, *P*, can be applied to the SO_3 groups.

Compare *M*15 and *M*16. $\mathscr{R}$ = 1·034, and the hypothesis is accepted at the 0·001 level.

(iv) *The TLS constraint*

Hypothesis 5: In thermal motion the sulphate groups behave as rigid bodies.

Compare *M*16 and *M*18. $\mathscr{R}$ = 1·030, and the hypothesis is rejected at the 0·001 level.

(v) *The* HSO_4^- *hydrogen atoms*

Hypothesis 6: The inclusion of hydrogen is significant.

Compare *M*18 and *M*21. $\mathscr{R}$ = 1·054, and the hypothesis is accepted at the 0·001 level.

Here it must be interjected that some difficulties were encountered in the refinement of models *M*20 and *M*21 – which included the HSO_4^- hydrogen atoms. Using the parameters of *M*16 and *M*18, difference Fourier maps were calculated for the asymmetric unit. In the region of the short $O(3)^+$–$O(4'')^+$ and $O(3)^-$–$O(4'')^-$ separations — O(4″) is related to O(4) by a translation of ± **b** (see Nelmes, 1971) — the positive density shown in Fig. 1 was found. Closely similar maps were obtained from both models. Fig. 1 suggests splitting of the H(9) hydrogen atom between two sites, $H(9)^+$ and $H(9)^-$, and in a way which is in accord with the positions of the O(H) atoms, $O(4)^+$ and $O(4)^-$ (see Table 6). Such a splitting is to be expected given the disordering of *S*1, but its manifestation in these maps could be an artefact arising from the disordered *S*1 model itself. Attempts to obtain stable refinements of the position, associated charge and isotropic temperature factors of $H(9)^+$ and $H(9)^-$ were unsuccessful when the parameters of the associated oxygen atoms, $O(4)^+$ and $O(4)^-$, were also allowed to refine.

Initial values for the hydrogen positional coordinates were obtained from the difference Fourier maps.

Table 4. *Parameters of model comparison and values of the* $\mathscr{R}$*-distribution points*

The number of observations is 3248 throughout. NPC is the number of parameters with the constraint being tested in force: NP is the number of parameters with that constraint removed. The values of the $\mathscr{R}$-distribution points are given at the 25, 10, 5, 1 and 0·1 percent significance levels. $\mathscr{S}$ is explained in the text (§ 4).

Hypothesis	Models	$\mathscr{R}$	NPC	NP	0·25	0·10	0·05	0·01	0·001	$\mathscr{S}$
1	*M*1/*M*21	1·265	119	169	1·009	1·010	1·011	1·012	1·014	22·1
2*a*	*M*6/*M*9	1·185	80	100	1·004	1·005	1·005	1·006	1·007	30·8
4	*M*9/*M*16	1·342	100	124	1·005	1·005	1·006	1·007	1·008	48·9
4*a*	*M*9/*M*11	1·266	100	108	1·002	1·002	1·002	1·003	1·004	88·7
4*b*	*M*13/*M*15	1·275	106	112	1·001	1·002	1·002	1·003	1·003	91·7
4*c*	*M*11/*M*14	1·017	108	110	1·000	1·001	1·001	1·001	1·002	17·0
4*d*	*M*14/*M*15	1·008	110	112	1·000	1·001	1·001	1·001	1·002	8·0
4*e*	*M*15/*M*16	1·034	112	124	1·002	1·003	1·003	1·004	1·005	8·5
5	*M*16/*M*18	1·030	124	154	1·006	1·006	1·007	1·008	1·010	3·8
6	*M*18/*M*21	1·054	154	169	1·003	1·004	1·004	1·005	1·006	10·8

Table 5. *Thermal parameters and* α *for M*8 *and M*16

$\mathbf{T}_1^+=\mathbf{T}_1^-$ and $\mathbf{L}_1^+=\mathbf{L}_1^-$ for *M*8.

T_{ij} and L_{ij} (see Table 2) are listed only for $i=j$.

T_{ij} are in units of 10^{-3} Å²; L_{ij} in 10^{-3} radian².

The least-squares errors on the elements of $\mathbf{T}_1^+$, $\mathbf{T}_1^-$, $\mathbf{L}_1^+$ and $\mathbf{L}_1^-$ are of the order of 1 unit. Those on the elements of $\mathbf{T}_2$ and $\mathbf{L}_2$ are of the order of 0·3 units.

Sulphate group			*M*8	*M*16			*M*8	*M*16
		T_{11}	29	27		L_{11}	7	20
$S1^+$	$\mathbf{T}_1^+$	T_{22}	21	26	$\mathbf{L}_1^+$	L_{22}	9	17
		T_{33}	37	30		L_{33}	31	10
		T_{11}	29	38		L_{11}	7	22
$S1^-$	$\mathbf{T}_1^-$	T_{22}	21	18	$\mathbf{L}_1^-$	L_{22}	9	10
		T_{33}	37	39		L_{33}	31	21
		T_{11}	25	25		L_{11}	9	9
*S*2	$\mathbf{T}_2$	T_{22}	22	22	$\mathbf{L}_2$	L_{22}	10	10
		T_{33}	26	26		L_{33}	12	12
		α	0·68 (1)	0·5		α	0·68 (1)	0·5

For $M20$ and $M21$ these coordinates were refined together with the associated charge – but keeping all other parameters fixed and the isotropic temperature factor, B, for each hydrogen set at 3·0 (Å^2/8π^2).

For H(9)$^+$, H(9)$^-$ and H(10) respectively, the final values of the associated charges were 0·30, 0·31 and 0·55 electrons ($M20$), and 0·24, 0·28 and 0·52 electrons ($M21$) (compare Table 1 of Nelmes, 1971). The higher values to be expected for both the associated charge and the temperature factors could be obtained by allowing the neighbouring oxygen atom parameters to refine. But then, as said, the H(9)$^+$ and H(9)$^-$ parameters became unstable, although H(10) refined as before (Nelmes, 1971).

The hydrogen atoms are discussed further in § 5.

Throughout the above testing of hypotheses it has been assumed that the various constraints are not significantly correlated – with the exception of [$\alpha = 0{\cdot}5$ and $\text{TLS}_\text{I}^+ = \text{TLS}_\text{I}^-$]. For example there is no model in which a shape constraint is applied without the TLS constraint. An attempt to refine models with all combinations of constraints would meet the constraint of available computing time. But, in any case, the assumption can be shown to be reasonable. Firstly the effect of removing a particular constraint can be seen not to depend on the other constraints in force to a degree that would vitiate any of the conclusions reached. Examples are (*a*) removing the shape constraint (compare $M3/M5$, $M7/M8$ and $M9/M16$); (*b*) freeing the O(H) atom (compare $M3/M4$ and $M9/M11$); and (*c*) removing the TLS constraint (compare $M2/M1$ and $M16/M18$). Secondly the relevant correlation coefficients obtained from the least-squares refinement were small ($\le 0{\cdot}15$). The correlation coefficients between α and the $\text{TLS}_\text{I}^+ = \text{TLS}_\text{I}^-$ parameters were significantly larger in comparison ($\le 0{\cdot}30$). This second argument is evidently weakened by the fact that each constraint is generally described by several parameters and thus correlation between constraints is expressed – somewhat inscrutably – by several coefficients. It would be a useful addition to these techniques to devise and calculate a single coefficient of correlation for each pair of constraints.

For the reasons outlined earlier (§ 2) it is difficult or impossible to assess physical significance rigorously for a given level of statistical significance. An empirical approach can be adopted. For single (free) refinements it has been assessed that with current models and data the errors obtained from least-squares refinement should be increased by a factor of up to three or more to be realistic (Hamilton, 1969). (This is to be borne in mind in the subsequent section in relation to Tables 6, 7 and 8.) In the context of the methods used here this estimate of unaccounted error might be incorporated by calculating the standard deviation of R_w; but Pawley (1972, §12) suggests another empirical approach.

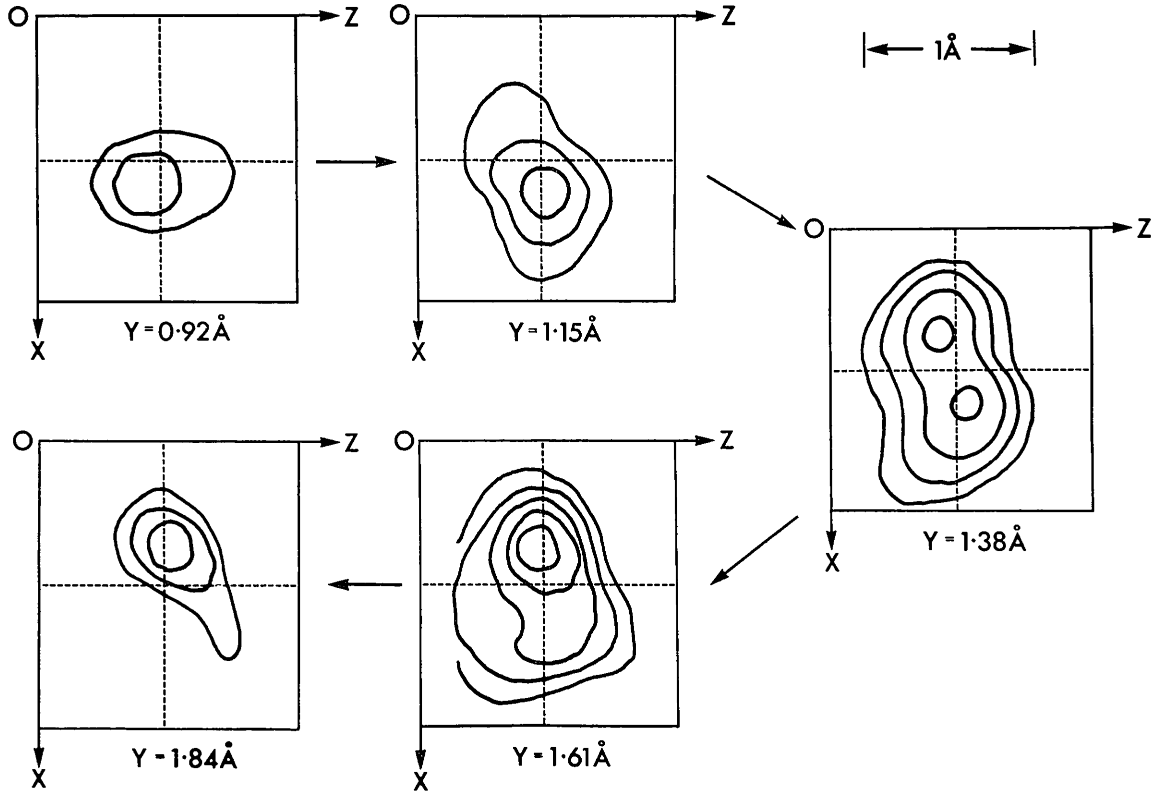

Fig. 1. Sections of the difference Fourier map taken at increasing Y (shown →) in the region of the short hydrogen bonds linking $S1_D$ groups along Y. The X, Z coordinates of the origin O, remain constant.

He employs the ratio $\mathscr{S}$ as an approximate index of the statistical significance of the same constraint applied in different materials.

$\mathscr{S}=(\mathscr{R}-1)/[\mathscr{R}(0{\cdot}01)-1]$, where $\mathscr{R}(0{\cdot}01)$ is the 0·01 point of the $\mathscr{R}$ distribution for the appropriate degrees of freedom. A conservative inference is that $\mathscr{S}$ values of the order of 3 or less may not indicate *physical* significance. Values of $\mathscr{S}$ for the AHS refinements are given in Table 4. Clearly all the conclusions reached are very strongly indicated, except that removing the TLS constraint (*M*16/*M*18) may not be physically significant within the resolution of the data.

5. The structure

The AHS structure has been fully described and discussed by Nelmes (1971). Here only those new features which have emerged from this study will be described.

The conclusions reached in §4 are

(i) that the *S*1 group is disordered and is equally distributed between its two sites,

(ii) that the inclusion of the HSO_4^- hydrogen atoms in the model is significant,

(iii) that the displacement of the O(H) atoms from positions conforming to regular trigonally shaped SO_4^{2-} groups (§2) is very significant,

(iv) and that although strictly the TLS (rigid-body thermal motion) and shape ($P_1^+=P_1^-$, P_2) constraints should not be applied, the indication against the shape constraint is relatively weak and that against the TLS constraint is of possibly marginal physical significance. They are 'reasonable' constraints giving a description closely approximating the 'true' structure.

Table 6 lists the final parameters for the unconstrained disorder model (*M*21). In view of (iv) above the final parameters of *M*14 are also given (see Table 7).

The disordering of the *S*1 group is illustrated in Figs. 2 and 3.* The occupancies of the two configurations have been shown to be equal within error. Although *S*2 is in a very similar environment (Nelmes, 1971) there is no indication that it is disordered.

The sulphate groups have been shown to be distorted, principally in the displacement of the O(H) atoms. In Table 8 the S–O bond lengths for *M*21 and *M*14 are compared. In the free refinement each pair of disordered oxygen atoms [*e.g.* $O(1)^+$ and $O(1)^-$] move closer together along *Y* and apart along *Z*, while $S(1)^+$ and $S(1)^-$ move closer together along *X* and *Z* (see Tables 6 and 7). It is very doubtful whether this is of any physical significance – this effect, and also the markedly greater errors found in *M*21 for the bond lengths of $S1^+$ and $S1^-$ compared with those of *S*2, are both attributable to high correlation.

The figures in Table 8 illustrate well two features of the constrained refinement technique referred to earlier (§2). In the presence of this high correlation it would be difficult indeed to test any shape hypothesis given only the free refinement (*M*21) results; and if a constraint does apply (as *M*14 assumes) it is seen how the accuracy of parameters in the constrained set (*i.e.* the

Table 6. *Final values of structural parameters and their standard deviations for M*21

Temperature factor $=\exp[-2\pi^2(U_{11}(ha^*)^2+2U_{12}(ha^*kb^*)+\ldots)]$.
The coordinates, *X*, *Y* and *Z* are given in Å, and the thermal parameters, U_{ij}, in Å^2.

Standard deviations (on the last quoted decimal place) are given in brackets. They do not take account of the errors in the cell dimensions.

	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
$S(1)^+$	1·524 (3)	3·296 (4)	1·605 (5)	0·0250 (9)	0·027 (1)	0·0302 (7)	−0·0053 (8)	0·0048 (6)	−0·0091 (9)
$O(1)^+$	0·414 (10)	2·734 (12)	2·277 (11)	0·050 (3)	0·053 (4)	0·056 (3)	−0·027 (2)	0·029 (2)	−0·024 (3)
$O(2)^+$	2·687 (8)	3·417 (8)	2·328 (8)	0·036 (2)	0·073 (3)	0·061 (3)	0·016 (2)	−0·018 (2)	−0·021 (2)
$O(3)^+$	1·131 (5)	4·476 (7)	0·837 (5)	0·058 (2)	0·033 (2)	0·048 (2)	0·005 (1)	0·001 (2)	0·007 (2)
$O(4)^+$	1·947 (8)	2·293 (11)	0·488 (10)	0·047 (3)	0·048 (3)	0·052 (4)	−0·020 (2)	0·024 (3)	−0·003 (2)
$S(1)^-$	1·548 (4)	3·276 (4)	1·689 (5)	0·044 (1)	0·019 (1)	0·048 (2)	−0·001 (1)	0·006 (1)	0·004 (1)
$O(1)^-$	0·358 (9)	2·940 (12)	2·345 (10)	0·033 (2)	0·044 (3)	0·035 (2)	−0·010 (3)	0·009 (2)	−0·001 (2)
$O(2)^-$	2·735 (7)	3·045 (8)	2·538 (7)	0·048 (2)	0·092 (5)	0·046 (2)	−0·012 (3)	−0·008 (2)	0·022 (3)
$O(3)^-$	1·549 (7)	4·607 (7)	1·187 (7)	0·108 (5)	0·025 (2)	0·117 (5)	0·013 (3)	0·004 (3)	0·002 (3)
$O(4)^-$	1·569 (8)	2·382 (11)	0·402 (10)	0·054 (4)	0·043 (3)	0·026 (1)	0·002 (2)	0·005 (2)	−0·001 (2)
S(2)	7·7335 (3)	3·5044 (4)	1·5873 (3)	0·0262 (1)	0·0228 (1)	0·0265 (1)	0·0018 (1)	−0·0013 (1)	−0·0030 (1)
O(5)	6·580 (1)	3·162 (1)	2·370 (1)	0·0367 (5)	0·0580 (8)	0·0417 (6)	0·0010 (6)	0·0110 (5)	−0·0115 (5)
O(6)	8·801 (1)	4·070 (1)	2·371 (1)	0·0372 (5)	0·0405 (6)	0·0360 (5)	0·0032 (5)	−0·0111 (4)	−0·0112 (5)
O(7)	7·263 (1)	4·590 (1)	0·570 (1)	0·0484 (6)	0·0280 (5)	0·0415 (5)	0·0061 (5)	−0·171 (5)	−0·0022 (5)
O(8)	8·184 (1)	2·405 (1)	0·748 (1)	0·0459 (6)	0·0257 (5)	0·0430 (6)	−0·0040 (5)	0·0035 (5)	0·0032 (5)
N(1)	1·546 (1)	2·939 (2)	5·225 (1)	0·0294 (6)	0·0393 (7)	0·0397 (7)	0·0003 (6)	−0·0009 (5)	−0·0013 (5)
N(2)	7·719 (1)	3·671 (2)	5·186 (1)	0·0356 (6)	0·0485 (9)	0·0325 (6)	0·0001 (6)	0·0021 (5)	−0·0029 (7)
$H(9)^+$	1·84 (5)	1·29 (6)	0·70 (4)						
$H(9)^-$	1·41 (5)	1·78 (6)	0·69 (4)						
H(10)	7·63 (2)	0·77 (3)	0·68 (2)						

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* I thank the referee for suggesting that it be made clear that the disorder as shown in Fig. 2 can be distinguished from a case in which the *S*1$_D$ sites are occupied systematically by $S1^+$ for one and $S1^-$ for the other, thereby degrading the symmetry to $P2_1/a$ or $P2_1/c$, pseudo *B* centred. Cu *Kα* Weissenberg photographs of the *h*0*l* layer show none of the weak *l* odd or *h* odd reflexions which this alternative would require.

Table 7. *The final values of the structural parameters and their standard deviations for M*14

The parameters for N(1) and N(2) are given as X, Y, Z (Å) and U_{ij} (Å^2). For each sulphate group the coordinates of C – denoted (C) – are given in Å in order X_c, Y_c and Z_c, the Euler angles (E) in order φ, θ and ψ are given in radians, and the shape parameters CO_B and CS in Å (see §3). The coordinates X, Y and Z of the unconstrained O(H) atoms (U) are given in Å. The TLS thermal parameters are listed for each group: **T** parameters (in order T_{11}, T_{22}, T_{23}, T_{33}, T_{31}, T_{12}) are given in Å^2, **L** parameters (L_{11}, L_{22}, L_{33}, L_{23}, L_{31}, L_{12}) in radian^2, and **S** parameters (S_{23}, S_{31}, S_{12}, S_{32}, S_{13}, S_{21}, S_{33}–S_{22}, S_{11}–S_{33}) in Å.radians (see §3). For all refined parameters errors are given (in brackets) on the last quoted decimal place. These errors do not include the uncertainty in the cell dimensions. The coordinates of the shape constrained atoms are calculated (from the C, E, CO_B and CS parameters) and output by the refinement program. These coordinates are listed to the right of the Table (in Å). Their errors are ~0·009 Å for $S1^+$ and $S1^-$ oxygen atoms, ~0·004 Å for S(1)$^+$ and S(1)$^-$, ~0·001 Å for $S2$ oxygen atoms, and ~0·0006 Å for S(2).

		X	Y	Z	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
N(1)		1·546 (1)	2·939 (2)	5·225 (1)	0·0293 (6)	0·0395 (7)	0·0398 (7)	0·0004 (6)	−0·0010 (5)	−0·0012 (6)
N(2)		7·718 (1)	3·671 (2)	5·186 (1)	0·0352 (6)	0·0486 (9)	0·0328 (6)	0·0002 (7)	0·0019 (5)	−0·0033 (7)
					T	**L**	**S**	X	Y	Z
S(1)$^+$	(C)	1·415 (4)	3·546 (4)	1·833 (4)	0·0289 (6)	0·0183 (9)	−0·0046 (7)	1·504	3·279	1·562
O(1)$^+$	(E)	1·547 (6)	3·945 (3)	−0·323 (7)	0·0275 (8)	0·0213 (8)	−0·0006 (7)	0·413	2·727	2·309
O(2)$^+$	(CO_B)	1·378 (1)			0·0282 (6)	0·008 (2)	−0·0034 (8)	2·688	3·447	2·350
O(3)$^+$	(CS)	0·391 (1)			−0·0039 (4)	0·0012 (9)	0·0009 (7)	1·142	4·463	0·842
					0·0040 (4)	−0·0057 (6)	−0·0033 (7)			
					−0·0069 (6)	0·003 (1)	−0·0016 (8)			
O(4)$^+$	(U)	1·906 (7)	2·276 (7)	0·474 (6)			0·015 (2)			
							−0·006 (1)			
S(1)$^-$	(C)	1·546 (4)	3·537 (3)	2·036 (4)	0·0361 (8)	0·0159 (9)	−0·0018 (8)	1·567	3·293	1·731
O(1)$^-$	(E)	1·500 (7)	3·816 (4)	−0·086 (7)	0·0181 (7)	0·0124 (7)	−0·0038 (9)	0·353	2·961	2·413
O(2)$^-$	(CO_B)	1·378 (1)†			0·036 (1)	0·028 (2)	0·0004 (9)	2·736	3·034	2·518
O(3)$^-$	(CS)	0·391 (1)†			−0·0029 (6)	0·002 (1)	0·0046 (9)	1·551	4·615	1·179
					0·0026 (6)	−0·0044 (9)	0·0162 (9)			
					0·0006 (6)	−0·004 (1)	−0·0039 (9)			
O(4)$^-$	(U)	1·604 (7)	2·411 (7)	0·414 (5)			0·001 (1)			
							−0·004 (2)			
S(2)	(C)	7·8510 (4)	3·2166 (6)	1·8344 (5)	0·0259 (3)	0·0084 (3)	0·0012 (2)	7·7341	3·5033	1·5861
O(5)	(E)	1·5704 (7)	4·0365 (7)	−3·5286 (9)	0·0226 (2)	0·0108 (3)	−0·0003 (2)	6·575	3·165	2·376
O(6)	(CO_B)	1·3875 (7)			0·0264 (2)	0·0124 (4)	−0·0028 (2)	8·800	4·072	2·375
O(8)	(CS)	0·3969 (8)			0·0017 (2)	0·0002 (2)	−0·0012 (2)	8·178	2·413	0·752
					−0·0014 (1)	0·0029 (2)	−0·0001 (2)			
					−0·0029 (2)	0·0032 (3)	0·0007 (2)			
O(7)	(U)	7·265 (1)	4·589 (1)	0·569 (1)			0·0024 (5)			
							−0·0026 (5)			

† Note that these are not varied independently – they are constrained to be the same as for $S1^+$.

S–O bond lengths) is increased. Note that while the constraint thus reduces the error in the relative positions of atoms within each SO_3 group, the error on their coordinates relative to the origin – and thus to atoms not in the group – is the same in both models (compare Tables 6 and 7).

Because of the high correlation between the parameters of $S1^+$ and $S1^-$ in $M21$, their O–S–O bond angles are unlikely to characterize meaningfully the distortion of these groups. The O–S–O bond angles of the $S2$ group are the same within error as previously published; and the environments of N(1) and N(2) remain sensibly the same as previously discussed (Nelmes, 1971) – with the exception of any possible effect of the $S1$ disorder. The hydrogen atom parameters are somewhat uncertain, as discussed in §4 and below. For these several reasons no other bond lengths or angles are listed. They may be calculated readily from the parameters in Tables 6 and 7.

It has been indicated in §4 that the parameters of the HSO_4^- hydrogen atoms are somewhat uncertain. This is particularly true of the thermal parameters, the associated charges and the separation of H(9) onto two disordered sites – though this last is certainly to be expected given the disorder of $S1$. One important feature seems well established: the evidence of the difference Fourier maps (*e.g.* Fig. 1) and of the significant lengthening of S–O(H) with respect to the other S–O sulphate bonds support a conclusion in accord with Nelmes (1971) that $H(9)^+$, $H(9)^-$ and H(10) are on off-centre sites ('ordered') in the $O(3)^+$–$O(4'')^+$, $O(3)^-$–$O(4'')^-$ and O(7)–O(8'') bonds. Ashmore (1970) found similar ordering in the structure of isomorphous RHS.

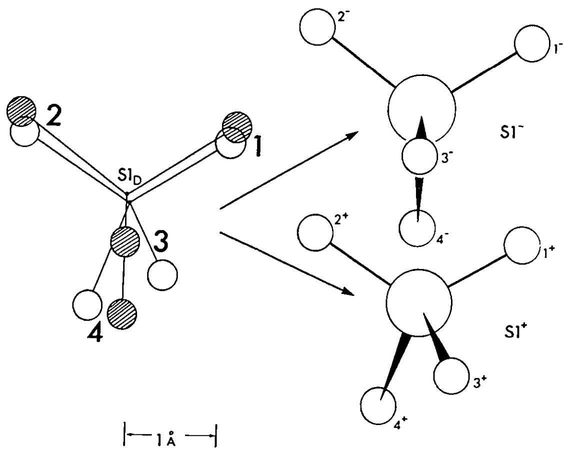

Fig. 3. The $S1_D$ group is shown at the left as it appears in Fig. 2, and on the right separated into its two configurations, $S1^+$ and $S1^-$. Here the sulphur atoms are represented by large circles. As indicated by the drawing, $O(3)^+$ and $O(4)^+$ are respectively above and below $S(1)^+$ relative to the plane of the diagram. Similarly for $O(3)^-$, $O(4)^-$ and $S(1)^-$.

The conclusion that the sulphate-linking hydrogens are ordered (in this sense) in the room-temperature phase is consistent with the recent study by Kasahara & Tatsuzaki (1970), who show that the transition in AHS at −3 °C is shifted by only 8 °C when the salt is 92% deuterated. Table 6 lists only the positional parameters of $H(9)^+$, $H(9)^-$ and H(10).

Thus the reliable information on these hydrogen atoms is limited to a very strong indication of being off-centre in the O–H···O bonds, and to reasonable

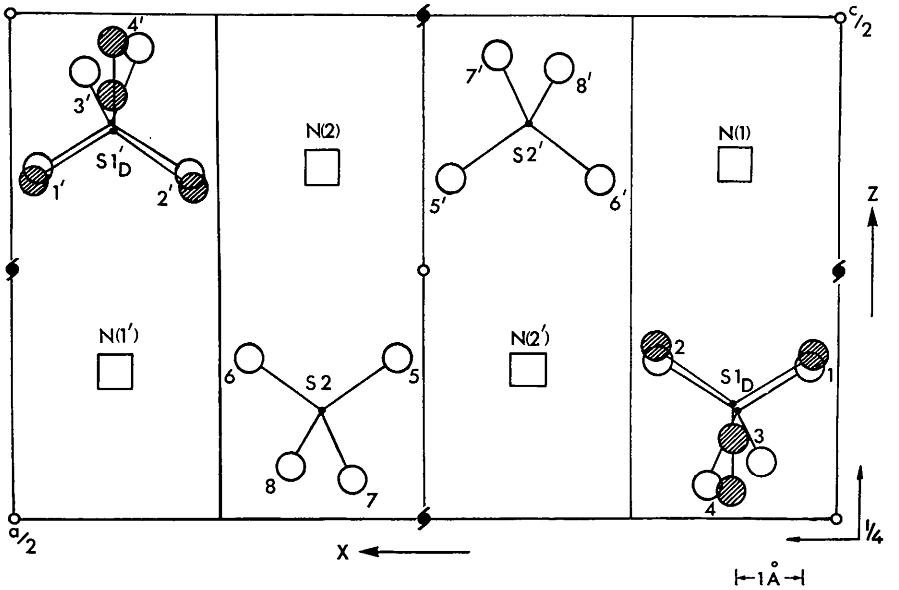

Fig. 2. A diagram of the structure projected onto (010). A quarter of the unit cell is shown, with the origin at a centre of symmetry. $B2_1/a$ symmetry elements are shown. Circles designate oxygen atoms, and squares the ammonium groups. The sulphur positions are shown as points. The single oxygen atom O(5) is labelled 5, and the disordered pair $O(1)^+$ and $O(1)^-$ is labelled 1, *etc.* The sulphate groups are labelled $S1_D$ ($S1^+$ and $S1^-$) and $S2$. Corresponding primed and unprimed symbols designate atoms or groups related by symmetry. Those which are unprimed constitute the asymmetric unit. In the $S1_D$ group the open circles are $S1^+$ oxygens and the shaded circles $S1^-$ oxygens (see Fig. 3). Compare the equivalent Fig. 1 of Nelmes (1971).

Table 8. *Sulphur–oxygen bond lengths for M*14 *and M*21

Bond lengths are in Å. Errors × 10^3 are given in brackets.

*M*14					
$S(1)^+$–$O(1)^+$ $S(1)^+$–$O(2)^+$ $S(1)^+$–$O(3)^+$	══	$S(1)^-$–$O(1)^-$ $S(1)^-$–$O(2)^-$ $S(1)^-$–$O(3)^-$	1·432 (1)	S(2)–O(5) S(2)–O(6) S(2)–O(8)	1·443 (1)
$S(1)^+$–$O(4)^+$	1·534 (8)	$S(1)^-$–$O(4)^-$	1·585 (8)	S(2)–O(7)	1·560 (2)
*M*21					
$S(1)^+$–$O(1)^+$	1·42 (11)	$S(1)^-$–$O(1)^-$	1·44 (10)	S(2)–O(5)	1·435 (1)
$S(1)^+$–$O(2)^+$	1·38 (8)	$S(1)^-$–$O(2)^-$	1·48 (8)	S(2)–O(6)	1·440 (1)
$S(1)^+$–$O(3)^+$	1·46 (8)	$S(1)^-$–$O(3)^-$	1·42 (9)	S(2)–O(8)	1·455 (2)
$S(1)^+$–$O(4)^+$	1·56 (11)	$S(1)^-$–$O(4)^-$	1·57 (11)	S(2)–O(7)	1·564 (2)

positional parameters – which accept the probability that H(9) is disordered. More complete and accurate information on this important feature of the structure should emerge from a full three-dimensional neutron structural study of ND_4DSO_4 currently being pursued by Mr K. D. Rouse at A.E.R.E., Harwell.

6. Conclusion

The techniques, value and application of a moderately straightforward extension of usual least-squares procedures have been illustrated. Some remaining difficulties have been outlined and a few possible improvements suggested. These techniques applied to AHS have led most importantly to the conclusion that in the phase above the ferroelectric transition the *S*1 sulphate group is disordered (equally) between two sites. The results of a recent study of the structure in the ferroelectric phase indicate that this feature plays an important role in the transition to the ferroelectric phase (Nelmes, 1972). The nature of the room-temperature disorder – principally its time scale – remains as an interesting problem for investigation by dynamical techniques. Advances in this direction are expected from some light-scattering experiments currently being performed in this Department.

The author wishes to thank Professor W. Cochran for his interest and encouragement in this work, Dr G. S. Pawley for his very generous help and guidance, and Dr P. Ashmore for kindly sending his unpublished results. The support of a Science Research Council Research Fellowship is gratefully acknowledged.

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X-ray Diffraction from Materials Containing Anti-Phase Domains

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(*Received* 24 *January* 1972)

A theory of X-ray diffraction from materials containing anti-phase domains is developed in terms of the characteristic function of the domain thickness distribution and the function J_p which is defined as the mean value of FF^* for cells separated by p domain boundaries. Also, an expression is derived for the domain thickness distribution which may be applied to the analysis of experimental data from any system in which the sizes of adjacent domains are uncorrelated.

Introduction

In certain order–disorder materials, Cu_3Au being the classic example, the transformation from the disordered to the ordered state is associated with the formation of anti-phase domains. When the domains in such a material are small the X-ray diffraction pattern exhibits broadened superlattice lines and lattice