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The Least-Squares Refinement of the Crystal Structure of $\text{Ce}(\text{IO}_3)_4 \cdot \text{H}_2\text{O}$ Ceric Iodate Monohydrate*

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The crystal structure of ceric iodate monohydrate has been refined by the least-squares method with a view toward studying the effects of the weighting system and of the number of data on the derived structure. It was found that the variations applied here to the weighting system had little or no effect on the derived structure. It was found that while inclusion of high-angle data allowed a more accurate location of the heavy atoms, it did not aid in the location of the oxygen atoms. Finally a discrepancy was found between standard deviations estimated from the least-squares procedure and by Cruickshank's method, and it is pointed out that this discrepancy could, at least in part, be due to systematic errors in the data.

Introduction

The crystal structure of ceric iodate monohydrate, $\text{Ce}(\text{IO}_3)_4 \cdot \text{H}_2\text{O}$, has been described previously (Ibers, 1956*a*) with accuracy sufficient for most purposes, and so our object in carrying out the least-squares calculations to be described here was not to obtain an extensive refinement of the structure parameters. Rather our primary object was to assess the dependence on the weighting system of the crystal structure derived by the procedure of least-squares from a given set of assumptions (the model). A further object was to assess the usefulness of high-angle data for the location of light atoms in the presence of heavy ones.

Ceric iodate monohydrate was chosen for this study

for several reasons. First, extensive data, collected previously from a spherical crystal using molybdenum radiation,† were available. Second, as noted above, a structure of sufficient accuracy for the commencement of refinements was available. Third, as a function of scattering angle the scattering power of oxygen atoms relative to cerium or iodine atoms is not too different from that of hydrogen atoms relative to carbon atoms, and so the conclusions reached in this study may be extrapolated with some certainty to crystal structure analyses of organic compounds where super-refinements are in vogue.

Description of the structure

Ceric iodate monohydrate crystallizes in space group $C_{2h}^5-P2_1/n$, with four molecules in the unit cell of dimensions $a = 9.57$, $b = 14.92$, $c = 8.00$ Å, and $\beta = 97^\circ 35'$. The crystal structure was determined

* A portion of this work was performed under the auspices of the Atomic Energy Commission.

† These data were collected by one of us (J. A. I.) while at the California Institute of Technology.

(Ibers, 1956a) from a three-dimensional Patterson function computed from all data within the sphere $\sin \theta_{Mo} \leq 0.71$. The structure was refined from a three-dimensional difference Fourier computed from data out to $\sin \theta_{Mo} \leq 0.46$. In this manner the 54 positional parameters (the parameters of the hydrogen atoms being neglected) and the three isotropic temperature factors (assigned to the heavy atoms, to the iodate oxygen atoms, and to the water oxygen atom) were determined. By means of Cruickshank's (1949) method standard deviations of the positional parameters were obtained.

The structure of ceric iodate monohydrate is composed of discrete, trigonal iodate groups. Each of two oxygen atoms per iodate group is shared with a cerium atom, but the third is not. The cerium atom has eight oxygen atoms arranged around it in a distorted Archimedes antiprism. Each iodine atom has six oxygen atoms around it in a distorted octahedron. Two of the iodine atoms require the oxygen atom of the water molecule to complete this octahedral arrangement. A more complete description of the structure and of the procedures used in determining it is given in the original paper.

Grouping and weighting of the data

In the present study two groups of data were used. The first included all non-zero observed intensities, of which there were 6,254. The second included the

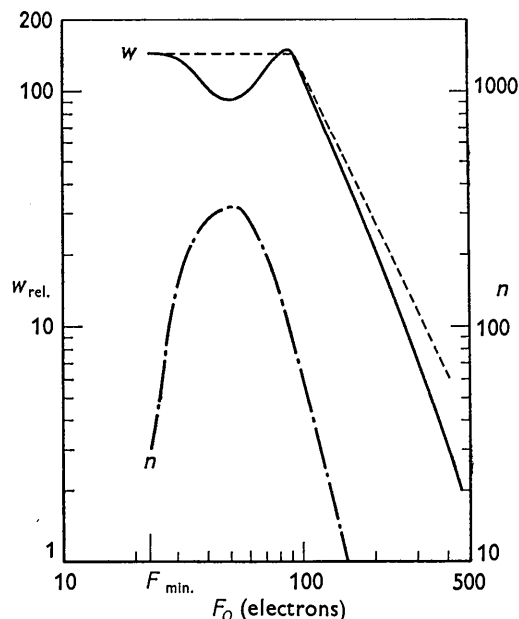


Fig. 1. The weighting and distribution of F_o . The upper curves depict the weights (left-hand axis) assigned to F_o : solid curve, Ibers' weights; dashed curve, Hughes' weights. The lower curve depicts the number n (right-hand axis) of reflections with observed structure amplitudes between $(F_o - \frac{1}{2})$ and $(F_o + \frac{1}{2})$ electrons. Unobservably small F_o 's have not been counted.

2,191 non-zero intensities within the sphere of radius $\sin \theta_{Mo} \leq 0.46$, that is within the copper limit.

In our procedure all unobserved reflections were given zero weight. The observed reflections were weighted either all equally (the unit weight system), on a scheme suggested by Ibers (1956b), or on the scheme of Hughes (1941). In Ibers' scheme the weights were derived as a smooth function of the magnitudes of the structure amplitudes on the basis of the average agreement of amplitudes of a given magnitude observed around both the a and c axes. The resultant set of weights, together with the distribution of magnitudes of observed structure amplitudes, is shown in Fig. 1. In the particular case of ceric iodate monohydrate there is only a two to one variation in weights assigned to $F_o \leq 4F_{min.}$ ($F_{min.}$ is 23 electrons), but there is a rapid decrease in the weight of F_o as it exceeds $4F_{min.}$. The maximum to minimum weight ratio is 75:1. The weighting scheme of Hughes is also shown in Fig. 1. In this scheme the weight is taken as a constant for $F_o \leq 4F_{min.}$ and inversely proportional to F_o^2 for $F_o > 4F_{min.}$. Hughes' weighting scheme was used here only in conjunction with the smaller group of data.

The three weighting schemes just described perhaps encompass most sets of 'reasonable' weights to be applied to photographic data visually interpreted. Hence, the comparison of results obtained using these systems should yield generally useful information on the problem of the weighting scheme in least-squares refinements.

Procedure

For the intercomparisons of the effects of various weighting schemes and of the groupings of data on the least-squares refinements the most general model is not required. For this reason a number of simplifying assumptions are made here. We wish to emphasize, however, that had our object been the determination of the most reliable set of structure parameters then some, if not all, of these simplifications would have been unsatisfactory. The first simplification, already noted, is the assignment of zero weights to unobserved reflections. A second is the use of individual, *isotropic* temperature factors for each atom. (Actually from the difference Fourier one may infer that this simplification is not a drastic one.) A third simplification is the assumption that the off-diagonal terms in the least-squares determinant can be neglected. We minimize the function $\sum w(|F_o| - |F_c|)^2$, although the minimization of $\sum w(F_o^2 - F_c^2)^2$ would be more in keeping with the spirit of the least-squares procedure.

The calculations were carried out on the Los Alamos computer MANIAC I in the usual manner, with the scale factor applied to F_c . The form factors and dispersion corrections were those used previously. Refinements were in all cases stopped when the shifts in parameters were less than about one-third the standard deviations σ estimated from the diagonal

error determinant. For this latter purpose the usual formula

$$\sigma^2(x_i) = \sum_j w_j (\Delta F_j)^2 / [(n-s) (\sum_j w_j (\partial F_j / \partial x_i)^2)] \quad (1)$$

was used, where n is the number of observations and s the number of variables, in our case 73 (54 positional parameters, 18 temperature factors, and a scale factor). Generally, three to five cycles were required to complete a refinement.

Results and discussion

The most important result obtained is an encouraging one: The parameters derived from the refinements based on the five pairings of weights and data do not differ significantly from one another as judged by application of the usual statistical tests to the standard deviations derived. However, there are some significant differences between the least-squares results and those of the Fourier work. The mean shifts from difference

Fourier results to those obtained by the least-squares procedure using all the data and Ibers' weights are: heavy atoms, 0.0065 Å; iodate oxygen atoms, 0.043 Å; and water oxygen atom, 0.44 Å. These shifts are not too surprising since the models differ and since no refinement in the usual sense was attempted in the previous work. In Table 1 are given the results of the least-squares refinement based on all the data and Ibers' weights, this refinement having yielded the smallest standard deviations for the heavy atoms.*

In Table 2 are given the individual averages of the twelve I-O and twelve O-O distances of the iodate groups as derived from the results of the five refinements and from the difference Fourier. Standard deviations (of a single observation), derived both from the refinements (σ) and on the assumption of equivalence of the distances of a given type (σ'), are given. The question of equivalence is a difficult one,

* The results, including F_o and F_c , of the separate refinements can be made available to those interested.

Table 1. *Least-squares results*

Atom		x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$	B	$\sigma(B)$
Ce		0.62286	0.00008	0.23839	0.00005	0.02946	0.00009	0.661	0.007
I	1	0.36698	0.00010	0.11566	0.00006	0.26454	0.00012	0.924	0.010
	2	0.83559	0.00009	0.42486	0.00006	0.26384	0.00011	0.820	0.009
	3	0.93387	0.00009	0.08665	0.00006	0.21683	0.00011	0.737	0.009
	4	0.28819	0.00009	0.37762	0.00006	0.14914	0.00011	0.771	0.009
O	1	0.3968	0.0027	-0.0009	0.0017	0.3285	0.0032	3.43	0.39
	2	0.5500	0.0025	0.1402	0.0016	0.2391	0.0030	3.06	0.34
	3	0.3630	0.0024	0.1667	0.0016	0.4687	0.0029	3.00	0.33
	4	0.7797	0.0025	0.4837	0.0016	0.4442	0.0030	3.12	0.35
	5	0.9552	0.0020	0.3491	0.0012	0.3792	0.0023	2.20	0.24
	6	0.6879	0.0023	0.3479	0.0015	0.2232	0.0028	2.80	0.31
	7	0.8478	0.0024	0.0348	0.0016	0.3806	0.0029	3.03	0.34
	8	0.0758	0.0026	0.1416	0.0017	0.3516	0.0032	3.27	0.37
	9	0.8175	0.0027	0.1843	0.0017	0.1860	0.0032	3.42	0.39
	10	0.4011	0.0030	0.4511	0.0019	0.2711	0.0035	3.81	0.44
	11	0.2266	0.0020	0.3209	0.0013	0.3212	0.0024	2.26	0.25
	12	0.4100	0.0026	0.2895	0.0017	0.1157	0.0031	3.27	0.37
w	0.0706	0.0044	0.2011	0.0029	0.0212	0.0054	6.25	0.83	

Table 2. *Standard deviations and average distances*

	Method*					
	A	B	C	D	E	F
$\sigma(\text{Ce, I})$ (Å)	0.00086	0.0013	0.0015	0.00095	0.0017	0.001
$\sigma(\text{O})$	0.024	0.025	0.027	0.023	0.030	0.014
$\sigma(w)$	0.043	0.039	0.036	0.038	0.038	—
$\langle \text{I-O} \rangle$	1.805	1.805	1.800	1.819	1.824	1.822
$\sigma \dagger$	0.024	0.025	0.027	0.023	0.030	0.014
$\sigma' \dagger$	0.024	0.030	0.028	0.021	0.024	0.022
$\langle \text{O-O} \rangle$	2.711	2.713	2.699	2.731	2.739	2.737
σ	0.034	0.036	0.038	0.033	0.042	0.020
σ'	0.051	0.050	0.045	0.047	0.045	0.034
$\sigma(B_{\text{Ce, I}})$ (Å ²)	0.009	0.019	0.021	0.010	0.024	—
$\sigma(B_{\text{O}})$	0.34	0.43	0.56	0.36	0.63	—
$\sigma(B_w)$	0.83	0.77	0.68	0.81	0.77	—

* Method: $A-E$, least-squares. F , difference Fourier (and Cruickshank's method for estimates of errors). A : all data, Ibers' weights; B : limited data, Ibers' weights; C : limited data, Hughes' weights; D : all data, unit weights; E : limited data, unit weights.

† σ , the standard deviation of the distance obtained from the individual standard deviations of the atomic positions; σ' , the standard deviation of the distance on the assumption of equivalence.

for in some of the refinements the distances test as equivalent, while in others they do not. The data are not sufficiently reliable to allow the question of equivalence to be answered unequivocally, but we note that those distances expected to differ from the others, namely those in which the oxygen atoms are not bonded to cerium atoms, do not. It is interesting to find that the mean distances are shortened when non-unit weights are employed in the refinements, and this shortening is possibly significant. A significant shortening is at least compatible with the fact that the parameters derived from the various refinements do not differ significantly. The weighting system might not cause a significant shift in the position of an oxygen atom as measured by the degree of overlap of the spheres* of error obtained from the separate refinements, and yet the center of the sphere of error could move toward an iodine atom when non-unit weights were employed. The limited accuracy of the data precludes further study of this fascinating possibility.

In Table 2 are given the average standard deviations of the positional parameters for the heavy atoms, the iodate oxygens, and the water oxygen. We give only average standard deviations, for the individual deviations do not differ by more than about 25% (Table 1). We also give in Table 2 the average standard deviations to be associated with the temperature factors, although such deviations are particularly susceptible to errors intrinsic in the diagonalization approximation. The average standard deviations of the positional parameters provide evidence that whereas the heavy atoms may be located more accurately using all the data, the oxygen atoms may be located with equal accuracy with either the limited or the entire data. These results confirm our intuitive notion that the location of an atom may be hindered, rather than aided, if that atom is not contributing sufficiently to the data being used. In fact it is not difficult to show, in the language of Fourier series, that the ratio of peak height of the atom to standard deviation of the electron density (ratio of signal to noise) as a function of scattering angle must go through a maximum. Unfortunately, there is no *a priori* basis on which to decide at what scattering angle is to be found such a maximum for a given type of atom in the structure. It does seem worth while to emphasize, however, that the indiscriminant collection of a large number of data, even quite accurate data, for the purpose of locating light atoms in the presence of heavy ones may be unnecessary or indeed fruitless.

Discrepancies in estimates of the standard deviations

The most striking feature of Table 2 is the discrepancy between standard deviations obtained from the least-

* The errors in the atomic positions are essentially spherical, as can be seen from the data of Table 1.

squares procedure and from Cruickshank's method. These latter standard deviations are only about one-half the former, and yet they are based on a less refined structure and a more approximate model. It is important to consider possible sources of this discrepancy, for upon estimates of standard deviations are based not only statements about the significance of various features of molecular geometry, but also a considerable amount of computing time.

In our case the basis on which the standard deviations are obtained from the least-squares analyses is not as firm as desired owing to the neglect of off-diagonal terms. However, from our experience and that of others (e.g., Trueblood, 1958) we feel that these estimates of standard deviations of positional parameters do not differ by more than some 25% from those we would have obtained using all the terms. Actually our experience is that the neglect of off-diagonal terms results in standard deviations which are too small. A possible objection to Cruickshank's method, when applied to a structure with atoms in general positions where the averaging process is reliable, is the approximation $\sigma(F) = |F_o - F_c|$, but this approximation is probably reliable to 20%, and is surely not wrong by a factor of two. (The factor 0.9 would enter if $|F_o|$ and $|F_c|$ were two measurements of the same quantity (Ibers, 1956b).) Hence we feel that the source of the discrepancy lies not in simplifications in either the theory or our treatment. It is interesting to note that we are not the first to find discrepancies of the direction and order of magnitude indicated here. Among others reporting similar discrepancies are Hughes & Lipscomb (1946). (These authors anticipated Cruickshank in the derivation of standard deviations of positional parameters from Fourier maps.)

Both of the methods discussed above for the estimation of standard deviations are based on the assumption that all errors in the data are random, and it is reasonable to investigate what effects, if any, certain systematic errors would have on such estimates. Let us assume that the systematic errors in the data are quite small so that neither the structure nor the curvature of a peak on the Fourier map is much affected. Then we may re-write equation (1) in the form

$$\sigma_1^2(x) = A \sum_j (\Delta F_j)^2 \quad (2)$$

where we have assumed unit weights. We can also write Cruickshank's formula for a particular x -coordinate in the form

$$\sigma_2^2(x) = B \sum_j h^2 (\Delta F_j)^2. \quad (3)$$

Both A and B are determinable constants. Let us now assume that for a particular plane $h = h'$ all F_o are in error by a constant factor. (That is, we visualize a scale error for a particular layer line. In actual practice, because of intercomparisons, this scale error

would tend to be spread over a wider range of layer lines, but the major error might still remain for the layer line h' .) It is not difficult to show that the condition that $(\sigma_1 - \sigma)$ be greater than $(\sigma_2 - \sigma)$, where σ is the standard deviation resulting only from random errors (and assumed to be the same in the two methods), is

$$A > Bh'^2. \quad (4)$$

In our case for an oxygen atom and the limited data with unit weights we have $A^{\frac{1}{2}} = 9.7 \cdot 10^{-5}$ and $B^{\frac{1}{2}} = 3.1 \cdot 10^{-6}$. Hence, any such error for $h' < 31$ (and hence any such error in our data) will cause a relatively greater increase in the least-squares estimate of the standard deviation of an oxygen parameter than in the estimate from Cruickshank's method.

Another type of systematic error might be described by

$$F_o = F_o^0 + Ch, \quad (5)$$

where F_o^0 is the structure amplitude that would be observed if there were no systematic errors. Equation (5) idealizes a common type of systematic error, namely one which increases (or decreases) with scattering angle. In this case $(\sigma_1 - \sigma)$ will be greater than $(\sigma_2 - \sigma)$ if

$$A \sum_j h^2 > B \sum_j h^4. \quad (6)$$

Our calculations indicate that the inequality (equation

(6)) holds here for the entire data as well as for the limited data.

Without direct evidence concerning the types and magnitudes of systematic errors in our data we cannot, of course, make any calculations of the order of magnitude of the discrepancy to be expected in the standard deviations. On the other hand, the rather qualitative and idealized calculations presented here make it reasonable to suppose that at least part of the discrepancy found between the least-squares and Cruickshank's estimates of standard deviations is due to systematic errors in the data. Clearly this example points once again to the often repeated but often forgotten fact that standard deviations obtained in crystal structure analyses are merely rough estimates, subject to many uncertainties, and are perhaps reasonable only when no systematic errors are to be found in the data. By placing an undue amount of faith in such estimates one may obtain a false impression of the accuracy of the structure determination.

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A Single Crystal Neutron Diffraction Study of Diaspore, $\text{AlO}(\text{OH})$

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A single crystal neutron diffraction study of diaspore has been made in which the intensities of ninety reflections of the $hk0$ and $0kl$ zones were measured. Unit-cell dimensions and their standard errors as redetermined by the X-ray powder method are $a = 4.401 \pm 0.001$, $b = 9.421 \pm 0.004$, and $c = 2.845 \pm 0.001$ Å.

The structure was refined by the method of least squares using an anisotropic temperature factor for each atom. The Al and O position parameters obtained in this way are in good agreement with the X-ray results reported by Hoppe. The hydrogen bonding postulated by Ewing (1935) was confirmed. The H atom is located 0.990 Å from O_{II} , but is not on the line of centers between O_{I} and O_{II} . Instead the $\text{O}_{\text{II}}\text{-H}$ bond makes an angle of 12.1° with the $\text{O}_{\text{II}}\text{-O}_{\text{I}}$ vector.

Introduction

The mineral diaspore, $\text{AlO}(\text{OH})$, has been the subject of several X-ray investigations (de Jong, 1930; DeFlandre, 1932; Takané, 1933). Its structure was cor-

rectly deduced by Ewing (1935) who based his conclusions partly on X-ray data and partly on considerations of ionic size and coordination numbers. A more complete X-ray determination was subsequently made by Hoppe (1941; 1942) who refined the aluminum and oxygen positions by Fourier methods. The present neutron diffraction investiga-

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