earlier neutron diffraction determination of the barium titanate structure referred to above, (Danner, Frazer & Pepinsky, 1955), so that abnormally large standard deviations of the parameters are not revealed. In view of the experience gained with barium titanate, there is good reason to suspect that they may be large, and the models proposed must be accepted with caution.

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Parameter Interaction in Least Squares Structure Refinement

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The correlation matrix gives a good indication of the interdependence of parameters in the course of refinement. Very strong interactions, i.e., high correlations, are essentially independent of the quality of the data, but depend on the trial structure model, including all parameters and atomic scattering factors, and to some extent on the number of data. Very strong interactions imply that the parameters involved could be indeterminate. Detailed illustration of the importance of the correlation matrix is given by results from investigations of the structures of a grossularite, of tetragonal $BaTiO_3$ and of $LiMnPO_4$.

Introduction

Temperature and scale factors obtained in structure refinements are perhaps not as reliable as might be indicated by error estimates. The character of the thermal parameter function whether isotropic or anisotropic is such as to invite into it errors of various sorts. These include errors in intensity measurement, in absorption and extinction correction and in atomic scattering factors, particularly when correction has not been made for dispersion or when the spherical symmetry approximation is not valid.

Templeton (1955) has predicted that neglect of the real part of the dispersion correction would strongly affect the scale and thermal parameters. This is equivalent to saying that strong interaction is expected between the atomic scattering factors and the scale and thermal parameters. In the case of the refinement of the yttrium iron garnet structure it was shown (Geller & Gilleo, 1959) that inclusion of the dispersion corrections resulted only in large changes in the scale factor (from 1·00 to 1·17) and in the thermal parameters of Y^{3+} (from 0·16 to 0·40 Å^2) and of O^{2-} (from 2·05 to 1·19 Å^2). The change in the temperature factor of the Fe^{3+} ion was negligible despite the fact that the real part of the dispersion correction for this ion was $-3{\cdot}7e$ as against $-1{\cdot}3e$ for the Y^{3+} ion.

The effects of the interactions described above, however, are usually not included in the error estimates. As another example, one may say that all theoretical atomic scattering factors are only an approximation particularly for atoms which have electronic clouds which in many structures deviate substantially from spherical symmetry. Such errors as may occur from this approximation could be absorbed in the thermal and scale parameters without necessarily being included in the error estimates of these parameters.

But now suppose that we decide on the use of certain atomic scattering factors in our model and assume that these are absolutely correct. We further assume a good trial structure which includes these atomic scattering factors and that our data weighting system is unbiased. Then the standard deviations calculated by solving *completely* the set of normal equations give, in the least squares sense, the correct estimates of error. It should be pointed out that these are the marginal standard deviations which include the effects of correlation. Therefore, theoretically, these error estimates may be considered to be conservative. That is to say, any conditional variance of a component of the parameter vector cannot be greater than the variance. (See, e.g., Anderson, 1958.)

The interdependence of two or more structural parameters can cause great difficulty in attempts to refine structures. Strong interactions may completely prevent refinement even when the data used are of high precision. The least squares refinement program written by Busing & Levy* (1959) now makes it possible to see what such interactions may be like. In recent work, to be reported separately, on the refinement of the structure of guanidinium aluminium sulfate hexahydrate (Geller & Katz, 1962), it became apparent that although the general features of the structure were correct and as originally reported for the gallium isomorph (Geller and Booth, 1959), the structure was unrefinable from the available data. This is despite the fact that the three-dimensional data used appear to be quite accurate. In the present paper,the relation of the correlation coefficients to the observed results of least squares calculations on the structures of a grossularite, of tetragonal $BaTiO_3$ and of $LiMnPO_4$ will be detailed.

The correlation matrix

The Busing–Levy least squares program sets up the entire matrix **a** and the vector **v** of the normal equations inverts **a** and solves the equations exactly. The matrix of normal equations, **a**, and its inverse **b** may be obtained from the binary tape translated into decimal by an auxiliary program. A special program patch for obtaining **v** in the output has been written by Miss D. C. Leagus of these Laboratories. For completeness the various relations† are listed below:

$$a_{ij}=\Sigma(\sqrt{(w)}D_i)(\sqrt{(w)}D_j)$$
$$v_i=\Sigma(\sqrt{(w)}D_i)(\sqrt{(w)}\Delta)$$
$$b_{ij}=A_{ji}/d$$
$$\Delta p_i=\Sigma_j b_{ij}v_j\ .$$

In these relations, the D_i are the derivatives;

$$\Delta=[(\text{sign of } s_qF)|F_o|]-s_qF_c\ ,$$

where s_q is the scale factor; A_{ji} is the cofactor of a_{ij}; d is the value of det **a**; the p_i are the parameters.

At the end of a least squares cycle the standard error of Δp_i, which is then also that of p_i, is given by

$$\sigma(p_i)^* = \sqrt{b_{ii}}\{[\Sigma(\sqrt{(w)}\Delta)^2-\sum_{k=1}^{n}\Delta p_k v_k]/(m-n)\}^{\frac{1}{2}}\dagger\ .$$

By analogy, the covariance

$$\sigma(p_ip_j)^* = b_{ij}[\Sigma(\sqrt{(w)}\Delta)^2-\sum_{k=1}^{n}\Delta p_k v_k]/(m-n)\dagger\ .$$

The correlation coefficient

$$\varrho(p_ip_j)\ddagger = \frac{\sigma(p_ip_j)}{\sigma(p_i)\sigma(p_j)} = \frac{b_{ij}}{\sqrt{b_{ii}}\sqrt{b_{jj}}} = \varrho_{ij}\ .$$

The normalized inverse matrix, with terms ϱ_{ij}, is the correlation matrix; that is, all the information needed to obtain the correlation matrix is obtained by the Busing–Levy program in the course of the least squares refinement cycle. A program patch to normalize the inverse matrix has been written by Misses D. C. Leagus and B. B. Cetlin and the correlation matrix is now obtained routinely by the author.

From the above expression for ϱ_{ij}, it is seen that in any cycle the correlation coefficients are independent of the sum of the residuals and are directly related to the structure model. That is, the ϱ_{ij} values depend on the derivatives evaluated with the given set of parameter values and atomic scattering factors. It is possible that some fairly strong interactions between parameters could be caused by large error in one or more of the parameters; on the other hand, it is also possible that large parameter errors could cause uncoupling of two strongly interacting parameters (Geller & Katz, 1962). But there is only one way in which data of poor quality could lead to large interaction: by deviating a parameter from its true value in such a way as to cause such interaction.

As indicated earlier, the interest of the author in

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* A program for two-dimensional refinement written by W. C. Hamilton mainly for use with neutron diffraction data also makes this possible.

† Wherever possible, the Busing–Levy notation will be used.

* It should be kept in mind that theoretically the quantities we call standard error, covariance and correlation coefficient have no relevance to the parameter values until convergence has been attained. However, it will be clear that examination of the correlation matrix and the σ's gives important practical information in any stage of the analysis.

† In these expressions the Δ's are the initial ones; that is to say, the term

$$\Sigma(\sqrt{(w)}\Delta)^2-\sum_{k=1}^{n}\Delta p_k v_k$$

is an estimate of the correct sum of squares of the residuals. If the problem were truly linear, the result would be exact.

‡ It should be kept in mind that theoretically the quantities we call standard error, covariance and correlation coefficient have no relevance to the parameter values until convergence has been attained. However, it will be clear that examination of the correlation matrix and the σ's gives important practical information in any stage of the analysis.

the correlation matrix derived from work on the refinement of the structure of guanidinium aluminum sulfate hexahydrate. In this case there are many large interactions of all types* except between scale and positional parameters. Now in order to gain confidence that these numerous interactions were preventing determinacy of the structure, some definitive work has been done on three previously investigated structures. Even though only four structures have now been looked at in this fashion, there is substantial evidence that it is advisable always to examine the correlation matrix or the equivalent before drawing final conclusions as to the meaning of the least squares refinement.

Refinement of the structure of a grossularite

The structure of a grossularite crystal was recently refined by Abrahams & Geller (1958) by means of the Sayre program and with the use of selected data which were particularly sensitive to the oxygen positional parameters, the only variable positional parameters in the structure. The reflections used were those for which h, l are odd, k even (h, k, l permutable). The Al atoms contribute nothing to these reflections and only O atoms contribute to those with $k=4n$. The net contribution of the Ca and Si atoms to the remaining reflections is of the form $\pm 8(f^T_{\rm Ca}-f^T_{\rm Si})$. Now, the refinement proceeded easily to convergence giving reasonable values for the isotropic temperature factors of the atoms involved. These are 1·88, 0·59 and 0·77 Å² for O, Si and Ca respectively. The oxygen positional parameters are (−0·0389, 0·0456, 0·1524). Two completely unrelated weighting methods gave essentially the same results.* Standard deviations especially for the O positional parameters (0·0004–0·0005) were low.

When we obtained the Busing–Levy program, we tried it on the same data with at first rather disturbing but interesting results. The temperature factors of the metal ions virtually exploded. The O temperature factor decreased, but changes in the O positional parameters were not statistically significant. The course of the refinement cycles is shown in Table 1.

It was noticed in the cases of 15 of the reflections, that the Δ's had values greater than 8 and so a rejection test was included. This of course, did not help the situation (Table 2). It seemed rather obvious that the trouble stemmed from the complete interdependence of the metal ion temperature factors. We had chosen data which did not have any independent contributions from the metal atoms. The use of the Sayre program, which neglects the off-diagonal terms, had nevertheless produced physically reasonable results.

Having remembered this case, it was a simple matter to return to it for further investigation. Using 100 reflections and no rejection test we started with the same initial parameters shown in Table 1. It was necessary to carry out only two cycles to make the points we wish to make. Of course, the resulting parameter values are exactly the same as those shown for the first two cycles in Table 1. In Table 3, we show the correlation matrices for these two cycles. The parameters are designated by the numbers given in Table 1.

Note that although some of the smaller values, such as for $\varrho_{1,2}$ and $\varrho_{1,3}$ decrease in the second cycle, the really large ones such as those of $\varrho_{1,7}$ and $\varrho_{2,3}$ stay

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* The interdependence of the parameters of guanidinium aluminum sulfate hexahydrate can be understood on a structural basis.

* The parameter values given here are the averages of the results of refinement by the two different weighting schemes.

Table 1. *Course of refinement of grossularite structure*

All 100 reflections included, G.G. weights*

Parameter number	Parameter	Starting values	Cycle 1	Cycle 2	Cycle 3	Cycle 4
1	s	1·000	0·9685	0·9624	0·9624	0·9607
2	$T_{\rm Ca}$ (Å²)	0·77	3·14	4·69	3·79	3·89
3	$T_{\rm Si}$ (Å²)	0·59	3·63	6·35	5·01	5·33
4	$x_{\rm O}$	−0·039	−0·0382	−0·0383	−0·0382	−0·0383
5	$y_{\rm O}$	0·046	0·0464	0·0460	0·0460	0·0461
6	$z_{\rm O}$	0·152	0·1521	0·1520	0·1520	0·1521
7	$T_{\rm O}$ (Å²)	1·88	1·39	1·35	1·34	1·34
		Standard deviations				
1			0·0266	0·0248	0·0256	0·0252
2			0·50	0·84	0·84	0·77
3			0·63	1·26	1·59	1·36
4			0·00058	0·00052	0·00053	0·00053
5			0·00057	0·00052	0·00052	0·00052
6			0·00056	0·00051	0·00051	0·00051
7			0·17	0·15	0·15	0·15

* See Abrahams & Geller (1958).

Table 2. *Course of refinement of grossularite structure*
Reflections rejected if $\Delta > 8{\cdot}00$, G.G. weights

Parameter number	Parameter	Starting values	Cycle 1	Cycle 2	Cycle 3	Cycle 4
1	s	1·00	0·9981	0·9766	0·9666	0·9659
2	T_{Ca} (Å^2)	0·77	2·47	3·87	4·34	4·33
3	T_{Si} (Å^2)	0·59	2·73	4·84	5·81	5·87
4	x_O	−0·039	−0·0384	−0·0387	−0·0387	−0·0387
5	y_O	0·046	0·0458	0·0455	0·0454	0·0454
6	z_O	0·152	0·1515	0·1511	0·1510	0·1510
7	T_O (Å^2)	1·88	1·76	1·53	1·44	1·44
Number of reflections included			85	87	88	88

Parameter number	Standard deviations			
1	0·0221	0·0220	0·0222	0·0223
2	0·36	0·48	0·57	0·55
3	0·45	0·69	0·96	1·02
4	0·00040	0·00039	0·00038	0·00038
5	0·00040	0·00039	0·00038	0·00037
6	0·00039	0·00039	0·00038	0·00037
7	0·13	0·12	0·12	0·12

essentially constant, as they would for subsequent cycles. The value of $\varrho_{2,3}$, 0·99, suggests a very strong interdependence of the thermal parameters of the metal ions, which is what would be expected. There is also a strong unsuspected interdependence of the scale factor and oxygen thermal parameter as suggested by the values, 0·80–0·81, of $\varrho_{1,7}$. This is further ascertained by examining the results in Tables 4 and 5 obtained from the refinement based on the 37 reflections which have contributions from oxygen ions only. Again the value of $\varrho_{1,5}$ indicates a strong interdependence of the scale factor and oxygen thermal parameter. The value of $\varrho_{3,4}$ appears to indicate a weak interdependence of the x and y parameters of the oxygen ion.

Table 3. *Correlation matrices from two cycles of refinement of grossularite structure.*
All 100 reflections used

Cycle 1

	1	2	3	4	5	6	7
1	1·00	0·25	0·21	0·04	−0·11	0·01	0·80
2		1·00	0·99	−0·10	−0·12	−0·10	0·19
3			1·00	−0·10	−0·12	−0·10	0·16
4				1·00	0·13	0·02	0·02
5					1·00	0·05	−0·10
6						1·00	0·00
7							1·00

Cycle 2

	1	2	3	4	5	6	7
1	1·00	0·06	0·02	0·05	−0·09	0·02	0·81
2		1·00	0·99	−0·14	−0·10	−0·07	0·02
3			1·00	−0·14	−0·09	−0·07	−0·01
4				1·00	0·13	0·02	0·03
5					1·00	0·06	−0·09
6						1·00	0·01
7							1·00

Table 4. *Refinement of grossularite oxygen parameters only*
G.G. weights

Parameter number	Parameter	Starting values	Cycle 1	Cycle 2	Abrahams & Geller*
1	s	1·000	0·8914	0·8938	1·000
2	x	−0·0383	−0·0382	−0·0381	−0·0386
3	y	0·0460	0·0458	0·0458	0·0456
4	z	0·1520	0·1518	0·1518	0·1522
5	T	1·40	1·11	1·10	1·79
		Standard deviations			
1			0·0350	0·0339	
2			0·00062	0·00066	0·00054
3			0·00059	0·00061	0·00053
4			0·00067	0·00070	0·00052
5			0·19	0·20	0·096

* Weights same as those used here. Sayre's least-squares program used on 100 reflections.

Table 5. *Correlation matrices from two cycles of refinement of grossularite structure*
37 reflections to which only oxygen ions contribute

Cycle 1

	1	2	3	4	5
1	1·00	0·06	0·05	−0·05	0·87
2		1·00	0·14	0·01	0·06
3			1·00	0·23	0·06
4				1·00	0·01
5					1·00

Cycle 2

	1	2	3	4	5
1	1·00	0·07	0·04	−0·05	0·87
2		1·00	0·15	0·03	0·06
3			1·00	0·23	0·06
4				1·00	0·01
5					1·00

We notice that the Sayre program gave values of thermal parameters which on first inspection appear to differ markedly from those obtained by the Busing–Levy program. First, we mention that because the

Sayre program we used applies the scale factor to the F_0, there will be a tendency for the thermal parameters to calculate high and the scale factors low when this program is used (see Cruickshank, 1959; Geller and Durand, 1960). Secondly, if there is any correlation at all, the error estimates given by the diagonal term approximation will be low.

Thirdly, if both the complete solution and diagonal term approximation *truly* converge, the parameter *values* obtained by both methods should be the same. When there is large correlation, both methods may fail to converge (i.e., there will be oscillations) or one or both methods may only *appear* to converge. When the complete solution does not really converge, and the diagonal term approximation *appears* to converge as in the present case, then only fortuitously could the results so obtained be *physically* correct, since it is not in the data to provide the true values of the parameters. That is to say, if enough iterations were made with the diagonal term approximation one should expect the ultimate parameter behavior to be the same as would be obtained by the use of the complete normal equations matrix. It should be kept in mind, however, that when high correlation exists, rounding-off errors in the matrix inversion could also cause difficulty in convergence.

We now examine the results of the calculations on the grossularite data to see what further conclusions we may obtain from the results.

The complete solution of normal equations for the 100 data problem gave physically impossible values of the Ca and Si isotropic thermal parameters. This is true not only of the mean values, but of the lower 3σ limit values: Cycle 4 values, Tables 1 and 2, are respectively 1·58 and 2·68 Å^2 for Ca and 1·25 and 2·81 Å^2 respectively for Si. Because it *looks* as though convergence was attained for these parameters in the two cases, in the least squares sense these look like the correct values. The indeterminacy is shown mainly by the large standard deviations. No seemingly 'correct' calculation, however, which gives physically impossible results even *upon actual convergence* can have a really sound basis. In this case, it is obvious that the fundamental difficulty was a biased weighting of the data.

In a statistical problem involving two or more parameters, it is customary to speak of a *confidence region* similar to the confidence limits in the univariate case. If there are n parameters, the confidence region can be represented by an ellipsoid in the n-dimensional space. Having decided on the level of significance this ellipsoid will contain the true values of $p_1, p_2, \ldots, p_n$ with the desired probability. The center of the ellipsoid is given by the vector of the estimated mean values of the parameters $\hat{\boldsymbol{\mu}}(\bar{p}_1, \bar{p}_2, \ldots, \bar{p}_n)$; the size and shape of the ellipsoid will depend on the inverse of the covariance matrix, in our case, $\mathbf{a}$, and on the desired significance level.

In order to make use of the theorems of mathematical statistics we assume a linear model and normally distributed errors. Then $(\hat{\boldsymbol{\mu}}-\boldsymbol{\mu}_0)'\mathbf{a}(\hat{\boldsymbol{\mu}}-\boldsymbol{\mu}_0)$ is distributed as $\sigma^2\chi_n{}^2$. Here $\hat{\boldsymbol{\mu}}$ is the estimate of $\boldsymbol{\mu}_0$, the true $\boldsymbol{\mu}$. The squared standard error of fit, $s^2 = \Sigma(\sqrt{(w)}\Delta)^2/(m-n)$, is distributed as $\sigma^2\chi^2_{m-n}/(m-n)$. The ratio of the two

$$\frac{(\hat{\boldsymbol{\mu}}-\boldsymbol{\mu}_0)'\mathbf{a}(\hat{\boldsymbol{\mu}}-\boldsymbol{\mu}_0)}{\dfrac{\Sigma(\sqrt{(w)}\Delta)^2}{m-n}} \sim \frac{\chi^2_n}{\chi^2_{m-n}/m-n} = nF_{n,\,m-n}\,.$$

Thus a confidence region for $\hat{\boldsymbol{\mu}}$, the mean vector, will be given by

$$(\hat{\boldsymbol{\mu}}-\boldsymbol{\mu}_0)'\mathbf{a}(\hat{\boldsymbol{\mu}}-\boldsymbol{\mu}_0) \le ns^2F_{n,m-n}(\alpha)$$

where $F_{n,m-n}(\alpha)$ is the α probability point for significance level of the F-distribution with n and $m-n$ degrees of freedom. That is, if we compute this for a particular $\hat{\boldsymbol{\mu}}$, we should have confidence $1-\alpha$ that the ellipsoid (the expression with the = sign) contains $\boldsymbol{\mu}_0$.

We could test the null hypothesis, that is: whether a given vector $\hat{\boldsymbol{\mu}}^{(1)} = \boldsymbol{\mu}_0$ by putting the vector $\hat{\boldsymbol{\mu}}^{(1)}$ into the above expression also. On the other hand, should we wish to test the hypothesis $\hat{\boldsymbol{\mu}}^{(1)} = \hat{\boldsymbol{\mu}}^{(2)}$, $(\hat{\boldsymbol{\mu}}^{(1)}-\hat{\boldsymbol{\mu}}^{(2)})'\mathbf{a}(\hat{\boldsymbol{\mu}}^{(1)}-\hat{\boldsymbol{\mu}}^{2})$ should be compared with $2ns^2F_{n,m-n}(\alpha)$. If the problem is essentially linear, the matrix $\mathbf{a}$ should be essentially the same for the two samples.

We now look at the different $\hat{\boldsymbol{\mu}}^{(k)}$ obtained for grossularite. We know that the data from which these vectors were obtained are highly correlated: they are not only from the same population, but are the total sample or subsets of it. However, we shall proceed *as if* the $\hat{\boldsymbol{\mu}}^{(k)}$ result from independent samples. We shall treat only the oxygen and scale parameters and assume that the $\mathbf{a}$ matrix obtained from the second cycle of the 'oxygen only' calculation is common to all sets of data. The $\mathbf{a}$ matrix is

5	523	5	−508	3	152	6	156	4	−785
		8	337	7	−521	4	−723	4	151
				8	404	7	−791	4	−665
						8	307	5	−233
								4	154

These numbers have the following meaning: The first digit is the power of 10 by which the remaining number beginning with a decimal point is multiplied. For example 5 523 means $0{\cdot}523\times10^5$ and 4 −785 means $-0{\cdot}785\times10^4$. (The a_{ji}, $i \neq j$, are not written because $a_{ij} = a_{ji}$.) We designate by:

$\hat{\boldsymbol{\mu}}^{(1)}$, the results of cycle 2, Table 4
$\hat{\boldsymbol{\mu}}^{(2)}$, the results of cycle 4, Table 1
$\hat{\boldsymbol{\mu}}^{(3)}$, the results of cycle 4, Table 2
$\hat{\boldsymbol{\mu}}^{(4)}$, the results of Abrahams and Geller (see Table 4).

We shall test the differences $\hat{\boldsymbol{\mu}}^{(2)}-\hat{\boldsymbol{\mu}}^{(1)}$, $\hat{\boldsymbol{\mu}}^{(3)}-\hat{\boldsymbol{\mu}}^{(1)}$ and $\hat{\boldsymbol{\mu}}^{(4)}-\hat{\boldsymbol{\mu}}^{(1)}$. These have the elements:

	$\mu^{(2)}-\hat{\mu}^{(1)}$	$\hat{\mu}^{(3)}-\hat{\mu}^{(1)}$	$\hat{\mu}^{(4)}-\hat{\mu}^{(1)}$
s	0·0669	0·0721	0·1062
x	−0·0002	−0·0006	−0·0005
y	0·0003	−0·0004	−0·0002
z	0·0003	−0·0008	0·0004
T	0·24	0·34	0·69

The value of s^2 is 14·09; the values of $F_{5,32}(\alpha)$ and of $2ns^2F_{5,32}(\alpha)=140{\cdot}9F_{5,32}(\alpha)$ are:

α(significance level)	$F_{5,32}(\alpha)$	$2ns^2F_{5,32}(\alpha)$
0·10	2·04	287
0·05	2·51	354
0·025	2·99	421
0·01	3·65	514
0·005	4·17	588

and the values of $(\hat{\mu}^{(k)}-\hat{\mu}^{(1)})\mathbf{a}(\hat{\mu}^{(k)}-\hat{\mu}^{(1)})'$ are:

k	$(\hat{\mu}^{(k)}-\hat{\mu}^{(1)})\mathbf{a}(\hat{\mu}^{(k)}-\hat{\mu}^{(1)})'$
2	77·4
3	95·9
4	194·4

In order that a difference be significant at a given level, $(\hat{\mu}^{(k)}-\hat{\mu}^{(1)})\mathbf{a}(\hat{\mu}^{(k)}-\hat{\mu}^{(1)})'$ must be greater than $2ns^2F_{5,30}(\alpha)$. It is seen that *under the assumptions made* none of these differences is significant, and thus, with the present data at least, the scale and oxygen thermal parameters are also effectively indeterminate.

It should be pointed out that in the above calculation, the application of the complete **a** matrix to $\hat{\mu}$ gives the values of these parameters obtained from the diagonal term approximation, the error estimates that would be obtained from the Busing–Levy program when amplitudes are evaluated with these particular parameter values. These error estimates are certain to be higher than those obtained from the diagonal term approximation but are also apt to be somewhat higher than those obtained for $k=1, 2, 3$.

Even if we simply took univariate confidence limits around each member of each set we would see results in agreement with those obtained above. Since it is quite obvious that the positional parameters are not significantly different, we shall only examine the scale and thermal parameters in this manner. We first take 3σ limits using the estimated errors of each case.

k	1	2	3	4
s	0·7864–0·9964	0·8856–1·0392	0·8990–1·0328	
T	0·50–1·70	1·04–1·64	1·08–1·80	1·50–2·08

We see that the overlap is such as to indicate that these parameters are not significantly different.

We might also examine the results of applying the Student t-test to the differences of results for individual parameters. This test makes use of the diagonal terms in the inverse matrix; that is, to test a difference:

$$(p_i^{(1)}-p_i^{(2)})/(2b_{ii}s^2)^{\frac{1}{2}} \leq t_{m-n}(\alpha)\ .$$

Therefore t also includes effects of correlation. However a confidence region resulting from the total number of confidence intervals

$$(p_i^{(1)}-p_0)/(b_{ii}s^2)^{\frac{1}{2}} \leq t_{m-n}(\alpha)$$

will be a rectangular parallelotope in the n-dimensional space, and therefore only an approximation to the ellipsoid described earlier.

As an example, let us apply the t-test to $p_5^{(4)}-p_5^{(1)}$. We have:

$$\begin{aligned}(p_5^{(4)}-p_5^{(1)})/(2b_{55}s^2)^{\frac{1}{2}} &= (T_0^{(4)}-T_0^{(1)})/(0{\cdot}20\sqrt{2})\\ &= 0{\cdot}69/0{\cdot}28=2{\cdot}46\ .\end{aligned}$$

This *appears* to be significant at the 2% level. Actually because there are five parameters being considered, the difference is really significant at the 10% (i.e., $1-(0{\cdot}98)^5$) level. It is seen that this test gives somewhat greater significance to the difference than the earlier test in which the parameter *vector* differences were tested by means of the F-distribution.

We caution the reader that the above results are in theory no better than the assumptions on which they are based. The assumption of independence of the sets of data is unwarranted. The results of the test using the Snedecor F-statistic appear to corroborate the conclusion that could been drawn intuitively namely, the temperature and scale parameters are not determinable from the data, but the positional parameters of the oxygen ions are accurately determinable.

The test described here should be very useful in deciding whether differences in results of structural analysis on different crystals of the same compound are significant. Also the standard errors obtained from the least squares calculation are not alone sufficient to describe the results when there is high correlation. Such correlation could make unlikely certain combinations of values of parameters. Thus in order to obtain an idea of the parameter behavior, one should really compute a confidence region by use of the F-distribution as described earlier. This is only meaningful however, when there is confidence that convergence has been attained.

The tetragonal $BaTiO_3$ structure

Some time ago Evans (1952) carried out an investigation of the $BaTiO_3$ structure. He collected extremely accurate $h0l$ data with Mo $K\alpha$ radiation employing a Geiger counter. Despite the fact that he attained extremely good agreement between calculated and observed amplitudes, he was forced to conclude that the structure was essentially indeterminate. From careful consideration of the values of certain pairs of derivatives, Evans concluded that there was strong interdependence in five pairs of parameters. In fact, he also concluded that it appeared that the only parameters that could be established unambiguously were β_{11}(Ba), β_{11}(O$_{\rm I}$), and β_{33}(O$_{\rm II}$) (Table 6). We decided to examine the correlation matrix obtained from at least one refinement cycle.

Table 6. *Results of least squares calculation on* BaTiO$_3$

Parameter number	Parameter	Starting values	'Corrected' values	σ
1	s	1·000	0·9682	0·0142
2	z(O$_{\rm II}$)	0·5000	0·6460	0·0967
3	β_{11}(O$_{\rm II}$)	0·00941	0·01113	0·00351
4	β_{22}(O$_{\rm II}$)	0·01412	0·09369	0·03598
5	β_{33}(O$_{\rm II}$)	0·01381	−0·01848*	0·01544
6	z(O$_{\rm I}$)	−0·0260	−0·0551	0·0171
7	β_{11}(O$_{\rm I}$)	0·01412	0·01598	0·00484
8	β_{33}(O$_{\rm I}$)	0·00767	0·00428	0·01514
9	z(Ti)	0·5120	0·5313	0·01651
10	β_{11}(Ti)	0·00722	−0·00515*	0·00547
11	β_{33}(Ti)	0·00460	−0·00465*	0·00892
12	β_{11}(Ba)	0·00424	0·00371	0·00033
13	β_{33}(Ba)	0·00430	0·00611	0·00120

For starting values

R factor (neglecting multiplicity) = 0·049

Weighted R factor, $[\Sigma(\sqrt{(w)}\Delta)^2]^{\frac{1}{2}}/[\Sigma(\sqrt{(w)}F_o)^2]^{\frac{1}{2}} = 0{\cdot}049$

$[\Sigma(\sqrt{(w)}\Delta)^2/(m-n)]^{\frac{1}{2}} = 0{\cdot}810$

After calculation, estimated $[\Sigma(\sqrt{(w)}\Delta)^2/(m-n)]^{\frac{1}{2}} = 0{\cdot}794$

* Physically impossible.

In the calculation of structure factors, the atomic scattering factors for Ba^{2+} were taken from the tables calculated by Thomas & Umeda (1957) with correction for dispersion* (Dauben & Templeton, 1955). The atomic scattering factors for Ti^{4+} were taken from the tables of James & Brindley (1931) also with correction for dispersion*. The atomic scattering factors of O^{2-} are those of Berghuis *et al.* (1955) for O corrected for ionicity as described elsewhere (e.g., Abrahams & Geller, 1958). The data used were those given in Evans' report. All data with $\sin^2\theta/\lambda^2 \leq 0{\cdot}25$ which suffered from extinction were weighted zero, the remainder being weighted unity. The starting parameters were essentially those which Evans felt to give the most reasonable structure. The results of the least squares cycle are given in Table 6. These results are expected, in view of the discussion given by Evans. The Δp_i and standard deviations are very large and it is obvious that real convergence is unattainable. Now let us look at the correlation matrix given in Table 7. Evans had concluded that the strongest interactions occurred between z(Ti) and β_{33}(Ti), z(O$_{\rm I}$) and β_{33}(O$_{\rm I}$), z(O$_{\rm II}$) and β_{22}(O$_{\rm II}$), β_{11}(Ti) and β_{22}(O$_{\rm II}$), and z(Ba) and β_{33}(Ba). We do not observe a ϱ value for the last one because in our calculation, z(Ba) was held constant. The ϱ_{ij} values for the others are respectively $\varrho_{9,11} = -0{\cdot}99$, $\varrho_{6,8} = 0{\cdot}19$, $\varrho_{2,5} = -0{\cdot}82$ and $\varrho_{4,10} = -0{\cdot}99$.

The value of $\varrho_{6,8}$ appears to be quite low; the other three definitely corroborate Evans' findings. The parameter z(O$_{\rm I}$) does interact strongly however with the β_{33} of the O$_{\rm II}$ atom, that is, $\varrho_{5,6}$ has the value 0·83. In fact, there are several other very strong interactions as can be seen in Table 7, e.g., $\varrho_{1,12}$, $\varrho_{2,6}$, $\varrho_{5,13}$, $\varrho_{11,13}$. The large interactions, especially $\varrho_{9,11}$ and $\varrho_{4,10}$, cause the indeterminacy of the positional parameters as well as of the scale factor and of most of the thermal parameters, at least based on the pinacoidal data used.

Table 7 indicates that the parameters β_{11}(O$_{\rm II}$), β_{11}(O$_{\rm I}$) and β_{33}(O$_{\rm I}$) are only weakly correlated with other parameters. However, we have not tested for interaction with the Ba parameters.

To show further the reliability of some of the above conclusions, we give the results of a calculation on the BaTiO$_3$ in which we inadvertently interchanged the values of the Evans' (1952) O$_{\rm II}$ thermal parameters α and γ. The starting parameters were those given in Table 8. Without considering statistical significance, many of the results differ from those obtained when the O$_{\rm II}\beta$-values of Table 6 were used. Those which are not too different (see Tables 6 and 8) are for s, β_{11}(O$_{\rm II}$), z(O$_{\rm I}$), β_{11}(O$_{\rm I}$), β_{11}(Ba), β_{33}(Ba).

The correlation matrix obtained from this calculation is given in Table 9. Note that in all cases of large ϱ in Table 7, the analogous values are large in Table 9. This includes values down to 0·5 in Table 7. (Analogous values for some of these are somewhat lower in Table 9.) The value for $\varrho_{6,8}$ in Table 9 is the only one that differs largely from that in Table 7, thus indicating a high sensitivity of $\varrho_{6,8}$ to the values of the β's

Table 7. *Correlation matrix from* BaTiO$_3$ *least-squares calculation*

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1·00	−0·58	−0·02	0·26	0·57	0·55	0·04	−0·08	−0·25	−0·22	0·27	0·82	−0·34
2		1·00	−0·06	−0·13	−0·82	−0·88	−0·01	0·22	0·22	0·11	−0·23	−0·52	0·63
3			1·00	−0·03	−0·20	−0·10	0·07	−0·07	0·11	−0·03	−0·08	−0·08	0·13
4				1·00	0·02	0·11	0·02	−0·01	0·11	−0·99	−0·10	0·26	0·08
5					1·00	0·83	0·01	−0·08	−0·61	−0·01	0·59	0·55	−0·85
6						1·00	−0·03	0·19	−0·20	−0·09	0·19	0·48	−0·57
7							1·00	−0·25	−0·11	−0·03	0·12	0·01	−0·08
8								1·00	0·31	0·01	−0·35	−0·10	0·32
9									1·00	−0·09	−0·99	−0·33	0·86
10										1·00	0·08	−0·23	−0·07
11											1·00	0·34	−0·86
12												1·00	−0·42
13													1·00

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* Real part only.

Table 8. *Least-squares calculation on* $BaTiO_3$

Incorrect β's for O_{II}

Parameter number	Parameter	Starting values	'Corrected' values	σ
1	s	1·0000	0·9713	0·0130
2	$z(O_{II})$	0·5000	0·6143	0·0890
3	$\beta_{11}(O_{II})$	0·01412	0·01076	0·00448
4	$\beta_{22}(O_{II})$	0·01412	0·05586	0·03655
5	$\beta_{33}(O_{II})$	0·00921	−0·01143*	0·01527
6	$z(O_I)$	−0·0260	−0·0606	0·0234
7	$\beta_{11}(O_I)$	0·01412	0·01557	0·00507
8	$\beta_{33}(O_I)$	0·00767	−0·00820*	0·01654
9	$z(Ti)$	0·5120	0·5230	0·0193
10	$\beta_{11}(Ti)$	0·00722	0·00040	0·00577
11	$\beta_{33}(Ti)$	0·00460	−0·00004*	0·01022
12	$\beta_{11}(Ba)$	0·00424	0·00371	0·00032
13	$\beta_{33}(Ba)$	0·00430	0·00578	0·00138

For starting parameters

R factor (neglecting multiplicity) = 0·051

Weighted R factor, $[\Sigma(\sqrt{(w)}\Delta)^2]^{\frac{1}{2}}/[\Sigma(\sqrt{(w)}F_o)^2]^{\frac{1}{2}}$ = 0·051

$[\Sigma(\sqrt{(w)}\Delta)^2/(m-n)]^{\frac{1}{2}}$ = 0·833

After calculation, estimated $[\Sigma(\sqrt{(w)}\Delta)^2/(m-n)]^{\frac{1}{2}}$ = 0·825

* Physically impossible.

of O_{II}. The results of this calculation are also indicative of the non-linearity of the model.

Refinement of the structure of $LiMnPO_4$

In a recent paper (Geller & Durand, 1960) on the refinement of the structure of $LiMnPO_4$, it was pointed out that neglect of off-diagonal terms of the normal equations matrix did not significantly affect the results of the least-squares refinement. In fact, even when only pinacoidal data were used and the off-diagonal terms neglected, the results (including error estimates), especially on the positional parameters, did not differ significantly from those obtained with the Busing–Levy Program. This could be, but is not necessarily, an indication that the parameters are not *highly* correlated.

The last refinement cycle was rerun to obtain the correlation matrix. Of the 136 $\varrho_{ij}(i \neq j)$ terms, only 25 had $|\varrho_{ij}|$ values greater than 0·05; only 12 values were greater than 0·10. Only four of the values were greater than or equal to 0·35. These were for $s-T_{Mn}$, 0·78; $s-T_P$, 0·57; $s-T_{O_3}$, 0·35 and $T_{Mn}-T_P$, 0·47; these numbers indicate fairly substantial interdependence of the scale factor and the thermal parameters of Mn and P and between the Mn and P thermal parameters. The values for $s-T_{O_1}$ and $s-T_{O_2}$ were each 0·23 and for $T_{Mn}-T_{O_1}$, $T_{Mn}-T_{O_2}$ and $T_{Mn}-T_{O_3}$, they were 0·15, 0·17, and 0·26 respectively. All twelve greater than or equal to 0·10 involved interactions between a scale factor and thermal parameter or between two thermal parameters.

Discussion

We arrive now at the discussion of several questions regarding interactions among parameters:

1. How do strong interactions arise?
2. In what ways do they manifest themselves?
3. Is it possible to avoid them?
4. What do we do about them if we cannot avoid them?

1. *Origins of strong interactions*

Initial indication of strong interactions which are removed when the structure is ultimately refined are caused by an initial trial structure which is far from the true structure.* Data of poor quality might also lead to coupling of parameters which are particularly sensitive to certain of the more poorly estimated intensities. (But see earlier discussion of the correlation coefficient.)

The most important cause of interactions arises from the nature of the structure on which the evaluated derivatives depend. This has been amply demonstrated by the detailed report by Evans on his work on $BaTiO_3$ and will be further corroborated by the forthcoming report on the guanidinium aluminum sulfate hexahydrate structure refinement attempts. In particular, considerable overlap of crystallographically non-equivalent interatomic vectors in the three-dimen-

Table 9. *Correlation matrix from* $BaTiO_3$ *least-squares calculation with incorrect* β's *for* O_{II}

	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1·00	−0·40	0·01	0·18	0·41	0·40	0·08	0·18	−0·12	−0·14	0·12	0·78	−0·20
2		1·00	0·02	0·01	−0·79	−0·92	−0·10	−0·29	−0·02	−0·02	0·05	−0·42	0·56
3			1·00	0·00	−0·15	−0·06	0·08	−0·10	0·07	0·00	−0·04	−0·05	0·08
4				1·00	−0·12	−0·04	0·05	−0·01	0·20	−0·99	−0·22	0·16	0·22
5					1·00	0·85	0·07	0·41	−0·51	0·12	0·46	0·50	−0·87
6						1·00	0·06	0·58	−0·08	0·05	0·03	0·43	−0·60
7							1·00	−0·21	−0·08	−0·06	0·09	0·04	−0·10
8								1·00	0·09	0·03	−0·15	0·17	−0·12
9									1·00	−0·18	−0·99	−0·25	0·79
10										1·00	0·20	−0·14	−0·21
11											1·00	−0·24	−0·76
12												1·00	−0·38
13													1·00

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* It should be kept in mind that an initially bad trial structure may also tend to uncouple parameters which in the 'true' structure are coupled (Geller & Katz, 1962). Similarly data of poor quality might tend to uncouple parameters which should be coupled.

sional Patterson would be indicative of potentially strong interactions in pairs of positional parameters.* This would occur most often for structures which have a substructure.

Strong interactions could arise from extremely incorrect weighting. For example, in the grossularite case, we gave zero weight to all amplitudes with large and independent contributions from the metal ions. To obtain physically meaningful thermal parameters for the metal ions, it would be necessary to include at least some of these structure amplitudes in the calculation. But to obtain the most accurate values of the oxygen positional parameters either those amplitudes to which only oxygen ions contribute should be used or those actually used in the original determination.

Another source of difficulty could be the nature of the atomic scattering factors (see Introduction and Discussion, Part 3).

2. *Manifestation of strong interactions*

The correlation matrix gives a measure of interactions or correlations between pairs of parameters.

It is probable that difficulty in attaining convergence is often a manifestation of strong interaction among parameters. This is not to imply that the discrepancy factor does not decrease to a low value, but rather that it does and that the general features of the structure are obviously correct. Yet oscillations occur with each subsequent iteration and/or interatomic distances obtained are improbable. Very large error estimates resulting from the least-squares calculation also may indicate strong interactions.

It can be shown that if any $|\varrho_{ij}|$, $i \neq j$, is exactly equal to unity, then the correlation matrix is singular. It then follows that the determinant of $\mathbf{a}$ is zero and therefore its inverse would not exist. In this case, the equations would not have a unique solution. It also follows that if two parameters are very nearly completely interdependent, the determinant of the normal equations will be very small. In such a case, there will be a tendency for the error estimates to be large. However, it should be kept in mind that the values of the A_{ii} for weakly correlated parameters are often lower than those for highly correlated ones although this is not universally true. Also, as pointed out earlier when the value of the determinant of $\mathbf{a}$ is very small, rounding-off errors in the matrix inversion also may cause difficulty in convergence.

3. *Possibility of avoiding strong interactions*

If the interactions are known to arise purely from the nature of the structure, as in the cases of $BaTiO_3$ and guanidinium aluminum sulfate hexahydrate, it is improbable that they can be entirely avoided either by changing the structure analysis technique or by changing the weighting. Because of the difference in the nature of the X-ray and the neutron scattering factor, neutron structure amplitude derivatives might not couple parameters which X-ray structure amplitude derivatives tend to couple.

Measurement of absolute intensities would decrease the dependence of other parameters on scale factors. However, because these intensities will have an error associated with them, if the scale factors are not allowed to vary, this error will be absorbed by the thermal parameters or others with which the scale factors would tend to interact.

In simple cases, reconsideration of the weighting technique might lead to uncoupling. However, from a realistic point of view, all weighting procedures are essentially arbitrary. Thus, if substantially different results are obtained by two different but seemingly logical weighting methods, the lack of reliable information for weighting has created an indeterminacy in the problem.

It is interesting to contemplate the possibility of finding by some means the exact relation between highly correlated parameters. In such a case, it should then be possible also to refine an otherwise 'unrefinable' structure.

4. *Procedure to follow if it appears that strong interactions cannot be avoided*

It is certainly frustrating to find after having collected and processed the data and carried out a number of refinement cycles, sometimes at substantial financial expense, that although a structure is generally correct, it is indeterminate in detail. This is an extreme case. However, the X-ray structure analyses of $BaTiO_3$ (Evans, 1952), of HCN (Dulmage & Lipscomb, 1951) and of guanidinium aluminum sulfate hexahydrate are in this category. In the extreme case one should call a halt to the work at the point that one is convinced and report the experience. It is hoped that this paper and the subsequent one on the guanidinium aluminum sulfate hexahydrate will contribute to early recognition of such cases.

In fact, the present work suggests that whenever possible a structure should be *solved* with the minimum possible data. Once a fair trial structure is obtained, it is then possible to calculate the correlation matrix with the inclusion of any number of calculated deriva-

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* For example, in the guanidinium aluminum sulfate hexahydrate structure (Geller & Katz, 1960; Geller & Booth, 1959) there are two sets of crystallographically non-equivalent N atoms in 3*c* and 6*d* of $P31m$. The N atoms in 6*d* are related to those in 3*c* very nearly by $\frac{1}{3}\frac{2}{3}0$, $\frac{2}{3}\frac{1}{3}0$—($x0z$; $0xz$; $\bar{x}\bar{x}z$). Because the Patterson function, of course, adds a center of symmetry, sets of C–N and Al–N vectors will overlap. And because of the nature of the structure, other peaks involving these nitrogens will overlap. It is seen that derivatives of the structure amplitudes with respect to the nitrogen positional parameters will have closely related values, the exact dependence breaking down only as a result of different anisotropic thermal parameters and differences from the exact relationship indicated above. This is the kind of situation found by Evans in his analysis of the $BaTiO_3$ situation.

tives even though the total data have not been measured. A judgment of s^2 could be made from those data used to solve the structure and an estimate of the confidence region could then also be made.

All this might not suffice, however, to give the individual investigator the confidence needed to abandon the work even if there is strong indication that a refined structure is not feasible.

The cases which are not extreme are those in which there may be apparent convergence but some large correlations and error estimates. The calculation of confidence regions should be worthwhile in such cases, although with a *large* number of correlated parameters, it is doubtful that it will be extremely useful. It is especially important however to note by examination of the correlation matrix which of the parameters appear to be correlated and which of them do not.

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Several books and a paper by Box & Coutie (1956) were useful in this work. The books are: Acton (1959), Anderson (1958), Scheffé (1959) and Wilks (1946).

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Potassium Osmyl Chloride — Refinement of the Crystal Structure*

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The crystal structure of $K_2OsO_2Cl_4$, first reported by Hoard & Grenko (1934), has been refined by least-squares and Fourier calculations using three dimensional data. The crystals are tetragonal, $I4/mmm$, with $a_0 = 6\cdot991 \pm 0\cdot004$ and $c_0 = 8\cdot752 \pm 0\cdot006$ Å. The two primary bond lengths in the $OsO_2Cl_4^{--}$ ion were refined to: Os–O: $1\cdot750 \pm 0\cdot022$ Å and Os–Cl: $2\cdot379 \pm 0\cdot005$ Å.

Introduction

The crystal structure of potassium osmyl chloride, $K_2OsO_2Cl_4$, was first determined by Hoard & Grenko (1934) (referred as H.&G. in remaining text). At that time the unit cell dimensions, space group and approximate values for the variable parameters of oxygen and chlorine were established, as well as the location of the osmium and potassium atoms in special positions. In conjunction with an extensive study of the

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