

An X-Ray Diffraction Study of the Structure of Guanidinium Aluminum Sulfate Hexahydrate

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The Busing-Levy IBM 704 least squares program has been applied to three-dimensional X-ray diffraction data from crystals of guanidinium aluminum sulfate hexahydrate taken with the Bond-Benedict single-crystal automatic diffractometer. Indications of interactions between parameters were evident in the early stages of refinement and were not removed in the subsequent cycles. Strong interactions were subsequently corroborated by large values of many of the correlation coefficients of pairs of parameters. In this case these interactions prevent refinement. The correctness of the general features of the structure as given in a previous paper on the gallium isomorph is nevertheless corroborated by the present investigation.

To enable those who have had similar difficulties to compare results, a fairly detailed account is given of the course of the attempt to refine the structure. The effects of highly correlated parameters are emphasized.

I. INTRODUCTION

The purposes of the investigation to be described were manifold. An approximate structure of the isomorphous gallium compound has already been reported.¹ The gallium compound with the heaviest metal atom among the isomorphs appeared to be best for establishing the general features of the structure.² However, in the hope of finding a closer relation between the structure and its electrical properties, it appeared that a refinement of the structure would be very worthwhile. In such a case, one would wish to have all of the atoms of more nearly the same scattering power; thus the guanidinium aluminum sulfate hexahydrate (G.A.S.H.) compound seemed most suitable for this pur-

† The contribution of H. Katz to this work was made during a period of employment at Bell Telephone Laboratories in the summer of 1959.

pose. Furthermore, this crystal would have the lowest linear absorption coefficient for all practical radiations; the importance of this feature will be discussed later. But probably most important, it was anticipated that the aluminum compound would be the one on which most measurements of various sorts would be made. This has indeed been the case.

While our earlier paper¹ was in press, a note³ appeared in *Kristallografiia* which gave an approximate structure for G.A.S.H. and its isomorphs which differed from that reported by us. A check with our data indicated that the structure reported by Varfolomeeva *et al.*³ was incorrect,² but this did not mean that the structure reported by us was necessarily correct. We had to face the question as to whether the correct structure might lie between the two structures or as mentioned in our first paper, perhaps some subtle disorder existed in the structure. In any case the appearance of the other result gave additional impetus to completion of work that had been started several years ago.

There is a further importance of this work. The quantitative X-ray data were taken with the Bond-Benedict single-crystal automatic diffractometer.⁴ It is the only crystal so far studied with this equipment and perhaps is the first X-ray structure analysis to be based on three-dimensional data collected automatically. Thus at least a small part of this paper will be devoted to an assessment of this equipment and suggestions as to future plans.

Perhaps the most frustrating experience encountered is to find indeterminate a problem which has taken considerable expenditure of time and effort of various sorts. One such reported problem in the field of X-ray crystallography is that of the determination of the structure of tetragonal BaTiO_3 ; this problem was found by Evans⁵ to be indeterminate by X-ray analysis, at the very least on the basis of the data collected. The results of the work on the three-dimensional data of G.A.S.H. indicate that the structure as originally reported by us is essentially correct. But we find that although a low discrepancy factor and standard error of fit are obtained by the least squares method of refinement, the structure cannot be refined; that is, convergence is not attained: there are parameter oscillations in each least squares iteration; some improbable interatomic distances and large error estimates are obtained. The cause appears to be strong interdependence of many of the parameters.

In this investigation the correlation matrix is used to demonstrate the existence of the strongly interacting parameters. The importance of this approach has also been demonstrated by a recent investigation described in a paper written by one of us (S.G.).⁶

TABLE I — LATTICE CONSTANTS OF GUANIDINIUM ALUMINUM SULFATE HEXAHYDRATE

Investigators	$a, \text{\AA}$	$c, \text{\AA}$
Wood	11.77 ± 0.04	8.98 ± 0.03
Ezhkova, <i>et al</i>	11.737 ± 0.002	8.948 ± 0.002
This work	11.75 ± 0.02	8.94 ± 0.01

II. CRYSTAL DATA

Guanidinium aluminum sulfate hexahydrate, $\text{C}(\text{NH}_2)_3\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, is isostructural with the previously reported¹ gallium compound. The morphology and unit cell dimensions have been reported by Wood.⁷ Lattice constants have also been reported by Ezhkova *et al.*⁸ The central values of our lattice constants, obtained from careful measurement of Buerger precession camera photographs, differ from those reported in both of the aforementioned papers, but are in better agreement† with those of Ezhkova *et al.*⁸ For purposes of comparison, the variously reported values are listed in Table I.

As described earlier,¹ the most probable space group to which the crystal belongs is $P31m$ and the unit cell contains three formula units. The molecular weight of the Al compound is 387.29, the volume of the unit cell is $1,069 \text{ \AA}^3$, and the X-ray density is 1.804 g/cc .

III. DETERMINATION OF THE STRUCTURE

The determination of the structure has been described in the paper on the gallium compound. The evidence for the correctness of the general features of the structure described in that paper, including the orientation of the guanidinium ions, is conclusive as will be shown subsequently.

IV. EXPERIMENTAL

The Bond-Benedict single-crystal automatic diffractometer⁴ was used to collect the three-dimensional data. Some changes from the original design of the instrument and in the electronics were made before the final data were taken. A detailed description of these changes must be left to the original authors. However, it should be mentioned that for these particular data (which were taken in 1956), a proportional counter replaced the Geiger counter and the "back-set" correction⁴ was virtually

† Dr. E. A. Wood and Mrs. V. B. Compton have informed us that their recent measurements of lattice constants of G.A.S.H. give values which agree more closely with those of Ezhkova *et al.*⁸ and of the present work.

eliminated by circuitry changes. Also, the internal geometry of the collimator was changed to square cross section.

The need for a collimator with square cross section derived from the mechanics of the instrument. The "back-setter" produces a jarring of the goniometer head which could at times translate the crystal very slightly out of the original alignment in the X-ray beam. If the beam has a circular cross section, slight deviation from coincidence of crystal cylinder and rotation axes causes significant differences in intensity when the diameter of the crystal is large relative to the beam cross section. This is not true of a beam with a more or less square cross section.

Of course, one would not have to worry too much about this if small crystals were being used. However, for this instrument and the use of the usual type of sealed X-ray tube, it is necessary to use large crystals to obtain the data. (This will be discussed further later.)

Two cylindrical crystals were used to obtain the data attainable by this instrument with $\text{CuK}\alpha$ radiation and a pentaerythritol monochromator. The crystal aligned along the c -axis had a diameter of 0.67 mm; the crystal aligned along the $[20\cdot1]$ direction (orthohexagonal A -axis) had a diameter of 0.54 mm. With a linear absorption coefficient for $\text{CuK}\alpha$ radiation of 48.7 cm^{-1} , the values of μR for these crystals are 1.64 and 1.32 respectively.

As described in the paper by Bond,⁴ the single-crystal automatic diffractometer works on a principle similar to that of the equi-inclination Weissenberg camera. With $\text{CuK}\alpha$ radiation, seven levels were obtainable about the c -axis and fifteen about the orthohexagonal A -axis.

Data from a particular level n were collected as follows: The alignment of the crystal was checked. This was done in two ways whenever possible. A microscope could be used to align the crystal cylinder axis with the rotation axis of the instrument. The equi-inclination angle was calculated and the crystal set to this angle. The arrangement of the counter of the instrument is always set so that the diffracted beam is incident perpendicularly to the window. Thus the counter is actually moved to twice the angle of the crystal from the zero level situation. If a particular reflection (for example, $00\cdot l$ on the l th level about the c -axis) was observable when the counter angle was equal to zero degrees for a given layer, this reflection was used to readjust crystal and counter.

To obtain the weak intensities, the diffraction unit settings were usually 40 kv and 20 ma. To obtain the stronger reflections, proper settings of the voltage and tube current were made so as to record enough moderate reflections to establish a scale between the two patterns.

Integrated intensities, crystal angles and counter angles for each level were recorded automatically by the Leeds-Northrup two-pen recorder as described in the papers by Bond and Benedict.⁴ As indicated above, resetting was made manually for each new level.

Following the collection of the data by the recorder, it was necessary to index the data: This was the most time-consuming (i.e., on a man-hour basis) part of the data processing required to obtain the observed amplitudes. The indexing was carried out with the use of the plotting device.⁴ (The indexing problem will be discussed further later.)

Following the indexing of all the data, the usual absorption, Lorentz-polarization and Tunell⁹ rotation factors† were applied to extract the relative $|F_o|^2$. (The polarization correction is for monochromatized radiation.) The calculation was programmed for the IBM 704 by R. G. Treuting. The corrections calculated were based on the formulae‡ given by Bond and the tables used for the absorption corrections are those given in Bond's paper.¹⁰ The program written by Treuting put the resultant $|F_o|^2$'s or $|F_o|$'s out on cards as well as on a print-out. The individual Lorentz-polarization, absorption and Tunell rotation factors were also printed out for each reflection for each layer on which it appeared.

Having extracted the $|F_o|^2$'s for each layer about each of the two axes, the next step involved an iterative cross-calibration process to bring the values to the same basis. An IBM 704 program written by W. R. Romanow allowed us to apply constant factors to the sets of $|F_o|^2$ put out by the intensity correction program. Romanow's program also put out new cards so that we could apply a different constant to the new values if necessary.

When we felt we had arrived at the best values, it was decided to carry out the subsequent least squares refinement on the basis of the $|F_o|$ values. Using a short program written by Romanow, square roots were taken of all the $|F_o|^2$'s and put out on cards. Those that came from layers about the orthohexagonal *A*-axis were then sorted on the values of *l* for ease in setting up the data for the least squares refinement.

As described in the Bond-Benedict papers, some reflections do not get entirely into the counter; thus, in order to be sure that all are ob-

† The proportional counter employed had a linear response to counting rates of over 20,000 cps. Because for even the strongest reflections, observed counting rates over 10,000 cps gave integrated intensities which went off scale on the recorder, no dead-time correction⁴ was necessary for any of the reflections.

‡ The formula for P_L on p. 380 of Bond's paper should read

$$P_L = T \sin 2\theta / \left\{ 1 + \left(\frac{q - \sin^2 \nu}{(1 + q) \cos^2 \nu} \right) (1 + \cos 2\theta)^2 - \frac{2q}{1 + q} (1 + \cos 2\theta) \right\}.$$

tained, the instrument was designed to obtain each reflection twice. For this reason the counter has a 4° window. Even at that, not all the reflections of a given form will have the same intensity, but usually about a twofold axis, a form of reflections of moderate intensity will have two with the same intensity. About a threefold axis, perhaps eight of twelve reflections from a given $hk\cdot l$ form will have the same intensity or 12 out of 16 of a given $hk\cdot 0$ form. Unfortunately, the weaker reflections do not give as good results as the moderate to strong ones. In the case of the c -axis layers, if there was a variation in the height of peaks which appeared to have been fully in the window, the value taken for the integrated intensity was the average of the several peaks. In the case of the orthohexagonal A -axis layers, because there were fewer peaks contributing to a form and therefore a greater possibility that only one peak was squarely in the window, the value recorded in most cases was the measure of the highest peak.

In taking the averages of observed structure amplitudes, the weighting was in accord with the above. For example for a given $|F_{hk\cdot l}|$, $h, k, l \neq 0$, the value from the c -axis layer was weighted four times and a value from an orthohexagonal A -axis layer once. The standard deviation was calculated in accordance with the analysis given in Chapter 16 of the book by Dixon and Massey¹¹ and as suggested earlier by Ibers.¹² However, for the unobserved, the standard deviation was taken as equal to half the minimum observable. For $|F_{00\cdot l}|$'s which would have unity weight since they appear only once, the σ was taken in accordance with a subjective estimate comparing the particular $|F_{00\cdot l}|$ with others of similar value. The agreement between or among $|F_o|$'s from the same form but from different layers was quite good generally except for the weakest reflections.

In the $\text{CuK}\alpha$ sphere, there is a total of 895 X-ray forms of guanidinium aluminum sulfate hexahydrate. The geometry of the Bond diffractometer allows us to observe only 842 of these. Of those possibly observable by the instrument, only 546 were actually observed.

V. ATTEMPT TO REFINED THE STRUCTURE

Because the major point of this paper is to demonstrate that the refined structure under discussion is effectively unattainable from the X-ray diffraction data, it seems worthwhile to give some of the details of the calculations. To make such a discussion simpler, the pertinent data are collected in tables. In Tables II and IV the values of parameters and some other important information are listed. In Table II two columns are assigned to each cycle; the left one lists the starting parameters,

Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7	Cycle 8
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the right, the calculated "corrected" parameters. A blank space in the left column indicates that the last previous calculated value was the starting value for the particular parameter. In the cases of cycles 9 and 10, all of the parameters had the last previous calculated values of cycles 8 and 9 respectively.

The order in which the atoms are listed in Tables II and IV is not the same as that of the paper¹ on the gallium isomorph, but the atom labeling is. In writing the special position symmetry patch for the Busing-Levy¹³ IBM 704 least squares refinement program, it is most convenient to list the atoms in general positions first. Then to avoid mistakes in the listing of results, it is best to leave the order the same as that of the output of the program.

In the calculation of structure amplitudes the following atomic scattering factors were used: for O, Al³⁺, N and C, those of Berghuis *et al.*,¹⁴ and for S, those of Viervoll and Ögrim.¹⁵

In cycles 1 and 2, 895 reflections, all those representing independent forms and observable in the CuK α sphere, but perhaps not observable with the single-crystal diffractometer, were included. Eight of the parameters were scale factors, all of which were initially equal to 0.6667, one for each value of l from 0 to 6 and the eighth value for all the remaining l values. Also in the first two cycles, isotropic temperature factors were used despite the fact that it was obvious that the thermal motions of the atoms in this crystal must be highly anisotropic.

The starting structural parameters for the first cycle were those given for the gallium isomorph¹ except for changes in the S and Al temperature factors and the y -parameter of N(II), which was inadvertently taken as 0.418 instead of 0.333. Now it may be seen in Table II under cycle 1, that this y -parameter did not change as radically as one might have hoped, in fact as one might have expected, for an incorrect parameter. But the temperature factor of the atom did increase considerably, perhaps indicating that the atoms did not want to be at the positions indicated. On the other hand, the temperature factor of the N in the special position decreased considerably to a negative value as if to compensate for the other. This, in retrospect, was already indicative of strong interaction between the thermal parameters of these two atoms. Another important change was the large one, to -0.392 , in the value of the O(III) z -parameter; this implies a very short S—O distance, 1.31 Å, in one set of the SO₄ groups.

The *estimated* error of fit^{13,6} at the end of the least squares calculation of cycle 1 was very much lower than the first computed error of fit,¹³ and it appeared that by readjustment of some of the temperature factors we could go a step further toward convergence before changing to aniso-

tropic temperature factors. Initially cycle 2 showed that even with the readjustment of temperature factors, the R value† had dropped from 0.473 to 0.303, the weighted R from 0.299 to 0.193. But the error of fit was higher than that estimated in cycle 1 on the basis, of course, of the parameters computed in that cycle, some of which were physically impossible (i.e., negative temperature factors).

However, cycle 2 ended with an estimated error of fit somewhat lower than that of cycle 1. The N(II) y -parameter decreased toward the value which we believe to be the more nearly correct one, but the N(II) B value increased greatly and the N(I) B value became a large negative value. Also the x -parameter of N(I) decreased to imply an unlikely short C—N distance. Changes in the S and Al positional parameters were not large but several oscillations occurred. The O(III) (atom 10) z -parameter returned to -0.400 , but even this value implied a rather short S—O distance, 1.37 Å.

At this point, it seemed necessary to change to anisotropic thermal parameters. The Busing-Levy program will compute these from the isotropic thermal parameters using the following relations: $\beta_{11} = Ba^2/4$; $\beta_{12} = (Ba^*b^* \cos \gamma^*)/4$; etc.

The starting parameters were those computed in cycle 1 and adjusted for cycle 2 (see Table II). For cycle 3, a critical estimate of the reflections really observable by the single-crystal automatic diffractometer was made. This resulted in the removal from the calculation of 43 unobserved reflections, some of which had rather high calculated structure amplitudes when compared with the respective estimated threshold values. Included in cycle 3 was a rejection test: that is, when Δ/σ was >10.00 , the reflection was not counted in the calculation of the R values or the standard error of fit, nor was it included in the least squares calculation. This reduced the number of $F_{hk\cdot l}$'s used in the least squares calculation to 790. (Unfortunately the R values and the calculated amplitudes computed in this cycle have been lost.)

The estimated error of fit resulting from the cycle 3 least squares calculation decreased from 4.99 to 2.30, an apparently tremendous improvement. However, the still incorrect N(II) y -parameter did not improve; also the values of the N(II) thermal parameters greatly increased. The O(III) values still implied a short S—O distance. The C(I) z -parameter indicated possible nonplanarity of the guanidinium ion in the special position, but this parameter also had an apparently

† Unless otherwise stated, the R value is that for the independent $F_{hk\cdot l}$'s, i.e., multiplicity is neglected. This is the R value calculated by the Busing-Levy program.

large estimated error, 0.0115, indicative of potential difficulty. Twelve of the atoms had calculated thermal parameters which did not satisfy all the criteria for physical reality (see Ref. 13). Therefore, for cycle 4 some of the thermal parameters had to be adjusted to satisfy these criteria. Also, the N(II) y -parameter was corrected. The R value and error of fit decreased considerably since cycle 2, but the weighted R value increased slightly. The same rejection test as used for cycle 3 allowed 809 reflections to be included in the cycle 4 calculation. The least squares calculation led to an estimated error of fit of 2.23, not too different from that estimated in the previous cycle.

In cycle 4, the values of the N(II) thermal parameters decreased, indicating that the high values had been caused by the wrong y -parameter. One would prefer to think, however, that the y -parameter should have tended to approach the correct value rather than to have the thermal parameters act as if the atom should be removed. This time the x -parameter of N(I) (atom 6) became rather large, implying too large a C—N distance. A number of the other positional parameters showed oscillation, and again there were twelve atoms which had thermal parameters not satisfying the criteria for physical reality (Table II). The O(III) z -parameter continued to imply a short S—O distance. The C(II) and N(II) atoms did not have the same values in z -parameter, nor did the C(I) and N(I) atoms have the same z -parameter. Also, in this cycle many of the scale factors, especially s_8 , had almost reached their starting values after having at first decreased substantially.

The necessary adjustments were made on the thermal parameters before cycle 5 was carried out. Also, the rejection test was removed. Five reflections which appeared to have substantial contribution from the 54 hydrogen atoms or to have suffered from extinction were given zero weight. Thus, of the 852 reflections, 847 were used in the cycle 5 least squares calculation. Because some of the initially estimated $\sigma(F_o)$'s were really very small, a few of these also were readjusted. Initially the R value was 0.198, while the weighted R decreased to 0.139, this latter reduction resulting mostly perhaps from the few adjustments made on the $\sigma(F_o)$'s. The error of fit for the 847 reflections was larger than for the 809 of the previous cycle. The calculated estimated error of fit after the least squares calculation did decrease, however.

But in cycle 5 there was no improvement in the way the calculation was going. There were further oscillations, and, very important, the C(II)—N(II) distance continuing from cycle 3 was short, whereas the C(I)—N(I) distance continued to be long. Considering the guanidinium ion to be planar, the C—N distances were respectively 1.22 and 1.48 Å,

the average is 1.35 \AA in good agreement with the acceptable guanidinium C—N value 1.34 \AA .¹⁶ Again this indicated interaction between the N(II) *x*- and *y*-parameters and the N(I) *x*-parameter. Also, the parameter values of the S(I) and O(III) atoms still indicated an improbably short S—O distance. There were other indications of interaction: for example, the *y*-parameters of the O(V) and O(VI) atoms (2 and 3 respectively) behaved strangely, that of O(V) indicating an improbably large $[\text{SO}_4]$ O—O distance, that of O(VI), too small an $[\text{SO}_4]$ O—O distance.

It seemed at the time, however, that there might be other possibilities for explaining the course of events in the attempt to refine the structure. For example, there could be many reflections to which the hydrogen atoms would contribute, and, perhaps particularly because this is a non-centrosymmetric structure, the affected structure amplitudes were having a detrimental effect. Therefore, in cycle 6 all reflections for which $\sin^2/\lambda^2 < 0.0800$ were given zero weight. Necessary adjustments were made in thermal parameters (Table II); the N(I) and N(II) positional parameters were readjusted each to yield the C—N distance 1.34 \AA ; and the O(V) and O(VI) *y*-parameters were adjusted to yield more reasonable $[\text{SO}_4]$ O—O distances. The *R* value for the 755 amplitudes (with nonzero weights) was 0.200, weighted *R* = 0.128 and error of fit, 2.82.

In the cycle 6 least squares calculation, only 43 parameters were varied: the scale factors and all positional parameters except the N(I) *x*-parameter. The estimated error of fit decreased to 2.38, but this cycle was also discouraging in that again there were oscillations and some rather large changes in parameter. The S(I)—O(III) distance continued to remain improbably short; the O(VI) *y*-parameter again implied too short an $[\text{SO}_4]$ O—O distance; and the values of the N(II) *x*- and *y*-parameters implied a C(II)—N(II) distance of 1.25 \AA .

In the paper on the gallium isomorph,¹ we had concluded that the arrangement of the guanidinium ions on the threefold axes were related to that at 3m to close approximation by $\frac{1}{3}, \frac{2}{3}, 0$ and $\frac{2}{3}, \frac{1}{3}, 0 - (u, 0, w; 0, u, w; \bar{u}, \bar{u}, w)$. However, some doubt remained, and therefore it was decided to try some different orientations of the guanidinium groups.

For cycle 7, the N(II) parameters were readjusted, presumably back to the starting parameters of cycle 6. However, a card-punch error (0.5333 instead of 0.5533) was made in the *x*-parameter. The N(I) parameter was set to -0.1130 . This we shall call the $(-, -)^\dagger$ orienta-

[†] This symbolism is derived as follows: The \pm orientations of N(I) are those for which in $(x, 0, z)$ of positions 3c, $x_{\text{N(I)}} = \pm u$ where u is very nearly $+0.113$. The \pm orientations of N(II) are those for which in (x, y, z) of positions 6d, $x_{\text{N(II)}} = \frac{1}{3} \pm u$, $y = \frac{2}{3}$. Thus $(-, -)$ here means that $x_{\text{N(I)}} = -0.113$, $x_{\text{N(II)}} = 0.220$, $y_{\text{N(II)}} = 0.667$. By symmetry the latter two are equivalent to 0.553 and 0.333 respectively.

tion. The positional parameters of O(VI) were also readjusted. The R value for the 755 reflections increased to 0.250, the weighted R to 0.187, and the error of fit to 4.10. In cycle 7 all scale and positional parameters were varied. At the end of the cycle, the estimated error of fit was 3.53. The C(II)—N(II) distance again was too short, ~ 1.21 Å; again the O(VI) y -parameter decreased from the adjusted value; the difference in the C(I) and N(I) z -parameters increased. Also again there were oscillations. The results of cycle 7 did not look promising.

In cycle 8, the (+,+) arrangement of the guanidinium ions was tried with the other starting parameters the same as those used in cycle 7. In this case the R value for the 755 amplitudes was 0.231, weighted R , 0.155, and error of fit, 3.40. Again only scale and positional parameters were varied. The estimated error of fit obtained at the end of the least squares calculation was 3.14. The results of this cycle looked promising. The C—N distances looked good; the O(V) and O(VI) parameters were not too bad. However, the S(I)—O(III) distance still looked improbably short. The agreement for individual amplitudes actually did not look as good as it did in cycle 6, but it was felt that perhaps some of this poorer agreement resulted from hydrogen contributions and/or from required changes in thermal parameters.

It was decided to continue to cycle 9 using the values of scale and positional parameters obtained in cycle 8. The R value increased to 0.240; the weighted R value decreased to 0.140; the error of fit was very close to that previously estimated. Despite this, the parameter results of this cycle (Table II) looked even better than those of the previous cycle, but the S(I)—O(III) distance continued to be improbably short.

The scale and positional parameters resulting from cycle 9 were used in cycle 10. There was not much change in R , weighted R or error of fit. In cycle 10, all scale and positional parameters which had changed less than 1σ in cycle 9 were held constant and all thermal parameters were allowed to vary. The estimated error of fit at the end of the cycle was 2.55. It appeared that the thermal parameters of the N(II) atom increased considerably as if trying to eliminate this atom, and as before this seemed to be an indication that the N(II) atom was not placed correctly. Also as if to compensate, the previously large β_{33} of N(I), 0.01480, decreased to -0.00095 . Eight of the atoms had thermal parameter matrices which were not positive definite.

With this continued disappointment, another notion became more important. Was it possible that the structure given by Varfolomeeva *et al*³ was correct? It seemed advisable to make the calculation with the model proposed by those authors. The results proved that the structure

cannot possibly be correct. The initial R was 0.559, weighted R , 0.473 and error of fit, 10.38 for the 755 reflections. Examination of the calculated and observed amplitudes showed a great many very large discrepancies indicative of an improbable structure. Only the scale and positional parameters were varied in the least squares calculation. Thermal parameters for the N atoms were those initially used in cycle 6. All other thermal parameters were essentially those obtained in cycle 10 with necessary adjustments made. The initial and final positional parameters are shown separately in Table III. The estimated error of fit was 8.92, indicating no real possibility of convergence. The parameter changes were mostly drastic. The N(I) x -parameter, for example, would imply a C(I)—N(I) distance of 1.16 Å. Interestingly enough, the S(I)—O(III) distance continued to remain very short.

In cycle 12, the guanidinium ions on the two three-fold axes (i.e., at $\frac{2}{3} \frac{1}{3}$ and $\frac{1}{3} \frac{2}{3}$) were turned 30° from their original positions. The thermal parameters were the same as those used initially in cycle 11 and are shown in the next to the last columns of Table II. The R value was 0.238, weighted R , 0.154, and error of fit, 3.38 (the latter two being somewhat higher than for the starting parameters of cycle 10). The estimated error of fit obtained from the least squares calculation was 3.14. The results of this calculation did not look promising. The C(I)—N(I) distance was large; there was an extraordinarily large change in the z -parameter of O(VIII). Also, agreement of many individual amplitudes was poorer than for the very first orientation of the guanidiniums. In fact, from the calculations of cycles 7–10 and cycle 12, it had become apparent that the $(+, -)$ orientation was indeed the best. It also appeared that disorder or rotation† of the guanidinium ions was highly unlikely unless very subtle. In the case of complete disorder or the equivalent free rotation, there would be no contributions from the nitrogen atoms to the amplitudes $F_{hk \cdot l}$, $h - k \neq 3n$, exactly as in the case of the $(+, +)$ orientation. This alone makes it appear that the originally reported¹ $(+, -)$ orientation of the guanidinium ions was corroborated.

In cycle 12, the normal equations and inverse matrices were obtained.¹³ Examination of the inverse matrix showed that there were large values of correlation coefficients, $\rho_{ij} = b_{ij}/\sqrt{b_{ii}b_{jj}}$, for many pairs of parameters. A few examples are:

† Two reports^{17, 18} based on nuclear magnetic resonance investigations of G.A. S.H. mention the possibility of rotation of the guanidinium groups. We have learned (by private communication) from, and have been permitted to quote, the author, D. W. McCall, of one of these,¹⁷ that further investigation now indicates that this rotation is highly unlikely.

TABLE III — POSITIONAL PARAMETERS. CYCLE 11

Atom	Coordinates			Atom	Coordinates		
	x	y	z		x	y	z
1 - N(II)	0.2200 0.2047	-0.3330 -0.3304	0.0000 -0.0305	10 - O(III)	0.3699 0.3651	0 0	-0.0820 -0.1185
2 - O(V)	0.3449 0.3512	0.1166 0.1250	-0.3130 -0.3122	11 - O(II)	-0.4412 -0.4246	0 0	0.2764 0.2739
3 - O(VI)	-0.3211 -0.3281	-0.1137 -0.1123	0.2450 0.2025	12 - O(I)	0.4538 0.4688	0 0	-0.3260 -0.3351
4 - O(IX)	-0.4654 -0.4639	0.3272 0.3327	0.3400 0.3434	13 - S(I)	0.3479 0.3469	0 0	-0.2433 -0.2502
5 - O(X)	0.4647 0.4647	-0.3391 -0.3422	0.5600 0.5294	14 - S(II)	-0.3174 -0.3200	0 0	0.3144 0.3079
6 - N(I)	0.1132 0.0987	0 0	0.4500 0.4124	15 - C(II)	$\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$	0.0000 0.0110	0.0000 0.0110
7 - O(VIII)	-0.1304 -0.1375	0 0	-0.1208 -0.1073	16 - Al ³⁺ (II)	$\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$	0.4430 0.4306	0.4430 0.4306
8 - O(VII)	0.1426 0.1367	0 0	0.1175 0.1260	17 - C(I)	0 0	0 0	0.4500 0.4694
9 - O(IV)	-0.2912 -0.3180	0 0	0.4756 0.4471	18 - Al ³⁺ (I)	0 0	0 0	0 0

$z_{O(V)} - z_{O(II)},$	0.81
$z_{O(V)} - z_{O(I)},$	0.58
$z_{O(IX)} - z_{O(VII)},$	0.84
$z_{O(IV)} - z_{O(III)},$	0.65
$z_{S(I)} - z_{S(II)},$	0.96.

It is noteworthy that the correlation coefficient for $x_{N(II)}-x_{N(I)}$ was very low, 0.10; it will be seen later that this low value resulted from the incorrect orientation of the guanidinium (II) ions.

It seemed unlikely that the weighting scheme could be the cause of the difficulties encountered. Nevertheless, it was decided to try a weighting scheme radically different from that used in the first twelve cycles.

In cycle 1' (Table IV), all amplitudes with $\sin^2\theta/\lambda^2 < 0.0800$ were still weighted zero. Also all unobserved amplitudes were to be weighted zero and all observed, unity. However, a number of amplitudes which should have been weighted zero were weighted unity, and a few which should have been weighted unity were weighted zero. This left 534 reflections included in the least squares calculation. The initial parameters were those from cycles 9 and 10, except for the N's which were started at the exact (+, -) orientation and the O(III) z -parameter which was started at -0.405 to give an S—O value closer to 1.48 Å. The R value was 0.204, weighted R , 0.149 and error of fit 2.19 for the 534 amplitudes and these parameter values. The least squares calculation gave an estimated error of fit of 1.90. Again the S(I)—O(III) distance decreased to 1.38 Å, the C(I)—N(I) distance increased again and the C(II)—N(II) distance decreased again. Some of the other distances are listed in Table V.

Starting with this calculation, the vector $v_i = \Sigma(\sqrt{w}D_i)(\sqrt{w}\Delta)$ was obtained as output† as well as the direct and inverse matrices,¹³ the purpose being to see whether Δp_i 's from the diagonal term approximations would be much different from those obtained by the exact solution of the normal equations. Not many of these were checked in this and subsequent cycles, but enough differences were found to indicate the importance of the off-diagonal terms.

It appeared that it would be most convenient to have the correlation or normalized inverse matrix to examine in each cycle. A program patch to enable us to do this was written by Misses D. C. Leagus and B. B. Cetlin.

† The program patch for this calculation was written by Miss D. C. Leagus.

TABLE IV — RESULTS OF LEAST SQUARES CALCULATIONS (SECOND SET OF WEIGHTS)

		Cycle 1'		Cycle 2'		Cycle 3'		Cycle 4'		Cycle 5'						Par. I
Parameters								a	b	a	b	c	d	e		
Scale	1	0.5557	0.5846		0.5627											1
Factors	2	0.6186	0.6058		0.6069											2
	3	0.5933	0.5951		0.6032											3
	4	0.6161	0.5841		0.5903											4
	5	0.6449	0.6503		0.6539											5
	6	0.7327	0.6826		0.6849											6
	7	0.6854	0.6689		0.6760											7
	8	0.6856	0.6693		0.6751											8
Atom 1	x	0.2200	0.2211	0.2184	0.2237	0.2200	0.2171	0.2148	0.2155	0.2169	0.2169	0.2146	0.2176	0.0027		9
N (II)	y	-0.3330	-0.3377		-0.3393	-0.3330	-0.3386	-0.3412	-0.3415	-0.3147		-0.3419	-0.3432	0.0026		10
	z	0.5350	0.5465		0.5521		0.5579	0.5552	0.5559	0.5591	0.5590	0.5580	0.5584	0.0044		11
	β_{11}	0.00890			0.00229		0.00229	0.00431	0.00586	0.00424	0.00422		0.00456	0.00255		12
	β_{22}	0.00700			0.00970		0.00970	0.01172	0.01386	0.01191	0.01222		0.01221	0.00330		13
	β_{33}	0.01820			0.02051		0.02051	0.02269	0.02108				0.01509	0.00470		14
	β_{12}	0.00500			0.00227		0.00227	0.00345	0.00427		0.00494	0.00508	0.00571	0.00201		15
	β_{13}	0.00520			0.00293		0.00293	0.00185	0.00170		0.00228	0.00226	0.00191	0.00233		16
	β_{23}	0.00410			0.00039		0.00039	0.00181	0.00217		0.00299	0.00309	0.00292	0.00269		17
Atom 2	x	0.3449	0.3412		0.3429			0.3419	0.3419	0.3430	0.3428	0.3423	0.3428	0.0025		18
O (V)	y	0.1166	0.1178		0.1167			0.1201	0.1201	0.1174	0.1173	0.1140	0.1165	0.0022		19
	z	-0.1977	-0.2072		-0.2076			-0.2043	-0.2043	-0.2005	-0.2002	-0.2008	-0.2056	0.0043		20
	β_{11}	0.00843			0.00741			0.00689	0.00741	0.00689			0.00517	0.00248		21
	β_{22}	0.00307			0.00010			0.00010	0.00010	0.00335			0.00244	0.00173		22
	β_{33}	0.02193			0.2388			0.2388	0.2388	0.02161			0.00999	0.00473		23
	β_{12}	0.00375			0.00267			0.00267	0.00267	0.00396	0.00402		0.00357	0.00153		24
	β_{13}	-0.00333			-0.00262			-0.00262	-0.00262	-0.00054	-0.00085		-0.00060	0.00230		25
	β_{23}	-0.00206			-0.00217			-0.00217	-0.00217				-0.00255	0.00207		26
Atom 3	x	-0.3211	-0.3225		-0.3243			-0.3215	-0.3215	-0.3233	-0.3231	-0.3230	-0.3232	0.0022		27
O (VI)	y	-0.1137	-0.1155		-0.1162			-0.1143	-0.1143	-0.1148	-0.1148	-0.1166	-0.1155	0.0021		28
	z	0.2450	0.2437		0.2447			0.2385	0.2385	0.2427	0.2436	0.2444	0.2365	0.0042		29
	β_{11}	0.00287			0.00027			0.00027	0.00027	-0.00048	-0.00061		-0.00124	0.00163		30
	β_{22}	0.00149			0.00238			0.00238	0.00238	0.00261			0.00162	0.00180		31
	β_{33}	0.01905			0.02399			0.02399	0.02399	0.03084	0.03061		0.01944	0.00487		32
	β_{12}	0.00066			-0.00127			-0.00127	-0.00127	-0.00077	-0.00099		-0.00050	0.00113		33
	β_{13}	-0.00081			0.00014			0.00014	0.00014	0.00118	0.00117		0.00159	0.00176		34
	β_{23}	-0.00057			-0.00069			-0.00069	-0.00069				-0.00363	0.00216		35
Atom 4	x	-0.4654	-0.4682		-0.4701			-0.4702	-0.4702			-0.4688	-0.4717	0.0021		36
O (IX)	y	0.3272	0.3259		0.3258			0.3255	0.3255	-0.0549	-0.0552	-0.0581	-0.0515	0.0016		37
	z	-0.0520	-0.0573		-0.0571			-0.0629	-0.0629	-0.0522	-0.0522	-0.0581	-0.0515	0.0039		38
	β_{11}	0.00266			0.00357			0.00357	0.00357	0.00522	0.00522		0.00403	0.00166		39
	β_{22}	0.00120			0.00070			0.00070	0.00070	0.00379	0.00388		0.00323	0.00146		40
	β_{33}	0.01613			0.01697			0.01697	0.01697	0.00943	0.00926		0.00534	0.00401		41
	β_{12}	0.00127			0.00089			0.00089	0.00089	0.00271	0.00272		0.00218	0.00107		42
	β_{13}	-0.00122			0.00017			0.00017	0.00017	-0.00212	-0.00213		-0.00128	0.00172		43
	β_{23}	0.00174			0.00193			0.00193	0.00193				0.00194	0.00124		44
Atom 5	x	0.4647	0.4669		0.4661			0.4626	0.4626	0.4639	0.4637	0.4634	0.4630	0.0022		45
O (X)	y	-0.3391	-0.3377		-0.3373			-0.3369	-0.3369	-0.3377	-0.3377	-0.3374	-0.3372	0.0017		46
	z	0.1758	0.1748		0.1759			0.1735	0.1735	0.1784	0.1785	0.1753	0.1798	0.0044		47
	β_{11}	0.00200			0.00383			0.00383	0.00383	0.00285	0.00278		0.00194	0.00187		48
	β_{22}	0.00142			0.00269			0.00269	0.00269	0.00048	0.00039		-0.00055	0.00180		49
	β_{33}	0.01636			0.01668			0.01668	0.01668	0.00075	0.00071		0.01066	0.00465		50
	β_{12}	0.00135			0.00189			0.00189	0.00189	0.00105	0.00097		0.00029	0.00131		51
	β_{13}	0.00007			-0.00176			-0.00176	-0.00176	-0.00002	-0.00000		0.00029	0.00190		52
	β_{23}	-0.00150			0.00049			0.00049	0.00049				-0.00090	0.00143		53
Atom 6	x	0.1132	0.1192	0.1132	0.1218	0.1130	0.1178	0.1163	0.1172	0.1158	0.1157	0.1139	0.1159	0.0026		54
N (I)	z	0.5065	0.4959	0.5000	0.5043		0.5100	0.5055	0.5057	0.5110	0.5111	0.5100	0.5110	0.0044		55
	β_{11}	0.0038			0.00791		0.00791	0.00634	0.00600	0.00658			0.00488	0.00295		56
	β_{33}	0.01480			0.01356		0.01021	0.01021	0.01008	0.00970			0.00866	0.00430		57
	β_{12}	0.00320			0.00934	0.00800	0.00934	0.00934	0.00934	0.00792	-0.00711		0.00546	0.00412		58
	β_{23}	0.00000			-0.01098	-0.00500	-0.01098	-0.01098	-0.01098				-0.00307	0.00432		59
Atom 7	x	-0.1304	-0.1284		-0.1284			-0.1348	-0.1348	-0.1306	-0.1309	-0.1321	-0.1317	0.0025		60
O (VIII)	z	-0.1208	-0.1209		-0.1212			-0.1187	-0.1187	-0.1155	-0.1156	-0.1165	-0.1155	0.0053		61
	β_{11}	0.00649			0.00105			0.00105	0.00105	0.00484	0.00501		0.00464	0.00265		62
	β_{33}	0.01200			0.01251			0.01251	0.01251	0.00361	0.00376		0.00371	0.00512		63
	β_{12}	0.00514			-0.00147			-0.00147	-0.00147	-0.01211	-0.01208		-0.01273	0.00380		64
	β_{23}	-0.00700			-0.00487			-0.00487	-0.00487				-0.01273	0.00380		65
Atom 8	x	0.1426	0.1366		0.1333			0.1333	0.1333	0.1180	0.1176	0.1147	0.1130	0.0023		66
O (VII)	z	0.1175	0.1184		0.1185			0.1123	0.1123	0.1110	0.1111	0.1169	0.1119	0.0039		67
	β_{11}	0.00728			0.00459			0.00459	0.00459	0.00087	0.00071		0.00014	0.00228		68
	β_{33}	0.00710			0.00457			0.00457	0.00457	0.01211	0.01194		0.01199	0.00309		69
	β_{12}	0.00710			0.00414			0.00414	0.00414	0.00045	0.00021		-0.00011	0.00304		70
	β_{23}	-0.00545			-0.00608			-0.00608	-0.00608	-0.00294	-0.00276		-0.00440	0.00292		71
Atom 9	x	-0.2912	-0.2927		-0.2908			-0.2943	-0.2943	-0.2941	0.4755	-0.2933	-0.2935	0.0020		72
O (IV)	z	0.4756	0.4738		0.4762			0.4723	0.4723	0.4755		0.4725	0.4814	0.0039		73
	β_{11}	0.00823			0.00792			0.00792	0.00792	0.00748	0.00731		0.00342	0.00311		74
	β_{33}	0.00784			0.00919			0.00919	0.00919	0.00688	0.00686		0.00627	0.00324		75
	β_{12}	0.00627			0.00788			0.00788	0.00788				0.00192	0.00398		76
	β_{23}	0.00209			0.00155			0.00155	0.00155				-0.00473	0.00327		77
Atom 10	x	0.3699	0.3707		0.3695			0.3707	0.3741	0.3734	0.3736	0.3736	0.3735	0.0025		78
O (III)	z	-0.4050	-0.3958		-0.3940	-0.4050	-0.3928	-0.3946	-0.3974	-0.3919	-0.3921	-0.3954	-0.3878	0.0043		79
	β_{11}	0.00651			0.00743			0.00772	0.01052	0.01176	0.1206		0.00812	0.00357		80
	β_{33}	0.01627			0.01411			0.01235	0.01374				0.00369	0.00462		81
	β_{12}	0.00640			0.00495			0.00596	0.00862	0.01144	0.1182		0.00809	0.00467		82
	β_{23}	0.00233			0.00652			0.00401	0.00653				-0.00179	0.00437		83
Atom 11	x	-0.4442	-0.4433		-0.4428			-0.4402	-0.4402	-0.4444	-0.4445	-0.4475				

TABLE V — SOME INTERATOMIC DISTANCES OBTAINED FROM LEAST SQUARES CALCULATIONS (SECOND SET OF WEIGHTS)

Distance	Cycle 1' Å	Cycle 2' Å
C(I)—N(I)	1.40	1.43
C(II)—N(II)	1.29	1.25
S(I)—O(V)	1.46	1.44
S(I)—O(III)	1.38	1.38
S(I)—O(I)	1.46	1.44
S(II)—O(VI)	1.47	1.48
S(II)—O(IV)	1.48	1.50
S(II)—O(II)	1.50	1.49
Al(I)—O(VII)	1.92	1.89
Al(I)—O(VIII)	1.86	1.86
Al(II)—O(IX)	1.90	1.92
Al(II)—O(X)	1.91	1.91

In cycle 2' the starting parameters were the same as those resulting from cycle 1' (new weights) except for the x -parameters of N(I) and N(II) and the z -parameter of N(I). Also, it was found that under the conditions set for the weighting in cycle 1', only 496 amplitudes should have been weighted unity. For these reflections and the starting parameters shown in Table III, the R value was 0.176, weighted R , 0.119 and error of fit, 1.85. Again only scale and positional parameters were allowed to vary. Changes were not large except for the N and C(II) parameters. Some distances calculated from these parameters are given in Table V. (C—N distances are always on assumption of planarity of the guanidium group.) Note that again the C(I)—N(I) distance is short, the C(II)—N(II) long, but the average is the expected value for such a bond. Also noteworthy is the continued tendency of S(I)—O(III) to be short. In fact, there is a tendency throughout for the S(I)—O distances to be shorter on the average than the S(II)—O distances. Examining the correlation matrix for this cycle we may summarize the results as follows (Table VI). Only those pairs for which $|\rho| \geq 0.40$ are listed. Thus of the 946 ρ_{ij} ($i \neq j$) terms only 75 are ≥ 0.40 . Important also is the fact that a large number, 677, of the terms are less than 0.10, many *much* less than 0.10; 194 of the $|\rho_{ij}|$ lie between 0.10 and 0.40. These could be important especially if one parameter has many interactions of moderate size with other parameters.

Earlier we gave some examples of $|\rho_{ij}|$ that were calculated from the inverse matrix of cycle 12 (old weights). It is seen from examination of Table VI that the values for the particular $|\rho_{ij}|$ obtained from cycle 2' are essentially the same except for the value for the $x_{N(II)}-x_{N(I)}$ interaction. The value is much higher, 0.62, than the one, 0.10, obtained

from the incorrect orientation of the guanidinium ions. Thus, *incorrect values for parameters can uncouple parameters*. Furthermore, this appears to be the reason that there was not much change in the incorrect y -parameter of N(II) in the first three cycles. That is, a parameter which is given a value which tends to make it independent may not change *rapidly* to a value which tends to make it dependent.

The purpose of the next cycle was to see the results of allowing the parameters, both positional and thermal, of only the N and O(III) atoms to vary. Before carrying out this calculation, however, the positions of hydrogen atoms were estimated. The guanidinium ions were considered to be essentially planar, and the z -parameters of the guanidinium H's taken as 0.55 for those about the threefold axes at $\frac{1}{3}, \frac{2}{3}$ and $\frac{2}{3}, \frac{1}{3}$, and 0.505 for those about the axis at 0,0. For the water molecules, the links with the SO_4 oxygen atoms were considered and the tilt of the water molecule estimated accordingly. In any given level of H_2O molecules about either of the nonequivalent axes, the z 's were taken equal. The H—O—H angle was taken as 105° and the O—H distance, 0.96 Å. (The initial H-parameter values will not be listed; however, the last set used will be listed later.) First, H contributions to the $F_{hk\cdot l}$ for h, k, l positive were calculated for two different orientations of the guanidinium ions, namely: $(+, -)$ and $(+, +)$. (The program used for this calculation was written by R. G. Treuting; the atomic scattering factors for H were those of Viervoll and Ögrim.¹⁵) These calculations, together with consideration of previous calculations of the amplitudes, corroborated the conclusion that the $(+, -)$ orientation was the most probable one.

The N-parameters were readjusted to yield the most probable C—N distance, and the z -parameter of O(III) was started at -0.405 . Those observed amplitudes with $\sin^2\theta/\lambda^2 < 0.0800$ which were not strongly affected by extinction were reweighted unity. The total number of reflections weighted unity was 568. The H atoms were put into the calculation as "fixed atoms" (see Ref. 13) with isotropic temperature factor $B = 3.00 \text{ Å}^2$. The over-all R value was 0.177, weighted R , 0.117, and error of fit, 1.90.

The results of the least squares calculation are given in Table IV cycle 3'. It is seen that the O(III) z -parameter returned to that of the previous cycle. The N(I) x -parameter increased somewhat, implying a C(I)—N(I) distance of 1.37 Å. The parameters of N(II) imply a C(II)—N(II) distance of 1.33 Å.

In Table VII, we list those correlation coefficients greater than or equal to 0.40. If this table is compared with Table VI, one finds that the

coupling of N(I) and N(II) positional parameters is still as strong as in the previous cycle. In both cycles 2' and 3', the correlation matrices showed no strong interaction between O(III) and nitrogen atom parameters. The correlation matrix of cycle 3' indicated that there are some very strong interactions in pairs of thermal parameters. As expected, there was corroboration of a strong interaction between the β_{33} 's of the N atoms.

For this case, it might be worthwhile to show the Δp_i 's obtained from the complete solution of the 21 normal equations compared with those obtained from the diagonal term approximation. These are given in Table VIII together with the σ 's calculated by the Busing-Levy program. As expected, several of the Δp_i 's for particular i are quite different, particularly for those which are highly correlated (see Table VII).

Before proceeding to the next cycle, the calculated and observed data were examined for any outstanding discrepancies and rechecks were made on the intensity data. It was found that 27 of the reflections which were listed as observed should have been listed as unobserved. It was also found that 5 reflections which were recorded as unobserved should have been observed by the instrument but were missed. These were obtained from film data.

Slight changes were made in the H-parameters; the x -parameter of N(I) was returned to 0.113 and necessary changes made in the β_{12} and β_{13} thermal parameters of N(I). Now the Busing-Levy program calculates and stores all derivatives, so that it is possible to allow different sets of parameters to remain constant and solve for sets of Δp_i for each initial set of parameters. In cycle 4'a, therefore, we first allowed only the N(I), N(II), and O(III) parameters to vary and then in 4'b,

TABLE VII — CORRELATION COEFFICIENTS FROM CYCLE 3'

$ \rho $	i, j				
0.40-0.50	1,2	7,12	8,9	8,15	
0.50-0.60	4,7				
0.60-0.70	1,10	5,7	5,14		
0.70-0.80	3,11	6,13			
0.80-0.90					
0.90-1.00	12,14	18,20			

Parameter numbers									
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(II)	1	2	3	4	5	6	7	8	9
N(I)	10		11	12		13	14	15	
O(III)	16		17	18		19	20	21	

TABLE VIII — PARAMETER CHANGES AND ERROR ESTIMATES
FROM CYCLE 3'

Parameter number (see Table VII)	Busing-Levy	Diagonal term approx.	σ 's from Busing-Levy
1	-0.0029	-0.0020	0.0027
2	-0.0056	-0.0027	0.0022
3	0.0058	0.0046	0.0037
4	-0.00661	-0.00105	0.00268
5	0.00270	0.00418	0.00245
6	0.00231	0.00477	0.00420
7	-0.00273	-0.00136	0.00202
8	-0.00227	-0.00333	0.00271
9	-0.00371	-0.00053	0.00225
10	0.0048	0.0051	0.0025
11	0.0057	-0.0030	0.0048
12	0.00411	0.00023	0.00296
13	-0.00124	0.00172	0.00527
14	0.00614	0.00113	0.00466
15	-0.01098	-0.00983	0.00552
16	-0.0003	-0.0009	0.0014
17	0.0121	0.0120	0.0023
18	0.00092	0.00160	0.00228
19	-0.00216	-0.00133	0.00311
20	-0.00145	-0.00230	0.00307
21	0.00419	0.00025	0.00351

varied all parameters except the scale factors. The results are shown in Table IV. Again in both cases, the N(I) x -parameter increased; there were changes in the N(II) parameters, but the implied C—N distance 1.35 Å was good. Also the z -parameter of O(III) seemed to improve, especially when all the parameters were allowed to vary. But in 4'a, the thermal parameter matrix of the N(I) atom was not positive definite, while in 4'b, seven atoms had thermal parameter matrices which were not positive definite. Also there were continued oscillations and large error estimates. It was evident that real convergence would not be attained.

However, because the N and O(III) parameters did look encouraging, it was decided to try one more cycle. This time the parameters of the water hydrogen atoms were recalculated in a somewhat different way. In a recent paper,¹⁹ Aleksandrov, Lundin and Mikhailov report results of a study of the distribution of hydrogen atoms in guanidinium aluminum sulfate hexahydrate by means of proton magnetic resonance experiments. They report that the nearest neighbor p—p (proton-proton) vectors are perpendicular to the a_1 , a_2 and a_3 axes.† They argue that on the basis of symmetry considerations all H atoms bonded to O's in a

† Previously, Spence and Muller¹⁸ had reported this to be so for the p — p vectors of the water molecules, but had concluded that the p — p vectors of the guanidinium groups could be parallel to the c -axis with a separation of 2.05 Å.

single octahedron layer about a threefold axis must have the same z -parameter. Of course, this is true only for those hydrogen atoms bonded to N(I) atoms and to the water molecules about the threefold axis at 0,0. The trigonal axes and planes of symmetry are such that only three atoms about the axis at $\frac{1}{3}, \frac{2}{3}$ and three about the axis at $\frac{2}{3}, \frac{1}{3}$ must have the same value of z .

Thus contrary to the statements of Aleksandrov *et al.*,¹⁹ symmetry conditions do *not* require all the nearest neighbor H—H vectors to be parallel to the (00·1) plane, nor must they all be perpendicular to the a_1 , a_2 and a_3 axes. Only for those about the threefold axis where the mirror planes intersect, namely at 0,0 must this be the case. However, it is possible that the nearest neighbor H—H vectors about the threefold axes at $\frac{1}{3}, \frac{2}{3}$, $\frac{2}{3}, \frac{1}{3}$ are *close* to parallelism with the (00·1) plane and perpendicularity to the a_1 , a_2 , a_3 axes.

Furthermore, Aleksandrov *et al.*¹⁹ refer to the trial structure reported by Varfolomeeva *et al.*³ Although that structure is incorrect, it would have no noticeable effect on the conclusions of Aleksandrov *et al.*, since they discuss only the nearest neighbor H—H vectors.

Thus, in calculating the H parameters, the tilting of the water H—H bonds out of the (00·1) plane and skewness to the a_1 , a_2 , a_3 axes was permitted in those water molecules about the threefold axes at $\frac{1}{3}, \frac{2}{3}$, $\frac{2}{3}, \frac{1}{3}$. (The guanidinium ions, however, were assumed to be planar.) In calculating the H positions, the water molecules were assumed to lie in the planes connecting the water oxygen atom with the two sulfate oxygen atoms involved in the hydrogen bonding. The bisector of the H—O—H angle of 105° was taken as the line passing through the center of the water oxygen atom and the center of the line connecting the two sulfate oxygen atoms involved. The parameters of the N and O atoms involved were those from cycle 4'b. The H-parameters thus deduced are listed in Table IX. The new parameters caused some differences in the

TABLE IX — H PARAMETERS USED IN FINAL CYCLE

Description	x	y	z
on N(I)(atom 6)	0.205	0.086	0.51
on N(II)(atom 1)	0.465	0.256	0.56
	0.564	0.434	0.56
on O(VIII)(atom 7)	0.139	0.218	-0.148
on O(VII)(atom 8)	-0.072	0.134	0.156
on O(IX)(atom 4)	0.457	0.257	-0.124
	0.526	0.400	-0.111
on O(X) (atom 5)	-0.452	-0.260	0.205
	0.464	0.588	0.219

contributions to several amplitudes, but in general not very important ones.

Some necessary adjustments of thermal parameters resulting from cycle 4'b were made. In cycle 5'a,† only those positional parameters were varied in which changes greater than $\sigma/5$ occurred between previous cycles 2' and 4', all thermal parameters were varied in which there were changes greater than $\sigma/5$ between cycles 1' and 4'; all scale factors were kept constant. In 5'b, only those parameters were varied in which changes in 5'a were greater than $\sigma/5$. In 5'c, only positional parameters were varied. In 5'd all parameters were varied. All results are listed in Table IV. Differences range from very small to very large and are indicative of the unattainability of convergence. We list also the σ 's‡ in the Δp_i 's for the last cycle 5'd in the last column of Table IV. These are especially large for most of the thermal parameters and for most of the z -parameters, and reflect the strong interdependence in pairs of parameters.

The correlation matrix‡ for cycle 5'd contains 6,670 $\rho_{ij}(i \neq j)$ terms. Thus we shall again only list the values of $|\rho_{ij}| \geq 0.40$ (Table X). Of the 6,670 terms in the matrix, 176 have values greater than 0.40; 1,389 have values greater than 0.10.

On examining Table X, one finds that no interactions of scale factors with positional parameters are listed. In fact, the correlation coefficients for such combinations are all *very* low. However, there are all the other types of interactions, namely: scale factor-thermal parameter, thermal parameter-thermal parameter, positional parameter-positional parameter, and several (those with asterisk) positional parameter-thermal parameter. Most often, also, the interdependence is between analogous parameters; for example, a z -parameter of an atom interacts with z -parameters of other atoms. Even when a positional parameter interacts with a thermal parameter, an analogy exists, e.g., a z -parameter interacts with a β_{33} -parameter. This makes physical sense, of course, and gives us some confidence that the correlation coefficients reflect the structural interdependence of the parameters. Correlation may be caused partially by the experimental technique§ but it is unlikely to result mainly from the ill-conditioning of the normal equations by a

† It should be kept in mind that all cycles 5' refer to the derivatives evaluated with the parameters of cycle 5'a.

‡ It is worth emphasizing that statistical theory precludes the use of the error estimates or normal equations matrix to determine the statistical significance of the parameters listed. Only if convergence is actually attained can these numbers be so used. Nevertheless, in a practical way, the error estimates and correlation coefficients do give us important information in the course of refinement or, as in the present case, relative to the unattainability of convergence.

§ X-ray vs neutron diffraction.

TABLE X — CORRELATION COEFFICIENTS FROM CYCLE 5'd.†
(ONLY $|\rho_{ij}| > 0.40$ ARE LISTED)

$ \rho $	$i - j_1, j_2, j_3, \dots$
0.40-0.50	3-4,5; 4-105; 6-75; 7-75; 8-75; 11-38,47,61,67,85; 15-56; 18-19,34; 20-47†,61,97,103; 21-30; 24-30,86,88; 25-26,27; 29-47,61; 30-33; 36-37; 38-61,103; 40-51,62; 42-68; 43-66†; 44-46†; 45-46; 47-55; 67,73,85,91,103; 51-64; 52-53; 55-97,103; 57-59; 61-73,79,85,91; 63-69; 67-103; 75-81; 77-79†,83; 79-83†,97,103; 81-83; 97-108,114; 103-108,114; 105-113; 108-110†; 113-116
0.50-0.60	4-5,6,7,8; 5-113; 8-99,113; 11-97,103; 12-15; 13-15,58; 16-59; 19-84; 20-91; 22-24; 26-89; 27-94†; 29-85,97,103; 30-94; 37-53†; 38-47,97; 39-42; 41-50,63,69; 43-71; 47-97; 48-51; 50-69; 51-62; 61-97,103; 67-97; 73-83†,97,103; 85-91,97,103; 110-115
0.60-0.70	5-105; 13-56; 14-57; 20-29; 21-24,88; 23-86; 27-92†; 28-90; 30-92; 37-46; 40-42,49,68,70; 49-64; 52-65; 72-78,80†,82†; 74-78†; 76-78†; 86-88; 96-104†,106†; 98-102†; 100-102†; 108-115†; 111-116†
0.70-0.80	5-6,7,8; 8-105; 9-54; 18-27; 21-86; 32-93; 35-95; 36-66; 45-60; 49-51,62; 50-63; 96-102; 108-114; 111-113†
0.80-0.90	6-7,8; 11-55; 25-91; 38-67; 62-64; 73-79; 98-100
0.90-1.00	7-8; 47-61; 56-58; 68-70; 74-76; 80-82; 92-94; 97-103; 104-106

† See last column of Table IV for parameter numbers.

‡ Positional-thermal parameter correlation.

reasonable but not necessarily ideal weighting technique. It will be noticed also that the same pairs of parameters show very nearly the same measure of interdependence as indicated by earlier calculations, again corroborating the point that it is the structural model (including atomic form factors) which causes the interactions.

For the sake of completeness, we show in Table XI a list of observed amplitudes compared with those calculated from the parameters used initially in cycle 5' and including the contributions of the H atoms with parameters shown in Table IX. Including consideration of multiplicity and the differences when calculated amplitudes are greater than the threshold values (with half the threshold value included in the denominator) for reflections not observed, the discrepancy factor is 0.11.†

The over-all agreement is quite good despite several discrepancies in which a calculated amplitude is above the threshold value for an unobserved reflection.‡ Table XI attests to the validity of the conclusion that the general features of the structure are correct.

† Six amplitudes, those of reflections 30·0, 11·1, 21̄·1, 22·1, 42̄·1 and 21̄·2, suffering from extinction were excluded in calculation of this discrepancy factor.

‡ These are a product of the instrument which sometimes missed reflections, which, according to visual estimates of photographic intensities, it should not have missed.

TABLE XI — OBSERVED AND CALCULATED AMPLITUDES BASED ON PARAMETERS USED INITIALLY IN CYCLE 5

[illegible]

VI. FURTHER COMMENTS ON THE INDETERMINACY OF THE EXACT STRUCTURE OF GUANIDINIUM ALUMINUM SULFATE HEXAHYDRATE

6.1 *Importance of the Weighting Procedure*

The use of two very different weighting procedures did not break down the high correlations existing between parameters. It is doubtful, especially in the case of so large a number of parameters, that any reasonable weighting procedure would succeed in uncoupling the parameters sufficiently to lead to greater determinacy.

6.2 *Effect of Keeping Some of the Parameters Constant while Allowing Others to Vary*

In the case that there is correlation between parameters, it would seem that, at least in the final stages of the refinement, holding of such parameters constant could lead to erroneous results. In a case involving a smaller number of parameters it might be possible to obtain a confidence region⁶ for all the parameters by holding some of the parameters constant, but at several different values. For example, suppose the problem involves n almost independent parameters and two almost completely dependent parameters which appear to prevent convergence. Choosing several judicious values of one of the latter and making the calculation for each one will give sets of values for the other parameters which will allow the construction of the equiprobability ellipsoids.

However, in a problem involving many parameters, and many large and multiple correlations, such a technique would appear to be impractical. It should be mentioned that if the model were very nearly linear, only those correlations very near ± 1 would be important in the unattainability of convergence. However, it is possible that the more nonlinear the model, the more important the other correlations become.

6.3 *Possible Effects of Increasing the Number of Observed Data*

There are two ways in which the number of data might be increased. One is to obtain more of the weak intensities by increasing the detector sensitivity. It does not seem that this would have the effect of decreasing the correlations. This was shown to some extent by the calculations based on the two different weighting schemes. In the first case the weighted evaluated derivatives for unobserved reflections were included; in the second, these were given zero weight and therefore excluded. Also, the exclusion of reflections for which $\sin^2\theta/\lambda^2 < 0.0800$ did not have an apparently significant effect on the correlations. (Compare, for example, analogous values in Tables VI and X.)

The other way in which to increase the number of data is to use shorter wavelength radiation. Now, it is not necessary actually to measure these data before determining the effect on the correlations because the correlation coefficients, as calculated, depend only on the model and the evaluated derivatives. It is unlikely that the situation would change very much if the additional terms were included because the relationship of the derivatives with respect to correlated parameters would probably not change very much.

In the case of tetragonal BaTiO_3 ,^{5,6} higher index reflections would have almost no important contributions from the oxygen atoms. Thus the interactions among oxygen ion parameters will not be affected. Similarly, interactions among the metal ion parameters will probably not be much affected. But interactions between the two groups could be reduced. However, in the case of an all light atom structure, it would appear that the extra data would probably not reduce the correlations.

6.4 Possible Effect of Greater Accuracy in Measurement of Observed Intensities

The effect of greater accuracy in measurement of the observed intensities is not really predictable in this case. To be sure, in each iteration the reduction of $s = \sqrt{\Sigma(\sqrt{w}\Delta)^2}/\sqrt{m-n}$ would reduce the apparent size of the equiprobability surfaces. This we certainly know.

However, we must ask first whether there is a limit to the accuracy of the observed amplitude. One would suspect that there is such a limit. Furthermore as pointed out by Caticha-Ellis and Rimsky,²⁰ there will always be a discrepancy between the calculated and true values of the amplitudes. Thus s has a lower positive limit.

Reduction of s would not only decrease the size of the equiprobability surfaces (and therefore, of course, the standard estimates of error) but it would also decrease the components of the vector v , $v_j = \Sigma(\sqrt{w}D_j) \cdot (\sqrt{w}\Delta)$, where the D_i are the evaluated derivatives. Thus, for example, if cycle 5'd were repeated with each Δ decreased to $\frac{1}{2}$ of its value, each v_j , and therefore each $\Delta p_i = \sum_j b_{ij}v_j$ would be reduced to the same extent. Of course an average reduction of $\frac{1}{2}$ might not do the same thing. In fact, with a poor distribution of the reduction in Δ , the Δp_i in some cases could even be larger, depending on the algebraic values of the D_j .

Actually the nature of the shape of the equiprobability surfaces might give the best clue to what might happen if increased accuracy of measurement were attainable. The nonlinearity of the model would probably play an important part. The more nonlinear, the more important are apt

to be those correlations which are not perfect. Of course, even one perfect correlation ± 1 , renders the whole problem indeterminate⁶ if insistence is made on allowing all parameters to vary in an iteration. This is not necessary, however, and one could learn a great deal about the parameters of a structure which has only one perfect correlation and the rest very small ones (see Section 6.2). In the present case, there are many correlations having absolute values between 0.90 and 1.00 (Table X). These have the specific values: 0.917, 0.905, 0.913, 0.907, 0.975, 0.963, 0.901, 0.979, and 0.902, respectively. Perhaps the most important ones are the three closest to unity.

In the case of gross nonlinearity it seems possible that these and so many of the other high correlations of Table X could cause unattainability of convergence even if the lowest limit of s were attained. That is, the shape of the equiprobability surface may be such as to prevent the practical attainment of separate estimates of the parameters (see also Ref. 21) from the given data. This seems to be true of the BaTiO₃ case.^{5,6}

Needless to say, a measure of doubt remains. Further work might aid in removing this doubt. This would involve trying to obtain more data and of greater accuracy, and further calculations. Our doing this is not presently contemplated.

6.5 *Fourier Synthesis vs Least Squares*

In the case of tetragonal barium titanate, Fourier synthesis produced no improvement on the least squares method.²² It is likely that with the present data, the situation in the case of the G.A.S.H. would be the same. On the other hand, there is no requirement of linearity in the Fourier synthesis: the actual amplitudes are the Fourier coefficients. In the least squares technique, an approximation is used: i.e.,

$$\begin{aligned} F_{hkl}(p_1, p_2, \dots, p_n) &= F_{hkl}(\bar{p}_1 + \Delta p_1, \bar{p}_2 + \Delta p_2, \dots, \bar{p}_n + \Delta p_n) \\ &= F_{hkl}(\bar{p}_1, \bar{p}_2, \dots, \bar{p}_n) + \sum_{j=1}^n \left. \frac{\partial F_{hkl}}{\partial p_j} \right|_{\bar{p}_j} \Delta p_j \end{aligned}$$

where $\bar{p}_1, \bar{p}_2, \dots, \bar{p}_n$ are approximate but nearly true values of the parameters. It is possible that higher order terms could be important here, but it is *not* clear that inclusion of the next higher order terms would necessarily lead to improvement. Also, the calculation would increase in complexity.

Cochran has shown that a rather close relationship exists between the Fourier synthesis and least squares techniques. There are conditions on

this relationship given by Cochran²⁴ and Hoard and Geller²⁴, and in addition in the actual least squares calculation, an approximation is made and nearness to linearity is assumed. Therefore, if the nonlinearity is not serious, convergence should be attainable in either case. If it is serious, the relationship could break down further and the Fourier synthesis could conceivably converge when the least squares calculation tends not to converge.

VII. COMMENTS ON THE SINGLE-CRYSTAL AUTOMATIC DIFFRACTOMETER

As mentioned earlier, the data used in this work were collected four years ago. Since that time only one or two attempts were made to use the instrument for other studies. These were unsuccessful because of difficulties which are probably surmountable, but require modification of the instrument.

The present instrument puts a lower limit on the sample size. To keep the time for recording a layer within reasonable bounds and to prevent the instrument from reacting to background scattering, only intensities above a certain preset count energize the circuitry which sets the crystal back and shifts speed. To obtain satisfactory counting rates the use of large crystals is required. (The intensity is proportional to the number of unit cells irradiated.) However, to obtain adequate or meaningful intensities from highly absorbing materials one must have small crystals. In short, the instrument presently is suited mainly to crystals with low absorption and from which sizable cylindrical specimens can be made.

The indexing of the reflections was a tedious process. The possibility of error, particularly at the high angles, was great, but the use of photographs and cross examination of data helped prevent errors. An improvement on the Bond-Benedict automatic single-crystal diffractometer would be provision for foolproof pre-indexing of the reflections.

VIII. SUMMARY

Extensive application of the least squares refinement technique (through the use of the Busing-Levy IBM 704 program) to three-dimensional X-ray data from crystals of guanidinium aluminum sulfate hexahydrate indicated that although the structure as originally reported for the isostructural guanidinium gallium sulfate is essentially correct, an *exact* structure is unattainable from the present data by means of the least squares method of refinement. The numerous high correlations of pairs of parameters, apparently linked with the nature of the structure, appear to be a primary cause of prevention of convergence.

The course of the calculations has been outlined with special emphasis on some of the more obvious parameter interactions, but tables are given to enable the more interested reader to examine the results in somewhat greater detail.

The work also further demonstrates the importance of the correlation matrix as a tool for establishing the existence or nonexistence of interdependence of structural parameters.

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