Acta Cryst. (1956). **9**, 967

A note on the least-squares method: the refinement of the structure of $KAsF_6$.

By JAMES A. IBERS, *Shell Development Company, Emeryville, California, U.S.A.*

(*Received* 5 *July* 1956 *and in revised form* 4 *September* 1956)

The usual normal equations of the least-squares method are linear in the changes in the variables since they are derived from equations of condition which are in linear form. The reduction of these equations of condition to linear form involves an approximation, namely the termination of the Taylor-series expansion of the known functions in terms of changes in the variables at the first derivative terms (Whittaker & Robinson, 1944). Particularly in the later stages of the refinement of atomic coordinates, this approximation does not lead to serious errors. It will be shown below, however, that the usual normal equations cannot be used in the first refinement of the structure found by Roof (1955) for $KAsF_6$. On the other hand, modified normal equations, derived from the Taylor-series expansion, in which a second derivative term in one of the variables is retained, prove to be effective.

A summary of the crystal structure of $KAsF_6$, as determined recently by Roof (1955), is:

$KAsF_6$: C_{3i}^2–$R\overline{3}$ (from Weissenberg photography);
$a = 7{\cdot}352$, $c = 7{\cdot}235$ Å (hexagonal); $Z = 3$.
As in (a), K in (b), F in (f) with $x = 0{\cdot}117$, $y = 0{\cdot}234$, $z = 0{\cdot}152$, as determined from Fourier projections based on powder data out to $\theta_{Cu} = 40°$.

It is reasonable to assume, both from structural considerations and from the general agreement between observed and calculated intensities as given by Roof, that the heavy-atom positions he describes for $KAsF_6$ are correct. However, a serious objection to Roof's work is the fact that his Fourier 'refinement', which was based on powder data, *had* to lead to the condition $y = 2x$, as required by the space group D_{3d}^5–$R\overline{3}m$, since with powder data it is impossible to distinguish $R\overline{3}$ from $R\overline{3}m$. Thus, Roof did not refine the structure in the space group he proposed. Moreover, Roof found an R factor of 0·19 (see below) for a structure in which the heavy atoms are fixed by symmetry. In view of these facts it is unreasonable to assume that the fluorine positions given by Roof are reliable. As far as is known, $KAsF_6$ is the first solid to be studied by X-rays in which there is an As–F bond distance. It is of interest, then, to establish this distance accurately, if possible, by a proper refinement of the fluorine positions. For this purpose the least-squares method offers many advantages over other methods of refinement, such as Fourier techniques. An important advantage in this particular case is the fact that a least-squares procedure can be applied separately either to the structure in $R\overline{3}m$ or in $R\overline{3}$, whereas with powder data Fourier techniques are applicable only to structures in $R\overline{3}m$. Moreover, all the data can be utilized in the least-squares method, whereas the high degree of overlap of the data is a severe handicap to the use of Fourier techniques. In $KAsF_6$ forty-six reflections contribute to the twenty lines observed on the powder photograph; only eight of these lines result from single reflections.

In order to carry out the least-squares refinement we define the function G_j as $G_j = (\sum_i p_{ij}F_{ij}^2)^{1/2}$, where the sum is over each reflection i having calculated structure factor F_{ij} and multiplicity p_{ij} which contributes to the observed intensity I'_j. Our object is to minimize the quantity $\sum_j w_j(I_j^{1/2}-G_j)^2$, where I_j is the reduced intensity, that is the observed intensity I'_j corrected for such effects as the Lorentz factor, the polarization factor, and absorption. The quantity we wish to minimize is analogous to $\sum_{hkl} w(hkl)(|F_o|-|F_c|)^2$, whose minimization for the refinement of atomic coordinates was first suggested by Hughes (1941).

It is not difficult to prove that for $R\overline{3}$, as long as $y = 2x$, the $\partial G/\partial x$, which arises from the linearization of the equations of condition is identically zero for all powder lines. The resulting normal equations will contain no Δx terms. If $2x$ is only approximately equal to y, a large spurious shift in x may result because the terms $\partial G_j/\partial x$ are relatively small. (That is, $\sum_j (\partial G_j/\partial x)^2$ may not be much larger than $\sum_j (\partial G_j/\partial x)(I_j^{1/2}-G_j)$.) Thus, to start with a small, arbitrary shift in x is not a generally useful way of attacking the problem. Rather, a successful least-squares refinement may be effected by using normal equations which are based on equations of condition whose Taylor-series expansions retain the terms $\frac{1}{2}(\partial^2G/\partial x^2)(\Delta x)^2$. Since $\partial G/\partial x \equiv 0$, the resulting normal equations are quite similar to the usual ones. In fact, replacement of $(\Delta x)^2$ for (Δx) and of $\frac{1}{2}(\partial^2G/\partial x^2)$ for $(\partial G/\partial x)$ are the only changes. It is immediately evident that these modified normal equations will not lead to a unique determination of x, since if $(\Delta x)^2 = C$, then $\Delta x = \pm C^{1/2}$. This is just what one expects, however, for there exist two equivalent sets of parameters, namely x_1, y, z and

Table 1. *Least-squares refinement of* $KAsF_6$

Parameter	Initial	First refinement $R\overline{3}$		Final refinement $R\overline{3}$		Final refinement $R\overline{3}m$
x	117	134	100	138±007	089±007	113±006
y	234	229		227±005	227±005	—
z	152	148		147±005	147±005	147±006
B_1	0·5	0·2		0·2	0·2	0·1
B_F	2·7	2·1		2·1	2·1	2·0
$\frac{1}{9}\sum_j (I_j^{1/2}-G_j)^2$	1320	888	944	774	774	806
R	0·09	0·06	0·06	0·050	0·050	0·051

x_2, y, z, where $x_1+x_2 = y$, which are related by a 30° rotation of the a axes in the a–a plane. Because both sets lead to identical interatomic distances and identical powder intensities, we need only consider one set. Actually, both sets were refined, for the condition $x_1+x_2=y$ in the final parameters serves as a convenient check on the accuracy of the calculations.

Structure factors were computed from Roof's parameters using form factors for K^+, F^-, and As (Berghuis *et al.*, 1955) and initial temperature factors $B_1=B_K=B_{As}$ and B_F for amplitude obtained essentially by a guess. The three fluorine parameters, the scale factor, and the two isotropic temperature factors constituted the variables whose most plausible values we wished to find from the twenty observational equations by use of the modified normal equations discussed above. All observational equations were given unit weight. All cross terms were retained in the normal equations. Table 1 indicates the results of the refinements for both shifts in x. It was found that the second and succeeding refinements could be carried out by use of the usual normal equations. This was possible because the x and y parameters had shifted far enough away from the condition $y = 2x$ to make $\partial G/\partial x$ comparable in size with the other first-derivative terms. The refinements were continued until changes in the parameters were less than 0·001. Four refinements in all were required for each set of parameters. The estimates of errors in the parameters given in Table 1 are those which result from the least-squares method; since absorption corrections ($\mu_{Cu} = 192$) presumably have been neglected by Roof in his reduction of the intensities, these estimates may be optimistic. For the sake of comparison, the structure was also refined for the space group $R\bar{3}m$ by use of the usual normal equations. The results of this refinement are also given in Table 1. Since the structure in $R\bar{3}m$ with only a moderately asymmetric temperature factor on the fluorine atoms would be expected to be compatible with the structure in $R\bar{3}$, it is not surprising that the two structures in Table 1 appear to be equally reliable.

Table 2. *Observed and calculated structure factors*

		$\frac{1}{3}F_c$*		$\frac{1}{3}G_c$		
Line No.	*hkl*	$R\bar{3}$	$R\bar{3}m$	$R\bar{3}$	$R\bar{3}m$	$\frac{1}{3}I^{\frac{1}{2}}$
1	101	26	26	63	65	66
2	110	42	44	103	107	99
3	012	40	42	97	103	102
4	021	24	25	58	61	62
5	003	−21	−21	63	62	62
	202	23	22			
6	211	1	−8	36	28	46
	$\bar{2}31$	−15				
7	300	22	21	55	52	55
8	113	14	12	183	184	181
	$\bar{1}23$	11				
	122	58	52			
	$\bar{1}32$	43				
9	220	35	36	85	88	83
10	104	23	23	56	56	59
11	131	18	19	63	67	78
	$\bar{1}41$	18				
12	303	14	15	133	133	123
	$30\bar{3}$	29	30			
	312	25	22			
	$\bar{3}42$	21				
	024	30	30			
—	401†	2	−1	5	2	—
13	223	13	11	174	179	169
	$\bar{2}43$	9				
	042	38	41			
	214	38	42			
	$\bar{2}34$	45				
14	321	20	16	58	57	59
	$\bar{3}51$	13				
—	015†	8	8	19	19	—
15	410	38	30	110	103	106
	140	24				
16	232	29	32	94	109	108
	$\bar{2}52$	25				
17	205	20	20	48	49	46
18	134	27	26	89	90	88
	$\bar{1}44$	24				
	051	3	1			
19	125	1	4	96	104	95
	$\bar{1}35$	8				
	330	38	42			
20	006	36	37	108	111	114
	413	4	10			
	$\bar{4}53$	14				
	143	13	10			
	$\bar{1}53$	4				
	502	33	35			

* For $R\bar{3}$ the values of F_c above are for $x = 0{\cdot}138$. If $x = 0{\cdot}089$ then $F(hkl)$ is interchanged with $F(\bar{h}, h+k, l)$. For $R\bar{3}m$ $F(hkl) \equiv F(\bar{h}, h+k, l)$ and the common value is given above without repitition. Values above are in electrons.

† Omitted from the calculation of the R factor.

Table 2 lists some pertinent data including the line numbers of Roof and the final values of G for both $R\bar{3}$ and $R\bar{3}m$. The values of $I^{1/2}$ were derived from the reduced intensities given by Roof. The reduction of the R factor $[\sum_j (I_j^{1/2}-G_j)]/\sum_j I_j^{1/2}$ from 0·19 to 0·050 may seem surprising in view of the shifts in the parameters and in view of the fact that the heavy atoms are fixed by symmetry. Actually, an R factor of about 0·11 is obtained here from Roof's structure. Roof obtains 0·19 because of a few indexing errors (line Nos. 13, 16, 20), and because he apparently defines R as $[\sum_j (I_j-G_j^2)]/\sum_j I_j$.

Table 3 summarizes the principal bond distances and angles which may be derived from the parameters found here and from Roof's parameters. $KAsF_6$ belongs structurally to a general class of substances typified by $TlSbF_6$ (Schrewelius, 1942) all of which crystallize in the space group $R\bar{3}m$. In view of this it is gratifying that the As–F distance found for the structure in $R\bar{3}$ agrees so well with that found for the structure in $R\bar{3}m$. The As–F distance may be given as 1·80±0·05 Å regardless of which space group is the correct one.

Table 3. *Bond distances and angles*

	$R\bar{3}$	$R\bar{3}m$	Roof
As–F (Å)	1·80±0·05	1·79±0·05	1·85
F–F (Å)	2·52	2·49	2·58
	±0·07	±0·07	
	2·58	2·57	2·66
K–F (Å)	2·81	2·81	2·75
	±0·05	±0·05	
	2·96	2·93	2·93
F–As–F (°)	88·7	88·3	88·3
	±2·2	±2·1	
	91·3	91·7	91·7

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* 8, 478.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* 63, 1737.

Roof, R. B., Jr. (1955). *Acta Cryst.* 8, 739.

Schrewelius, N. (1942). *Ark. Kemi Min. Geol.* 16B, No. 7.

Whittaker, E. & Robinson, G. (1944). *The Calculus of Observations*, p. 214. London: Blackie.

Acta Cryst. (1956). 9, 969

The isomorphous-replacement method applied to molecules containing like atoms.

By D. June Sutor, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

(*Received* 22 *June* 1956 *and in revised form* 17 *July* 1956)

The introduction of a 'heavy atom' into a compound often provides a convenient method of analysing its crystal structure. The coordinates of the heavy atom can generally be obtained from the Patterson function, and then it may be a relatively simple matter to locate the rest of the molecule. The method suffers from the disadvantage that the presence of the heavy atom results in less accurate values for the atomic coordinates than are usually obtained for a compound containing only like atoms. This disadvantage can be overcome by using, instead of the conventional heavy atom, one containing a similar number of electrons to the atoms comprising the rest of the molecule. Except for certain cases, such as those in which the compound can be obtained with varying amounts of water of crystallization, this extra atom will be part of the molecule. For example, in organic crystal structure analysis this method can be applied to two similar molecules one of which contains an extra substituent atom.

The two compounds chosen must show a close correspondence in unit-cell dimensions so that the atomic positions are not very different. A comparison of the two Patterson functions will then show whether the molecules not only have the same orientation but also occupy closely similar positions in their unit cells. I have applied the method with success to caffeine and theophylline, whose crystal structures I had not succeeded in solving by other means. In this case, the extra atom is the carbon of the methyl group, substituted in the five-membered ring of caffeine (see Fig. 1). The two *hk*0 Patterson functions showed that the orientation and position of the molecules are similar, but indicated that the plane of the theophylline molecule is more steeply inclined to the short (*c*) axis. This is to be expected from the unit-cell dimensions as the *c* axis shows an increase of 12% in theophylline whereas the *a* and *b* axes are 11% and 8% shorter respectively.

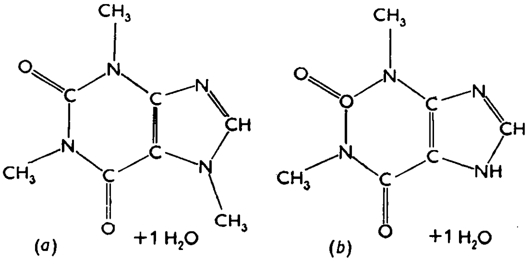

Fig. 1. (*a*) Caffeine. (*b*) Theophylline.

The difference Patterson introduced by Buerger (1942), and preferably sharpened, is used to locate the positions of the molecules in the unit cell, as this function will contain images of the molecules as seen from the extra atoms. In the calculation of the difference Patterson, terms which are sensitive to the non-exact correspondence of like atoms in the two compounds are not included. These terms are of two types, first a few reflexions occurring at low angles where the difference in F values for the two compounds is greater than can be due to the extra atom, and secondly, all reflexions occurring at high angles where the correspondence between the observed structure amplitudes is no longer good. Omission of these latter terms causes no errors due to series termination since it is a difference series which is used.

The difference Patterson (*hk*0 projection) of caffeine and theophylline, sharpened and with the origin peak removed, is shown in Fig. 2(*a*). The space group is $P2_1/a$, which has four general positions, and therefore this function represents sixteen images of the molecule as seen from the four extra atoms with each of the four molecules in turn. These sixteen images constitute four sets of four molecules related by the space-group elements, and the choice of one such set fixes the molecule with respect to one of the origins in this projection. The location of a set proved to be comparatively easy: the obvious starting point was the molecule situated with the extra atom on the origin of the difference Patterson. Positive regions could be obtained for the majority of atoms and the orientation of the six-membered ring agreed with that obtained from the ordinary sharpened Patterson functions of both caffeine and theophylline. By a process of trial and error lasting less than half a day, three other molecular positions were found satisfying the space-group symmetry and placing as many atoms as possible on positive regions. These four positions are shown in Fig. 2(*a*). Of the remaining maxima, those marked with crosses are the only ones compatible with the positions for the water molecules forming hydrogen bonds. More accurate coordinates for this water molecule were obtained from the first Fourier refinement and it is these coordinates which are marked in Fig. 2(*a*). Spurious maxima occur, due to the non-exact correspondence of like atoms in the two compounds, but there are very few peaks which have not been used. At present both structures have R factors below 20% and refinement is proceeding.