

- HAUPTMAN, H. & GREEN, E. A. (1976). *Acta Cryst.* **A32**, 45–49.
- HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem*. I. *The Centrosymmetric Crystal*. ACA Monograph No. 3. Pittsburgh: Polycrystal Book Service.
- HAUPTMAN, H. & KARLE, J. (1957). *Acta Cryst.* **10**, 267–270.
- HURT, M. F. & WAID, C. (1970). *SIAM (Soc. Ind. Appl. Math.) J. Appl. Math.* **19**, 547–550.
- KLUG, A. (1958). *Acta Cryst.* **11**, 513–543.
- NAYA, S., NITTA, I. & ODA, T. (1964). *Acta Cryst.* **17**, 421–433.
- SHELDRIK, G. M. (1976). Intercongr. Symp. Direct Methods Crystallogr., Buffalo, Abstr. SE2.

*Acta Cryst.* (1978). **A34**, 574–578

## Electronic Polarizabilities of Ions in Doubly Refracting Crystals

BY DIETER POHL

*Mineralogisch-Petrographisches Institut der Universität Hamburg, Grindelallee 48, D2000 Hamburg 13, Federal Republic of Germany*

(Received 20 September 1977; accepted 7 March 1978)

A method is described for determining electronic polarizabilities of ions in doubly refracting ionic crystals solely from crystal data. An expression for computing polarizabilities by a least-squares fit can be derived. Such a method is used to obtain values for the polarizability of cations for the sodium *D* line in Å<sup>3</sup>: Na<sup>+</sup> 1.7, K<sup>+</sup> 11.6, Rb<sup>+</sup> 19.1, Tl<sup>+</sup> 48.7, Ca<sup>2+</sup> 5.2, Sr<sup>2+</sup> 11.1, Ba<sup>2+</sup> 23.2, Pb<sup>2+</sup> 38.3. Evidence is given of decreasing polarizability of the O<sup>2-</sup> ion in aragonite-type carbonates with decreasing cation sizes.

### Introduction

Tessman, Kahn & Shockley (1953) (TK & S) reported a method for evaluating electronic polarizability values of ions in ionic crystals from both optical and structural data. By applying their method to a great number of crystals, they obtained a list of polarizability values of ions. TK & S polarizability values differ considerably from polarizability values that have been otherwise determined (Pauling, 1927; Born & Heisenberg, 1924; Mayer & Goepfert-Mayer, 1933; Fajans & Joos, 1924; Langhoff, 1965; Cohen, 1965, 1966; Lahiri & Mukherji, 1967). The cation polarizabilities are generally higher, and the anion polarizabilities lower, than those obtained by other methods for gaseous ions. Efforts have been made to account for these differences (Ruffa, 1963; Jain, Shanker & Khandelwal, 1975), as well as to develop the TK & S method so as to reduce the discrepancies (Pirenne & Kartheuser, 1964). As pointed out by Batsanov (1966), the main deficiency of the TK & S method stems from neglect of the fact that small cations tend to reduce the polarizability of the anions. The phenomenon of *interacting individual ions*, as suggested by Pirenne & Kartheuser (1964), is not sufficiently explained though it improves the correspondence between the polarizabilities of ions in ionic crystals and the polarizabilities of gaseous ions.

Since TK & S and Pirenne & Kartheuser (1964) restricted themselves to isotropic crystals, they could

only determine the sum of the polarizabilities from the refractive index. They lacked the additional data required to evaluate the individual polarizabilities. The difficulty of having more adjustable parameters than experimental measurements may be handled, at least in principle, by extending the TK & S method to doubly refracting crystals. The optical properties of a diatomic crystal, for example, can be described sufficiently by two polarizabilities while there are one, two or three indices of refraction measured, depending on symmetry. It has been suggested (Batsanov, 1966) that the use of salts with complex oxygen-containing anions could be advantageous in determining cation polarizabilities, since the polarizabilities of the complex anions alter but little with the cation sizes. With these arguments in mind, I decided to examine some sulfates and carbonates to obtain values for electronic polarizabilities of ions in doubly refracting crystals. In this paper a method is presented for determining the polarizabilities of ions in ionic crystals. The resulting polarizabilities do not depend as they do in the work of TK & S and of Pirenne & Kartheuser (1964) on an arbitrary selection of the electronic polarizability of one of the ions. Moreover, we shall see that the trend of decreasing polarizability of the anions with decreasing sizes of the cations is confirmed. The calculations remove the discrepancies between the electronic polarizabilities of ions in crystals and the values for gaseous ions.

### Fitting expression

In an anisotropic crystal the connection between crystal structure, electronic polarizabilities of the ions, and refractive indices is established by evaluating dipole lattice sums. General principles of the Ewald method for evaluating multipole lattice sums have been reviewed recently by Cummins, Dunmur, Munn & Newham (1976). According to these authors one may write [equation (10) of the reference]

$$\mathbf{F}(k) = \mathbf{E} + \sum_{k'} \mathbf{L}(kk') \mathbf{p}(k') / \epsilon_0 v. \quad (1)$$

The integers  $k, k'$  denote the sublattice or the site in the unit cell, and the summation is over all sites within the unit cell occupied by polarizable ions.  $\mathbf{F}(k)$  is the local electric field at site  $k$ ,  $\mathbf{p}(k')$  is the electronic dipole moment at site  $k'$ , and  $\mathbf{L}(kk')$  is the so-called Lorentz-factor tensor. The remaining quantities of equation (1) are the macroscopic electric field  $\mathbf{E}$ , the unit cell volume  $v$ , and the permittivity of a vacuum  $\epsilon_0$ .

Substitution of each of the ions by a point dipole located at the atomic centre, following Bragg (1924), defines the isotropic electronic polarizability  $\alpha(k')$  by

$$\mathbf{p}(k') = \epsilon_0 \alpha(k') \mathbf{F}(k'). \quad (2)$$

From the above equations it follows that

$$\mathbf{F}(k) = \mathbf{E} + (1/v) \sum_{k'} \mathbf{L}(kk') \alpha(k') \mathbf{F}(k'). \quad (3)$$

The Lorentz-factor tensor  $\mathbf{L}(kk')$  may be evaluated from the crystal structure by means of the formulae of Cummins, Dunmur, Munn & Newham (1976) or, as I did, by the plane-wise summation method due to De Wette & Schacher (1965). If the electronic polarizabilities  $\alpha(k')$  are known or at least can be estimated, then (3) becomes a solvable system of linear equations in the components of the  $\mathbf{F}(k)$ .

The electric dipole moment per unit volume due to all dipoles is given by summing equation (2) over  $k'$  and dividing by  $v$ ,

$$\mathbf{P} = (1/v) \sum_{k'} \mathbf{p}(k') = (\epsilon_0/v) \sum_{k'} \alpha(k') \mathbf{F}(k'). \quad (4)$$

By means of the dielectric susceptibility tensor  $\chi$  the electronic polarization can be written as

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E}. \quad (5)$$

The components of the dielectric susceptibility tensor are related to those of the dielectric constant tensor by

$$K_{ij} = \chi_{ij} + \delta_{ij}. \quad (6)$$

Since the dielectric constant tensor is associated with the squares of the refractive indices, comparison between theoretical and observed values becomes possible.

Once a set of polarizabilities  $\alpha_1, \alpha_2, \dots, \alpha_n$  for the different ions in a crystal is given, the electric fields  $\mathbf{F}(k)$

can be determined by solving equations (3). Using equations (4), (5) and (6), we get the components of the dielectric constant tensor as functions of the electronic polarizabilities

$$K_{ij} = K_{ij}(\alpha_1, \dots, \alpha_n). \quad (7)$$

Now the sum

$$\sum_{i=1}^3 (K_{ii}(\alpha_1, \dots, \alpha_n) - K_{ii}^{\text{obs}})^2 \quad (8)$$

can be minimized. The  $K_{ii}^{\text{obs}}$  denote the diagonal terms of the dielectric constant tensor, which are known by experiment. Minimizing (8) can give values for the electronic polarizabilities  $\alpha_1, \dots, \alpha_n$  provided their number  $n$  does not exceed that of the refractive indices, that is, two for a uniaxial crystal and three for a biaxial crystal.

If there are different crystals with certain ions in common which are believed to be of equal polarizability, the summation in expression (8) can be extended over this group of crystals. This procedure gives better results, since the number of adjustable parameters in comparison with the experimentally known values becomes more favorable.

Under isotropic symmetry the Lorentz-factor tensor is diagonal with elements equal to one third, and the local electric field is constant. Thus equation (3) may be written as

$$\mathbf{F} = \mathbf{E} + \frac{1}{3v} \mathbf{F} \sum_{k'} \alpha(k'). \quad (9)$$

This is the standard result of Lorentz for the local field in a polarized continuum. The result does not depend on the polarizability of the individual ions, but is determined solely by the sum

$$\alpha_m = \frac{1}{Z} \sum_{k'} \alpha(k'), \quad (10)$$

where  $Z$  is the number of chemical formulae per unit cell, as usual. Equation (10) states that the electronic polarizability of an isotropic crystal is simply the sum of the electronic polarizabilities of the individual ions. It was therefore called *assumption of simple additivity* (TK & S) or *interacting formula* (Pirenne & Kartheuser, 1964). The molecular electronic polarizability  $\alpha_m$  is then related to the refractive index by the familiar Lorenz-Lorentz formula

$$\alpha_m = \frac{3v}{Z} \frac{n^2 - 1}{n^2 + 2}, \quad (11)$$

which is used in the work of TK & S and Pirenne & Kartheuser (1964).

### Numerical results and discussion

#### (i) Details of the numerical calculation

I have written a computer program (Fortran IV) which evaluates dipole lattice sums and the dielectric

constant tensor. The input of data is easily managed. For the components of the dielectric constant tensor, accuracy within 1 part in  $10^6$  is obtained. To achieve this high degree of accuracy a great number of terms must be included when computing the dipole lattice sums. For the plane-wise summation method of De Wette & Schacher (1965) the rate of convergence of the sums is governed by the length of the vector joining two atoms within a unit cell and, more specifically, by the component in the direction of the basic reciprocal lattice vector  $\mathbf{c}^*$  [see for example equation (24) of De Wette & Schacher]. If this component is low, so is the rate of convergence. Moreover, as pointed out by Cummins, Dunmur, Munn & Newham (1976), some care is necessary in applying the usual test of convergence. This test is that a fixed number of contributions to each sum should fall below a pre-set value. To make quite sure that the intended accuracy of the dielectric constant tensor is achieved, the number of terms in the lattice sums is determined as a function of the above vector component. This procedure is adapted to unfavorable cases, since it normally overestimates the number of necessary terms. The speed of the computations is therefore greatly reduced, and the method is practically limited to structures containing less than about 50 ions per unit cell.

In addition to the program that evaluates lattice sums, I have written another program (Fortran IV) which uses the lattice sums as data and determines electronic polarizabilities by minimizing expression (8). The results of these calculations involve errors because the minimum of expression (8) is usually not very distinct. Thus, by the least-squares fit the parameters can be determined only to a low degree of accuracy.

In addition to the errors arising in connection with the least-squares fit, another source of error may originate because of inexact optical or structural data. An especial sensitivity is found if inaccuracies of very short distances between ions of high values of polarizability are involved.

### (ii) Carbonates

In order to investigate the relation between atomic arrangement and double refraction, calcite and aragon-

Table 1. *Aragonite-type carbonates: electronic polarizabilities of ions*

Cation	$\alpha_{\text{cation}}$ ( $\text{\AA}^3$ )	$\alpha_{\text{O}^{2-}}$ ( $\text{\AA}^3$ )	Structure
$\text{Ca}^{2+}$	5.2	18.0	<i>a, b</i>
$\text{Sr}^{2+}$	12.1	17.8	<i>a</i>
$\text{Ba}^{2+}$	23.6	18.5	<i>a</i>
$\text{Pb}^{2+}$	38.2	19.8	<i>c</i>

References: (a) Villiers (1971). (b) Dal Negro & Ungaretti (1971). (c) Sahl (1974).

ite have been used repeatedly since the paper of Bragg in 1924. I, therefore, also began with these structures, since both display strong double refraction, far away from the isotropic case where the optics depends solely on the sum of the electronic polarizabilities. But as work went on, it appeared that calcite-type structures are beyond the range over which the Bragg model of point dipoles is valid. I was therefore forced to restrict the calculations to aragonite-type carbonates. The problem of applying the Bragg model to calcite-type structures is discussed in detail by Pohl & Rath (1978).

The carbonates were assumed to consist of  $Me^{2+}$  ions ( $Me = \text{Ca, Sr, Ba, Pb}$ ) and  $\text{O}^{2-}$  ions; the carbon ion  $\text{C}^{4+}$  was omitted because of its negligible polarizability. Refractive indices are obtained from the compilation by Winchell & Winchell (1964). On the basis of recent structural data (references in Table 1) electronic polarizability values were computed for  $\lambda = 5893 \text{ \AA}$  (sodium *D* line) by minimizing expression (8). The results are given in Table 1.

For each of the aragonite-type carbonates, a polarizability value is determined for both the  $Me^{2+}$  ion and the  $\text{O}^{2-}$  ion. No other data apart from structural and optical constants are used in the computation. A trend of decreasing polarizability of the  $\text{O}^{2-}$  ion with decreasing size of the cation is indicated.

### (iii) Sulfates

For cations, the polarizability is thought to be almost independent of crystal structure or neighboring anions. To test this statement as well as to confirm the values of the polarizabilities obtained from the aragonite-type carbonates, the computations were extended to sulfates. All sulfates containing just one type of cation are included, provided that both optical data and a recent structure determination (references in Table 2) are available. As was the case with the carbonates, the refraction data are obtained from Winchell & Winchell

Table 2. *Sulfates: electronic polarizabilities of ions*

Cation	$\alpha_{\text{cation}}$ ( $\text{\AA}^3$ )	$\alpha_{\text{O}^{2-}}$ ( $\text{\AA}^3$ )	$\alpha_{\text{cation}}$ (at $\alpha_{\text{O}^{2-}} = 17.5$ ) ( $\text{\AA}^3$ )	Structure
$\text{Na}^+$	-0.8	18.6	1.7	<i>a</i>
$\text{K}^+$	12.8	16.9	11.6	<i>b</i>
$\text{Rb}^+$	15.8	18.9	19.1	<i>c</i>
$\text{Tl}^+$	41.2	21.7	48.7	<i>d</i>
$\text{Ca}^{2+}$	6.5	17.1	5.1	<i>e</i>
$\text{Sr}^{2+}$	12.2	17.0	10.2	<i>f</i>
$\text{Ba}^{2+}$	17.5	18.7	22.8	<i>g</i>
$\text{Pb}^{2+}$	no distinct minimum		38.4	<i>h</i>

References: (a) Nord (1973). (b) McGinnety (1972). (c) Nord (1974). (d) Pannetier & Gaultier (1966). (e) Cheng & Zussman (1963). (f) Hawthorne & Ferguson (1975). (g) Colville & Staudhammer (1967). (h) Sahl (1963).

Table 3. *Electronic polarizabilities of cations (in Å<sup>3</sup>)*

Cation	Theoretical work	Pauling	Mayer & Goepfert-Mayer	Fajans & Joos	TK & S	Present paper
Na <sup>+</sup>	{ 2.1 <sup>a</sup> 1.8 <sup>b,c</sup>	2.3	2.1	2.5	5.2	1.7
K <sup>+</sup>	14.3 <sup>a</sup>	10.6	10.1	11.1	16.7	11.6
Rb <sup>+</sup>		17.8	18.8 <sup>d</sup>	19.6	24.9	19.1
Tl <sup>+</sup>					65.3	48.7
Ca <sup>2+</sup>	8.2 <sup>a</sup>	5.9	6.8	6.4	13.8	5.2
Sr <sup>2+</sup>		10.9	12.6	10.8	20.1	11.1
Ba <sup>2+</sup>		19.6	26.1 <sup>d</sup>	21.1	31.4	23.2
Pb <sup>2+</sup>					61.6	38.3

References: (a) Langhoff (1965). (b) Cohen (1966). (c) Lahiri & Mukherji (1967). (d) Born & Heisenberg (1924).

(1964). As the polarizability of the sulfur ion S<sup>6+</sup> is negligible, the sulfates were assumed to consist of O<sup>2-</sup> ions and Me<sup>+</sup> ions (Me<sup>+</sup> = Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Tl<sup>+</sup>) or Me<sup>2+</sup> ions (Me<sup>2+</sup> = Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>). For each compound, polarizabilities were computed for  $\lambda = D$  by minimizing expression (8). The results are given in Table 2, columns 2 and 3.

The most striking features of the calculations are a negative value of the polarizability of the Na<sup>+</sup> ion and the failure to determine a polarizability for the Pb<sup>2+</sup>. The negative polarizability value gives an estimate of the error connected with the present method of computing polarizabilities; the breakdown of the method in case of PbSO<sub>4</sub> reflects the fact that the sulfates are nearly isotropic. Therefore expression (8) has only a weak minimum, as expected from equation (10), which claims that in the isotropic case, there is no distinct minimum at all.

Since it fails completely for PbSO<sub>4</sub> and gives too low a value of the polarizability for Ba<sup>2+</sup> (compared with the value determined from the carbonate, BaCO<sub>3</sub>, witherite), the method appears to be invalid for sulfates with heavy cations. However, no trend was observed in the polarizability of the O<sup>2-</sup> ion for the sulfates with the light cations Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>. In these circumstances, it seemed promising to extend the summation in expression (8) over the three sulfates of Na, K, and Ca. The extended expression (8) was then minimized, and a value of 17.5 Å<sup>3</sup> was computed for the polarizability of the O<sup>2-</sup> ion in sulfates. Keeping this value fixed, another set of polarizabilities of cations in sulfates was determined. The results are given in Table 2, column 4.

For the modified calculation the polarizability of Na<sup>+</sup> becomes positive and the values of the Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup> and Pb<sup>2+</sup> ion differ but little from those determined from aragonite-type carbonates. By and large, the assumption that the sulfates, at least those in Table 2, contain O<sup>2-</sup> ions of the same polarizability throughout seems to be justified by improved results. However, highly accurate results cannot be obtained because the sulfates are nearly isotropic.

#### (iv) Comparison with other investigations

A final list of electronic polarizabilities of cations is set up by averaging over the values which are determined for Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup> and Pb<sup>2+</sup> from carbonates and sulfates, and by taking the values of Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Tl<sup>+</sup> from the sulfates. Table 3 lists some polarizabilities calculated by theoretical methods together with polarizabilities determined by Pauling (1927), Mayer & Goepfert-Mayer (1933), Fajans & Joos (1924), TK & S, and the present method. Whereas the theoretical work, as well as the work of Pauling and Mayer & Goepfert-Mayer, refers to the static case ( $\lambda = \infty$ ), the determinations of Fajans & Joos, TK & S and this work are for  $\lambda = D$ .

I thank the Deutsche Forschungsgemeinschaft for financial support and the Rechenzentrum der Universität Hamburg and the DESY-Rechenzentrum, Hamburg for computer time.

#### References

- BATSANOV, S. S. (1966). *Refractometry and Chemical Structure*, pp. 53–55. Princeton: Van Nostrand.
- BORN, M. & HEISENBERG, W. (1924). *Z. Phys.* **23**, 388–410.
- BRAGG, W. L. (1924). *Proc. R. Soc. London Ser. A*, **105**, 370–386.
- CHENG, G. C. H. & ZUSSMAN, J. (1963). *Acta Cryst.* **16**, 767–769.
- COHEN, H. D. (1965). *J. Chem. Phys.* **43**, 3558–3562.
- COHEN, H. D. (1966). *J. Chem. Phys.* **45**, 10–12.
- COLVILLE, A. A. & STAUDHAMMER, K. (1967). *Am. Mineral.* **52**, 1877–1880.
- CUMMINS, P. G., DUNMUR, D. A., MUNN, R. W. & NEWHAM, R. J. (1976). *Acta Cryst.* **A32**, 847–853.
- DAL NEGRO, A. & UNGARETTI, L. (1971). *Am. Mineral.* **56**, 768–772.
- DE WETTE, F. W. & SCHACHER, G. E. (1965). *Phys. Rev.* **A137**, 78–91.
- FAJANS, K. & JOOS, G. (1924). *Z. Phys.* **23**, 1–46.
- HAWTHORNE, F. C. & FERGUSON, R. B. (1975). *Can. Mineral.* **13**, 181–187.
- JAIN, J. K., SHANKER, J. & KHANDELWAL, D. P. (1975). *Philos. Mag.* **32**, 887–889.

- LAHIRI, J. & MUKHERJI, A. (1967). *Phys. Rev. A* **153**, 386–387.
- LANGHOFF, P. W. (1965). *Phys. Rev. A* **139**, 1415–1425.
- MCGINNETY, J. A. (1972). *Acta Cryst.* **B28**, 2845–2852.
- MAYER, J. E. & GOEPPERT-MAYER, M. (1933). *Phys. Rev.* **43**, 605–611.
- NORD, A. G. (1973). *Acta Chem. Scand.* **27**, 814–822.
- NORD, A. G. (1974). *Acta Cryst.* **B30**, 1640–1641.
- PANNETIER, G. & GAULTIER, M. (1966). *Bull. Soc. Chim. Fr.* pp. 3336–3341.
- PAULING, L. (1927). *Proc. R. Soc. London Ser. A*, **114**, 181–211.
- PIRENNE, J. & KARTHEUSER, E. (1964). *Physica*, **30**, 2005–2018.
- POHL, D. & RATH, R. (1978). Submitted to *Acta Cryst.*
- RUFFA, A. R. (1963). *Phys. Rev.* **130**, 1412–1423.
- SAHL, K. (1963). *Beitr. Mineral. Petrogr.* **9**, 111–132.
- SAHL, K. (1974). *Z. Kristallogr.* **139**, 215–222.
- TESSMAN, J. R., KAHN, A. H. & SHOCKLEY, W. (1953). *Phys. Rev.* **92**, 890–895.
- VILLIERS, J. P. R. (1971). *Am. Mineral.* **56**, 758–767.
- WINCHELL, A. & WINCHELL, H. (1964). *The Microscopic Characteristics of Artificial Inorganic Solid Substances*. New York: Academic Press.

*Acta Cryst.* (1978). **A34**, 578–582

## An Optimized Conjugate Gradient Solution for Least-Squares Equations

BY A. D. RAE

*School of Chemistry, University of New South Wales, Kensington, New South Wales 2033, Australia*

(Received 19 January 1978; accepted 27 February 1978)

The conjugate gradient method allows the solution of least-squares equations  $\mathbf{A}(\mathbf{u} - \mathbf{u}_0) = \mathbf{B}$  without evaluating  $\mathbf{A}^{-1}$ . Storage limitations can thus be satisfied by approximating  $\mathbf{A}$  by a sparse matrix which need not be block-diagonalized. Optimization of the method allows a satisfactory solution within 10–12 iteration steps for any sized matrix, enabling an economic use of conditional slack constraints.

### Introduction

The least-squares refinement of a crystal structure uses residuals  $\Delta_{\mathbf{h}}$  which are not linear in variables  $\{u\}$  and iteration is required for the minimization of  $\sum_{\mathbf{h}} w_{\mathbf{h}} \Delta_{\mathbf{h}}^2$ . Modified equations can enable a more economic refinement strategy. The larger the problem, the more uneconomic it is to use a full-matrix solution involving all refinable parameters. If sparse-matrix approximations are considered, the advantage of a conjugate gradient solution for the least-squares equations  $\mathbf{A}(\mathbf{u} - \mathbf{u}_0) = \mathbf{B}$  becomes obvious. The traditional method of solution involves the evaluation of  $\mathbf{A}^{-1}$  so that  $\mathbf{u} - \mathbf{u}_0 = \mathbf{A}^{-1}\mathbf{B}$ . However, only in the special case of block-diagonalization is  $\mathbf{A}^{-1}$  confined to the same storage area as  $\mathbf{A}$ . The conjugate gradient solution says  $\mathbf{u} - \mathbf{u}_0 = \sum_{i=0}^{N-1} \alpha_i \mathbf{p}_i$  where successive approximations  $\sum_{i=0}^m \alpha_i \mathbf{p}_i$ ,  $m = 0$  to  $N - 1$ , are made by an iterative procedure involving multiplication by the matrix  $\mathbf{A}$ . The variance-covariance matrix for the variables  $\{u\}$  requires the evaluation of  $\mathbf{A}^{-1}$  but this is only of any consequence in the final refinement cycle. A simple strategy successfully employed by Konnert (1976) for large structures is to use a sparse matrix where the only off-diagonal elements are between parameters for nearest and second-nearest-neighbour atoms. For such an approximation  $\mathbf{A}^{-1}$  requires a much larger storage area than does  $\mathbf{A}$ . Slack con-

straints on interatomic distances were used to aid refinement by the conjugate gradient method.

The conjugate gradient method can be monitored to estimate the actual improvement in  $\sum_{\mathbf{h}} w_{\mathbf{h}} \Delta_{\mathbf{h}}^2$  for each iterative approximation to  $\mathbf{u} - \mathbf{u}_0$ . Each successive approximation further reduces  $\sum_{\mathbf{h}} w_{\mathbf{h}} \Delta_{\mathbf{h}}^2$  and a simple modification to the standard method can be found so that fewer iterations can be used to obtain a satisfactory approximate solution. This modification is the subject of this paper. It is found that as few as 10 iterations are sufficient to obtain 0.9999 of the maximum improvement. The rapidity of such an approximation means that conditional slack constraints can be used to aid refinement with very little cost in time. Restrictions can be imposed on the ranges of refinable parameters in three ways.

#### (a) Strict constraints

Strict constraints can be envisaged as replacing variables  $\{u\}$  by variables  $\{v\}$  where  $du_j = \sum_i C_{ji} dv_i$  so that

$$\frac{\partial \Delta_{\mathbf{h}}}{\partial v_i} = \sum_j \frac{\partial \Delta_{\mathbf{h}}}{\partial u_j} C_{ji}$$

Only a subset of the variables  $\{v\}$  is refined, the remainder being given fixed values.