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# **Techniques and Convergence Properties** of EFG Lattice Summations

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#### Abstract

The calculation of electric field gradient (EFG) lattice sums over point charges in ionic crystals is considered. Although the de Wette method gives rapidly converging sums under favourable circumstances, direct summations over a unit cell-shaped cavity are found to produce lattice sums which converge regularly as  $N^{-2}$  (*N* is the number of unit cells in a side of the cavity), allowing accurate extrapolation to their values for an infinite lattice by means of Neville tables. This convergence behaviour can be explained mathematically for orthogonal lattices using the Euler-Maclaurin formula. A point charge calculation of the EFGs at low symmetry sites in GdFeO<sub>3</sub> has been carried out to compare the convergence of the direct summation and de Wette techniques and to illustrate the  $N^{-2}$  convergence of the direct lattice sums.

### 1. Introduction

In an ionic crystal the electric field gradient (EFG) at a particular site depends on the charge distributions of the surrounding ions. The simplest electrostatic model of such a crystal is to consider the ions as stationary point charges located at the lattice sites. Then the EFG tensor components at the site of interest due to this periodic array of point charges may be expressed as summations over all the ions in the crystal, namely

$$V_{ij} = \sum_{\eta} Z(\eta) \frac{3x_{i\eta} x_{j\eta} - \delta_{ij} r_{\eta}^2}{r_{\eta}^5}, \quad i, j = 1, 2, 3,$$

where  $Z(\eta)$  is the charge and  $(x_{1\eta}, x_{2\eta}, x_{3\eta})$  the cartesian coordinates of the  $\eta$ th ion which is a distance  $r_{\eta}$  from the origin at the site of interest.

Although the point charge model only sometimes provides a realistic description of an ionic compound, it illustrates the techniques involved in the calculation of lattice EFGs. This paper investigates both the direct summation and de Wette methods of evaluating the EFG lattice sums with particular emphasis on their convergence behaviour. A mathematical foundation is given to the observed regular convergence of direct lattice sums. This convergence behaviour and the equivalence of the two summation techniques are illustrated by means of a point charge calculation for different sites in  $GdFeO_3$ .

### 2. Lattice Summation Techniques

A real crystal may be considered to be composed of a number of interpenetrating sublattices, one for each set of ions of a given type located at identical sites (defined here as sites at which the EFG has the same principal component, asymmetry parameter and principal axes).\* Then the *ij*th component of the EFG at a site of the  $\sigma$ th sublattice may be written as

$$V_{ij}(\sigma) = \sum_{\tau} Z(\tau) S_{ij}(\sigma, \tau),$$

where

$$S_{ij}(\sigma,\tau) = \sum_{\kappa} \frac{\partial^2}{\partial (r_{\tau\kappa})_i \partial (r_{\tau\kappa})_j} |1/r_{\tau\kappa}|$$
(1)

is the appropriate lattice sum over the  $\tau$ th sublattice with a site of the  $\sigma$ th sublattice as origin. The sum over  $\kappa$  is for all sites of the  $\tau$ th sublattice (except the origin when  $\sigma = \tau$ ) and  $\mathbf{r}_{\tau\kappa}$  is the position vector of the  $\kappa$ th site. Such lattice sums depend only on the crystal structure and not on the type of ion at each sublattice site.

Because it is impracticable to sum the contributions to the EFG from every ion in a quasi-infinite crystal, the lattice summations are performed over all the charges within a finite mathematical cavity which lies within the crystal and surrounds the site of interest. The size of the cavity is then increased until the sums converge. The two summation techniques which have been employed to calculate lattice EFGs on the basis of a point charge model of an ionic compound involve several different cavity shapes. Direct summations have been carried out over all the ions contained within either a spherical or a unit cell-shaped cavity centred at the site of interest, whereas in the de Wette method of planewise summation a slab-shaped cavity is considered. The relevant features of both techniques are now briefly reviewed.

In the earliest calculations of EFGs a direct summation was performed within a spherical cavity (Bersohn 1958; Bernheim and Gutowsky 1960; Belford *et al.* 1961). Not only did the lattice sums converge slowly, but they also oscillated as the radius was increased because the number of ions within a spherical boundary does not increase smoothly with the volume enclosed. When the cavity is changed to one having the same shape as the unit cell of the crystal and containing an integral number of such unit cells, the convergence of the lattice summations becomes regular because the ratio of the number of ions within the cavity to the volume of the cavity is a constant (Bolton *et al.* 1962).

Nijboer and de Wette (1958) introduced an alternative method for the computation of lattice sums and this was applied to the evaluation of lattice EFGs in crystals by de Wette (1961) and de Wette and Schacher (1965). If  $a_1$ ,  $a_2$ ,  $a_3$  denote the lattice basis vectors, the contributions from all point charges in an  $a_1$ ,  $a_2$  plane parallel to the faces of a slab-shaped cavity are summed in two-dimensional reciprocal space, allowing the contributions of all the planes to be added together analytically. The one exception is the summation over the plane in which the origin is situated. When this sum is not zero, it may be evaluated by using an auxiliary convergence function (Nijboer and de Wette 1957; de Wette and Schacher 1965) or by the direct summation technique with the ion at the origin excluded from the summation.

\* Note that this may not be the same as identical crystallographic sites. For example, gadolinium ions in  $GdFeO_3$  (see Section 4) are all located at 4c sites, but the EFG principal axes for two of the ions are mirror images across the a-c (or b-c) plane of the axes for the other two ions. Although this distinction between orientation of principal axes is not required for the point charge model, it must be taken into account when the ions are considered as nonspherical charge distributions.

The mathematical details of the de Wette method are described by de Wette and Schacher (1965) and Sholl (1966). The expressions for the EFG lattice sums quoted by these authors have been checked independently and agreement is obtained with the revised ones given by Massidda (1976).

#### 3. Convergence of the Summations

Although the lattice contribution to the EFG at a given site must be independent of the shape of the crystal, the lattice sums (1) are only conditionally convergent (Sholl 1966), i.e. their values depend on the shape of the cavity in which the summation is performed. However, it may be shown that the lattice sums over all the charges within an electrically neutral volume are absolutely convergent (Sholl 1966). When the contribution from one type of ion is being calculated, the cavity shape must be taken into account by the inclusion of the appropriate Lorentz factors  $\beta_{ij}$  defined by Sholl (1966). Then the invariant quantity is

$$Z(\tau)\{S_{ij}(\sigma,\tau)+z(\tau)\beta_{ij}/v\},\$$

where  $z(\tau)$  is the number of ions per unit cell in the  $\tau$ th sublattice and v is the unit cell volume.

When summing over unit cell-shaped cavities, care must be taken in treating the ions which lie on the surface of the unit cell. In order to preserve the symmetry of the site at which the EFG is being calculated, fractional charges should be assigned to ions located on the cell's corners, edges and faces. The appropriate fraction is given by the reciprocal of the number of cells which share the ion, i.e.  $\frac{1}{2}$  for ions on faces,  $\frac{1}{4}$  for ions on edges and  $\frac{1}{8}$  for ions at corners of the unit cell.

In the de Wette method the sums over the reciprocal lattice converge quite rapidly provided that the atomic parameter in the  $a_3$  direction is not too close to either 0 or 1 (Sholl 1966; Massidda 1976). Otherwise, oscillations due to the sine or cosine factor in the lattice sum expressions do not quickly die away with distance from the origin. With the added complication of having to evaluate the sum over the plane containing the origin either by a direct summation or by introducing an auxiliary convergence function, the de Wette technique appears to be straightforward only for certain lattices with small numbers of ions per unit cell. However, in a more recent paper Massidda (1976) shows how these difficulties can sometimes be overcome by transforming to a different coordinate system.

Because the de Wette method involves summations in only two dimensions, convergence to seven significant figures may be obtained in favourable circumstances after summing over a few hundred lattice points. On the other hand, the slow convergence rate of the direct summation method necessitates a three-dimensional summation over several thousand unit cells to achieve convergence to three or four significant figures. However, the regular convergence of lattice sums over a cavity with the shape of the unit cell may be exploited to extrapolate the sums to an infinite lattice.

A convenient method of extrapolating lattice sums is by means of Neville tables (see Section 4) as used by Bolton *et al.* (1962) in the calculation of the electric fields at the ionic sites in rutile due to induced dipoles at all the other sites. If N is the number of unit cells in the side of the rectangular cavity, these authors found that the extrapolations to  $N = \infty$  went as  $N^{-1}$  for cavities with ions on their faces or

edges and as  $N^{-2}$  for cavities with no surface ions. However, our calculations showed that, with fractional charges on the surfaces of unit cells, the EFG lattice sums for compounds with a variety of structures all converge to  $N = \infty$  at least as fast as  $N^{-2}$ . The rate of convergence was observed to be independent of whether the sum is over both positive and negative ions in the lattice or over ions of just one charge sign. Extrapolation procedures indicated that the lattice sums actually approach their convergence behaviour (proportional to  $N^{-2}$  etc.) even at N values as small as 4.

# Mathematical Justification of $N^{-2}$ Convergence

Since this regular convergence behaviour of direct EFG lattice sums cannot be explained simply on the basis of the multipolar order of the unit cell as described by Coogan (1967), a mathematical argument using the Euler-Maclaurin formula (see e.g. Mathews and Walker 1970) is now presented.

Consider a lattice with parameters  $a_1, a_2, a_3$  containing point charges of one particular sign. The site (0, 0, 0) at which the EFG, due to all such charges, is to be calculated is surrounded by a unit cell-shaped cavity with sides  $2Na_1, 2Na_2, 2Na_3$ .\* Since the assertion that the EFG lattice sums  $S_N$  over all the charges within the cavity converge as  $N^{-2}$  implies that the EFG summations over all charges outside the cavity are proportional to  $N^{-2}$  for sufficiently large N, it is adequate to show the latter property, i.e.

# $S_{\infty} - S_N = \text{const.} \times N^{-2} + \text{higher order terms}.$

The contribution to any component  $V_{ij}$  of the EFG tensor at the centre of the cavity due to the charges outside the cavity may be evaluated by summing over all such charges. Alternatively, one may integrate over the region outside the cavity assuming a uniform continuous distribution of monopoles and then subtract the difference between the integral and the sum. In other words, Sum  $\equiv$  Integral – (Integral – Sum). Although the former method is generally used to evaluate EFG components numerically, the latter has advantages in the algebraic determination of the convergence behaviour of the lattice sums.

No generality is lost by considering just the one charge with atomic parameters  $u_1, u_2, u_3$  in each unit cell outside the cavity. Let us first select the charges with  $u_1 = u_2 = u_3 = 0$ . The generalization to arbitrary  $u_i$  is carried out later. For the sake of simplicity the argument will also be restricted to lattices with orthogonal axes. Since the ionic charge Z is just a constant factor in the EFG expression, it may be omitted for the moment, leaving the function

$$X_{ij}(x_1, x_2, x_3) = (\partial^2 / \partial x_i \partial x_j) (x_1^2 + x_2^2 + x_3^2)^{-\frac{1}{2}}, \quad i, j = 1, 2, 3,$$

where  $x_1, x_2, x_3$  are the coordinates along the three mutually orthogonal crystal axes.

The region R outside a rectangular cavity with sides  $2Na_1, 2Na_2, 2Na_3$  may be divided into six semi-infinite rectangular volumes, allowing us to write the integral

<sup>\*</sup> Because the origin is chosen to be at one corner of a unit cell, there must be an even number of unit cells in each side of the cavity. In this section it is convenient to denote this number of unit cells by 2N rather than N.

of  $X_{ij}(x_1, x_2, x_3)$  over R as

$$\begin{split} I &= \int_{R} dx_{1} dx_{2} dx_{3} X_{ij}(x_{1}, x_{2}, x_{3}) \\ &= \sum_{\pm} \left( \int_{Na_{1}}^{\infty} dx_{1} \int_{-\infty}^{\infty} dx_{2} \int_{-\infty}^{\infty} dx_{3} X_{ij} \right. \\ &+ \int_{-Na_{1}}^{Na_{1}} dx_{1} \int_{Na_{2}}^{\infty} dx_{2} \int_{-\infty}^{\infty} dx_{3} X_{ij} + \int_{-Na_{1}}^{Na_{1}} dx_{1} \int_{-Na_{2}}^{Na_{2}} dx_{2} \int_{Na_{3}}^{\infty} dx_{3} X_{ij} \right), (2) \end{split}$$

where  $\sum_{\pm}$  indicates a summation over both  $\int_{N_a}^{\infty} dx$  and  $\int_{-\infty}^{-N_a} dx$ . When i = j, the integrand of I becomes

$$\begin{aligned} X_{ii}(x_1, x_2, x_3) &= (3x_i^2 - r^2)/r^5, \qquad i = 1, 2, 3, \\ r &= (x_1^2 + x_2^2 + x_3^2)^{\frac{1}{2}}. \end{aligned}$$

It may be shown that

where

$$\begin{split} \int_{\alpha_{i1}}^{\alpha_{i2}} \mathrm{d}x_i \int_{\alpha_{j1}}^{\alpha_{j2}} \mathrm{d}x_j \int_{\alpha_{k1}}^{\alpha_{k2}} \mathrm{d}x_k \, (3x_i^2 - r^2)/r^5 \\ &= \sum_{\lambda=1}^2 \sum_{\mu=1}^2 \sum_{\nu=1}^2 \, (-1)^{\lambda+\mu+\nu+1} \arctan\left(\frac{\alpha_{j\mu}\alpha_{k\nu}}{\alpha_{i\lambda}(\alpha_{i\lambda}^2 + \alpha_{j\mu}^2 + \alpha_{k\nu}^2)^{\frac{1}{2}}}\right), \\ &\quad i, j, k = 1, 2, 3, \quad i \neq j \neq k \,, \end{split}$$

provided that the region of integration does not include the origin of the coordinates. By applying this general result to each triple integral in equation (2), it is found that for i = j the contributions to I cancel to zero if the outer surface of R retains the shape of the unit cell when all three coordinates  $x_1, x_2, x_3$  simultaneously tend to infinite limits. Since  $X_{ij}(x_1, x_2, x_3)$  is an odd function of two coordinates when  $i \neq j$ , its integral is zero over a region such as R which is symmetrical with respect to the origin.

The fact that the EFG expressions are analytic functions at all points within the region R allows the Euler-Maclaurin formula to be invoked to calculate the difference between the integral and the sum. Since the EFG in a three-dimensional lattice is a function of three variables, the one-dimensional analysis given by Mathews and Walker (1970) is extended by considering the trapezoidal approximation for the triple integral. For a general rectangular volume of sides  $N_1a_1, N_2a_2, N_3a_3$  this approximation may be written as

$$S = \left(\prod_{l=1}^{3} a_{l}(\frac{1}{2} + E_{l} + E_{l}^{2} + \dots + E_{l}^{N_{1}-1} + \frac{1}{2}E_{l}^{N_{1}})\right) X_{ij}(n_{1}a_{1}, n_{2}a_{2}, n_{3}a_{3})$$
$$= \left(\prod_{l=1}^{3} a_{l}(E_{l}^{N_{1}} - 1)\{\frac{1}{2} + 1/(E_{l} - 1)\}\right) X_{ij}(n_{1}a_{1}, n_{2}a_{2}, n_{3}a_{3}),$$
(3)

where the  $n_l a_l$  are the initial values of  $x_l$  and the operators  $E_l$  are defined by

$$E_{i}X_{ij}(n_{1}a_{1}, n_{2}a_{2}, n_{3}a_{3}) = X_{ij}((n_{1}+1)a_{1}, n_{2}a_{2}, n_{3}a_{3}),$$
 etc.

It can be seen that the above approximation is simply the lattice sum over all the charge sites *within* the rectangular volume plus the appropriate fractions of sites on the surface. The corresponding lattice sum over all the charge sites within and on

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the surface of the region R may be obtained by adding together the contributions from the six rectangular volumes defined by the limits of integration in equation (2).

The exact value of the integral I over the rectangular volume of sides  $N_1a_1$ ,  $N_2a_2$ ,  $N_3a_3$  is given by

$$I = (E_1^{N_1} - 1)(E_2^{N_2} - 1)(E_3^{N_3} - 1) U_{ij}(n_1a_1, n_2a_2, n_3a_3),$$

where

$$U_{ij}(x_1, x_2, x_3) = \int \int \int X_{ij}(x_1, x_2, x_3) \, \mathrm{d}x_1 \, \mathrm{d}x_2 \, \mathrm{d}x_3 \, \mathrm{d}x_3 \, \mathrm{d}x_2 \, \mathrm{d}x_3 \, \mathrm{d}x_3 \, \mathrm{d}x_4 \, \mathrm{d}x_2 \, \mathrm{d}x_3 \, \mathrm{d}x_4 \, \mathrm{d}x_5 \,$$

With the definitions

$$Dx_k U_{ij}(x_1, x_2, x_3) = (\partial/\partial x_k) U_{ij}(x_1, x_2, x_3), \qquad k = 1, 2, 3,$$

we have

$$Dx_1 Dx_2 Dx_3 U_{ij}(x_1, x_2, x_3) \Big|_{n_q a_q} = X_{ij}(n_1 a_1, n_2 a_2, n_3 a_3), \qquad q = 1, 2, 3,$$

and therefore

$$I = (E_1^{N_1} - 1)(E_2^{N_2} - 1)(E_3^{N_3} - 1) Dx_3^{-1} Dx_2^{-1} Dx_1^{-1} X_{ij}(x_1, x_2, x_3) \Big|_{n_q a_q}.$$
 (4)

From equations (3) and (4), we have

Integral - Sum = 
$$(E_1^{N_1} - 1)(E_2^{N_2} - 1)(E_3^{N_3} - 1)Dx_3^{-1}Dx_2^{-1}Dx_1^{-1}$$
  
 $\times \left\{ 1 - \prod_{l=1}^3 a_l Dx_l \left( \frac{1}{2} + \frac{1}{\exp(a_l Dx_l) - 1} \right) \right\} X_{ij}(x_1, x_2, x_3) \Big|_{n_q a_q}$   
=  $(E_1^{N_1} - 1)(E_2^{N_2} - 1)(E_3^{N_3} - 1)Dx_3^{-1}Dx_2^{-1}Dx_1^{-1}$   
 $\times \left\{ 1 - \prod_{l=1}^3 \left( 1 + \frac{B_2(a_l Dx_l)^2}{2!} + \frac{B_4(a_l Dx_l)^4}{4!} + ... \right) \right\} X_{ij}(x_1, x_2, x_3) \Big|_{n_q a_q},$ 
(5)

where the substitutions  $E_l = \exp(a_l Dx_l)$  have been used and  $B_2$  and  $B_4$  are Bernoulli numbers which have the respective values 1/6 and -1/30. After expanding the expression in the braces in equation (5) and using the fact that

$$(E_1^{N_1}-1)Dx_1^{-1}X_{ij}(x_1,n_2a_2,n_3a_3)\Big|_{x_1=n_1a_1}=\int_{n_1a_1}^{\mathcal{N}_1a_1}X_{ij}(x_1,n_2a_2,n_3a_3)\,\mathrm{d}x_1\,,$$

and similarly for the other two cases, one finally obtains

Integral - Sum = 
$$-\frac{B_2}{2!} \sum_{l,m,n} \left( a_l^2 \int_{n_m a_m}^{\mathcal{N}_m a_m} dx_m \int_{n_n a_n}^{\mathcal{N}_n a_n} dx_n \frac{\partial}{\partial x_l} X_{ij}(x_1, x_2, x_3) \Big|_{n_l a_l}^{\mathcal{N}_l a_l} \right)$$
  
 $- \left( \frac{B_2}{2!} \right)^2 \sum_{l,m,n} \left( a_l^2 a_m^2 \int_{n_n a_n}^{\mathcal{N}_n a_n} dx_n \frac{\partial^2}{\partial x_l \partial x_m} X_{ij}(x_1, x_2, x_3) \Big|_{n_l a_l}^{\mathcal{N}_l a_l} \Big|_{n_m a_m}^{\mathcal{N}_m a_m} \right)$   
 $- \frac{B_4}{4!} \sum_{l,m,n} \left( a_l^4 \int_{n_m a_m}^{\mathcal{N}_m a_m} dx_m \int_{n_n a_n}^{\mathcal{N}_n a_n} dx_n \frac{\partial^3}{\partial x_l^3} X_{ij}(x_1, x_2, x_2) \Big|_{n_l a_l}^{\mathcal{N}_l a_l} \right)$ 

+ higher order terms.

In the above equations,  $\mathcal{N}_l = n_l + N_l$  and  $\sum_{l,m,n}$  denotes a cyclic permutation of the coordinates  $x_l, x_m, x_n$   $(l \neq m \neq n)$ . When these integrals and derivatives are evaluated over each of the six rectangular volumes which comprise the region R outside a unit cell-shaped cavity of dimensions  $2Na_1, 2Na_2, 2Na_3$ , the infinite limits give zero contributions and the finite limits of the lowest order terms produce contributions proportional to  $N^{-2}$  when i = j. There are no contributions of order  $N^{-3}$ , the remaining terms shown giving contributions proportional to  $N^{-4}$ . However, for  $i \neq j$  the  $N^{-2}$  and  $N^{-4}$  contributions are always zero because at least one integral or derivative in each term shown above is evaluated over an even function of the relevant variable.

Let us now consider the EFG at the origin due to the Kth sublattice of charges located at points  $(u_1a_1, u_2a_2, u_3a_3)$  within each unit cell outside the cavity. The above procedure gives the N dependence of the lattice sums at the point  $(u_1a_1, u_2a_2, u_3a_3)$ relative to the origin if the centre of the cavity is chosen to be at this site of interest. In order to calculate the sums at (0, 0, 0) the entire cavity is translated to make this point its centre. This translation does not change the lattice sums evaluated at  $(u_1a_1, u_2a_2, u_3a_3)$ .\* One may write

$$S_{ii}(0,K) = S_{ii}(J,K) + \{S_{ii}(0,K) - S_{ii}(J,K)\},$$
(6)

where the parameters 0 and J indicate that the sums are evaluated at (0,0,0) and  $(u_1a_1, u_2a_2, u_3a_3)$  respectively.

Again consider a general rectangular volume of sides  $N_1a_1, N_2a_2, N_3a_3$ . The difference in the braces in equation (6) then becomes

$$\begin{split} \Delta S_{ij} &\equiv S_{ij}(0,K) - S_{ij}(J,K) \\ &= \sum_{l=n_1}^{N_1} \sum_{m=n_2}^{N_2} \sum_{n=n_3}^{N_3} \left[ X_{ij}((l+u_1)a_1,(m+u_2)a_2,(n+u_3)a_3) - X_{ij}(la_1,ma_2,na_3) \right]. \end{split}$$

The expression in square brackets may be expanded in terms of the Taylor series for  $X_{ij}(x_1, x_2, x_3)$  about the point  $(la_1, ma_2, na_3)$ , i.e.

$$\Delta S_{ij} = \sum_{l=n_1}^{N_1} \sum_{m=n_2}^{N_2} \sum_{n=n_3}^{N_3} \left[ u_1 a_1 \frac{\partial X_{ij}(x_1, ma_2, na_3)}{\partial x_1} \right]_{x_1 = la_1} + u_2 a_2 \frac{\partial X_{ij}(la_1, x_2, na_3)}{\partial x_2} \Big|_{x_2 = ma_2} + u_3 a_3 \frac{\partial X_{ij}(la_1, ma_2, x_3)}{\partial x_3} \Big|_{x_3 = na_3} + higher order derivatives of X_{ij}(x_1, x_2, x_3) \Big].$$
(7)

\* In translating the centre of the cavity from  $(u_1a_1, u_2a_2, u_3a_3)$  to (0, 0, 0), equal numbers of ions in the Kth sublattice are gained and lost by the region outside the cavity. If an ion at  $(x_1, x_2, x_3)$  relative to  $(u_1a_1, u_2a_2, u_3a_3)$  enters this region another at  $(-x_1, -x_2, -x_3)$  is removed from it. Since  $X_{ij}$ components are invariant under inversion of cartesian coordinates, the cavity translation does not alter the lattice sums.

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Because of the symmetry of the region outside the cavity with respect to the origin, each index l, m and n either runs from  $-\infty$  to  $\infty$ , or from  $-\infty$  to -(N+1) as well as from N to  $\infty$ , or has -N and N-1 as its summation limits. Combined with the fact that each term in the first-order partial derivatives of  $X_{ii}(x_1, x_2, x_3)$  contains one of  $la_1, ma_2, na_3$  as a factor, the resultant cancellation of terms leaves at most one term in the summation over the corresponding index l, m or n. The remaining double summation yields a result proportional to  $N^{-2}$  at large N. Two of the first-order derivatives of  $X_{ij}(x_1, x_2, x_3)$  with  $i \neq j$  also have the same property, whereas the third such derivative has all of  $la_1$ ,  $ma_2$  and  $na_3$  as factors and the consequent cancellation of terms in the summations over l, m and n causes it to converge as  $N^{-4}$ . The summations over the cavity of the higher order derivatives converge at least as fast as  $N^{-2}$  in general.

This procedure may be repeated for each relevant ion in the unit cell and the results added without affecting the dependence on N. Therefore, it has been shown that in general the EFG summations for a periodic array of discrete charges converge to their values for an infinite lattice as  $N^{-2}$ , even when summing over ions whose total charge is nonzero.

Table	1.	Structural	information	for	GdFeO <sub>3</sub>	used	in	EFG
			calculati	ons				

The atomic parameters shown in parentheses are uniquely determined by the symmetry

Atom	Site	Site	Atomic parameters				
		symmetry	<i>u</i> <sub>1</sub>	<i>u</i> <sub>2</sub>	<i>u</i> <sub>3</sub>		
Gd	4c	m	0.98444	0.06284	(0.25)		
Fe	4b	1	(0.5)	(0.0)	(0.0)		
O(m)	4c	m	0.1005	0.4672	(0.25)		
<b>O</b> (1)	8d	1	0.6957	0.3016	0.0506		

In carrying out lattice summations over certain structures with cubic unit cells, it was found that the off-diagonal EFG components converged more rapidly than  $N^{-2}$ , appearing to be more closely proportional to  $N^{-4}$  for  $N \ge 4$ . The conditions under which both the  $N^{-2}$  and  $N^{-3}$  terms vanish in equation (7) (which gives the only nonzero contributions to off-diagonal components) have been examined. The necessary symmetry property at the origin which enables  $\Delta S_{ij}$  ( $i \ne j$ ) to behave in this manner seems to be inversion symmetry in the  $a_i$  direction with the atomic parameter along the  $a_j$  direction remaining constant in the inversion process, plus inversion symmetry in the  $a_j$  direction with the  $a_i$  axis parameter constant during the process. For example, in the case of  $\Delta S_{12}$  there must be identical crystallographic positions (footnote in Section 2) at  $(u_1a_1, u_2a_2, x_3), (-u_1a_1, u_2a_2, x'_3), (u_1a_1, -u_2a_2, x''_3)$ and  $(-u_1a_1, -u_2a_2, x''_3)$ .

#### 4. Illustration and Comparison of Techniques

To illustrate the summation techniques and convergence properties discussed above, the point charge EFGs at the various ionic sites in gadolinium orthoferrite  $GdFeO_3$  are considered. The calculations have been carried out both by the de Wette method and by direct summation over unit cell-shaped cavities. In the latter method the  $N^{-2}$  convergence behaviour of the lattice sums has been used to extrapolate to the EFG values in a quasi-infinite crystal.

Gadolinium orthoferrite is a distorted perovskite (space group *Pbnm*) and has an orthorhombic unit cell with lattice parameters  $a_1 = 0.5349$  nm,  $a_2 = 0.5611$  nm and  $a_3 = 0.7669$  nm (Wyckoff 1964; Marezio *et al.* 1970). This is the lowest symmetry lattice for which we have proved the  $N^{-2}$  convergence. Also, the ionic sites have low symmetries of 1,  $\overline{1}$  and m, providing a good test of the applicability of the convergence behaviour. Other structural information used in the calculations is given in Table 1.

# Table 2. Neville tables showing (a) the rapid convergence of $V_{12}(O(1), O(1))$ and (b) the slow convergence of $V_{33}(O(m), O(m))$

In (a), the number in parentheses is the rounding error in the last figure. Convergence is obtained in the first difference column. The units are  $10^{-2} \text{ mm s}^{-1}$  for the ground state splitting of  $^{155}\text{Gd}$ ; to convert to Vm<sup>-2</sup>, multiply by  $3.63102 \times 10^{21}$ . In (b), the units are  $10^{-3} \text{ mm s}^{-1}$ . The entries in the first difference column are changing monotonically so that convergence is not obtained until the second difference column. Rounding errors are the same as for (a).

N		(a) $V_{12}(O(1), O(1))$			(b) V <sub>33</sub> (O(m), O(m))		
	$V_{12}(N)$	$V_{12}(N, N+1)$	$V_{12}(N,, N+2)$	$V_{12}(N,, N+3)$	$V_{33}(N)$	$V_{33}(N, N+1)$	$V_{33}(N,, N+2)$
2	1.536188			ι	- 3 • 571016		
		$1 \cdot 520873(1)$				-1.875335	
4	1.524702		1.517639(2)		- 2.299255		-2.703738
		1.517999(2)		1.517982(3)		- 2.611694	
6	1 • 520978		1.517960(3)		-2.472832		-2.643121
		1.517970(2)		1 · 517967(4)		-2.635264	
8	1 • 519662		1 · 517966(4)		-2.543896		-2.637415
		1.517968(3)		1 · 517971(6)		-2.636640	
10	1 · 519052		1 · 517970(5)		-2.577284		- 2.637214
		1 • 517969(3)		1 · 517964(7)		-2.636959	
12	1.518721		1 · 517966(6)		-2.595518		-2.637217
		1 · 517967(4)		1 · 517965(9)		-2.637085	
14	1.518521		1 · 517965(7)		-2.606546		-2.637216
		1 · 517966(4)		1 • 517970(10)		-2.637142	
16	1.518391		1 · 517968(8)		-2.613717		-2.637210
		1 · 517967(5)		1 · 517956(12)		-2.637169	
18	1.518302		1 · 517962(9)		-2.618639		-2.637217
		1 · 517965(5)		1.517982(13)		-2.637186	
20	1.518238		1 · 517971(10)		-2.622163		-2.637215
		1 · 517967(6)		1 · 517950(15)		-2·637196	
22	1.518191		1 · 517962(11)		-2.624772		-2.637209
		1 · 517966(6)				-2.637200	
24	1 • 518155				-2.626757		

#### Direct Summation Results

To study the convergence properties of individual lattice sums, the EFG components due to each group of ions of the same type were calculated separately at each of the different ionic sites, i.e. the EFG components at a Gd site due to Gd ions, at a Gd site due to Fe ions, and so on. Each lattice sum was found to converge linearly with  $N^{-2}$  at least by N = 8 and in many cases as early as N = 4.

A convenient method of extrapolating lattice sums possessing this  $N^{-2}$  convergence property is by means of Neville tables (see e.g. Hartree 1952), which do not require the data to be tabulated at equal intervals of the independent variable. This may be seen in Table 2 where each entry in the columns for  $V_{12}(N)$  and  $V_{33}(N)$  represents the sum of EFG contributions from a cavity of side N unit cells with N an even integer. Since we are trying to estimate the EFG function at  $N^{-2} = 0$ , the next columns in the difference tables are given by

$$V_{ij}(N, N+1) = \frac{(N+1)^2 V_{ij}(N+1) - N^2 V_{ij}(N)}{(N+1)^2 - N^2},$$
  
$$V_{ij}(N, N+1, N+2) = \frac{(N+2)^2 V_{ij}(N+1, N+2) - N^2 V_{ij}(N, N+1)}{(N+2)^2 - N^2}, \quad \text{etc.}$$

Convergence is obtained quite rapidly, but care must be taken in estimating the rounding errors. For a conventional difference table and starting with an error of  $\pm 0.5$  in the last figure for  $V_{ij}(N)$ , the likely error increases slightly slower than a simple doubling for each successive column (see e.g. Hartree 1952). However, in our case this rounding error also increases as one goes down a column, being weighted by approximately  $(2N^2 + 2N + 1)/2(2N + 1)$  in the first difference column. This slightly reduces the expected increase in reliability of entries with larger N. This increased rounding error can be interpreted graphically because the points are getting closer together on the  $N^{-2}$  scale, hence allowing greater uncertainty in the slope of the line joining them. One could reduce this uncertainty by taking differences between EFG elements separated in N values by more than two when the convergence accuracy could be seen to be limited by rounding.

Two of the EFG components have been selected to illustrate the convergence properties. The first component, which exhibits one of the fastest convergence rates found, is  $V_{12}(O(1), O(1))$  where O(1) denotes the no-symmetry oxygen ions.\* Since this is an off-diagonal EFG element which involves only sites of symmetry 1, it may be regarded as a stringent test of the general validity of the  $N^{-2}$  convergence. No difference was observed between the behaviour of the diagonal and off-diagonal EFG components. The second example, illustrating one of the slowest convergence rates found, is  $V_{33}(O(m), O(m))$  where O(m) denotes the mirror-symmetry oxygen ions. This corresponds to one of the highest symmetry summations performed. Although both of these cases are for the effect of a group of ions at the site of another of the same type, no different properties were found for summations involving the effect of one group of ions at the site of an ion of another group.

The data for these two examples are presented in two different ways. In Fig. 1 the EFG components are plotted against  $N^{-2}$ , clearly showing the regular convergence. In the slowly converging example, the initial entries corresponding to N = 2, 4 and 6 (see Table 2b) are not monotonic, a feature observed in 20 out of the 77 summations performed. This effect, which is presumably due to large higher order terms, in no case continued beyond N = 4. It is interesting to note that in one case,  $V_{12}$ (Fe, Gd), the sum changed sign between N = 4 and 6, but still converged linearly with  $N^{-2}$ .

The Neville tables are also given for both examples (Table 2) with the rounding error in the last figure of each entry in Table 2a shown in parentheses to indicate its variation. The more rapidly converging example can be seen to have converged to the seven significant figures used by N = 8 (see the first column of differences) and the effect of differencing errors then becomes apparent as one moves successively to the right of Table 2a. In the slowly converging example of Table 2b, which is presented

<sup>\*</sup> More generally,  $V_{ij}(\sigma, \tau)$  denotes the *ij*th component of the EFG at a site of the  $\sigma$ th sublattice due to all the ions on the  $\tau$ th sublattice.

#### EFG Lattice Summations

in more abbreviated form, the entries in the first difference column are still changing monotonically whilst the second difference column gives a more accurate estimate of the final answer. In no case did we find that the answer improved after the second difference column.





In order to estimate the cavity size necessary to obtain a certain desired degree of accuracy, Table 3 shows the number of significant figures correctly obtained at different N values for the fastest and slowest convergence rates observed, starting from seven figure data. At worst, one can expect to gain one significant figure each time N increases by two units, but the accuracy usually increases considerably faster than this. The numbers in this table apply of course only to summation values of approximately the 'normal' size (EFG  $\sim 10^{22}$  V m<sup>-2</sup>); those smaller by n orders of magnitude will, on average, have n less significant figures since the effects of higher order terms would be expected to occur at the same absolute magnitude.

Attempts were made to fit the tabulated data to a polynomial in  $N^{-\alpha}$  as an alternative to the Neville table extrapolation. The extrapolated values obtained were not as reliable as those from the Neville tables, even when including coefficients up to  $\alpha = 8$ . However, it was instructive to see that the sizes of the coefficients did not decrease with increasing  $\alpha$  and it was easy to monitor the rapid decrease of the terms with increasing N.

## de Wette Method Results

The same EFGs at various ionic sites in  $GdFeO_3$ , calculated by means of the direct summation technique, were also evaluated using the de Wette method. As indicated

in Section 2, this method involves summing in two-dimensional reciprocal space the contributions from ions in  $a_1$ ,  $a_2$  planes parallel to the faces of a slab-shaped cavity. In obtaining the results for this paper, the sum over the plane which contains the origin was evaluated by a two-dimensional direct summation. Since this lattice sum was found to converge regularly as  $N^{-1}$  (here N is the number of unit cells in a side of the plane), it could also be extrapolated by means of a Neville table.

NDi	irect summatio No. of signi	n method ficant figures	М	de Wette method No. of significant figures		
	Slowest	Fastest		Slowest	Fastest	
4	1	4	4	0	1	
6	2	6	6	0	1	
8	3	7	8	0	2	
10	4	·	10	0	3	
12	5		12	. 0	4	
14	6		14	0	5	
			16	0	5	
			18	1	6	
			20	1	7	
			22	1		
			26	2	·	
			30	2	-	
			34	2		
			38	· · 2		

Table 3. Number of significant figures obtained at different values of N (or M) for the fastest and slowest convergence rates found in a normal magnitude summation

In the de Wette method the rate of convergence of the sums over the reciprocal lattice depends on the positions of ions along the  $a_3$  direction relative to the site at which the EFG is being evaluated. If  $u_3$  denotes the atomic parameter in the  $a_3$  direction relative to that at the origin, convergence is most rapid when  $u_3 = 0.5$  and becomes slower as  $u_3$  approaches either 0 or 1. In the cases where all  $u_3$  values lie between 0.2 and 0.8, EFG components of the order of  $10^{22}$  V m<sup>-2</sup> were found to converge to at least seven significant figures after summing over about 500 lattice points in two-dimensional reciprocal space. However, for  $u_3$  values of approximately 0.05 or 0.95, the sums could be estimated to only three or four significant figures after 1600 lattice points had been included because oscillations due to the sine or cosine functions were still evident. The irregular behaviour of these poorly converging sums does not allow them to be extrapolated by means of a Neville table.

It is useful to be able to estimate the minimum size of the planes in two-dimensional reciprocal space over which the summations must be carried out in order to obtain a certain desired degree of accuracy. Let M be the number of basis vectors in a side of such a plane. Table 3 shows the number of significant figures correctly obtained at different M values for the cases of fastest and slowest convergence of a normal magnitude summation (EFG  $\sim 10^{22}$  V m<sup>-2</sup>). The sums which converged most rapidly gain approximately one significant figure each time M increases by two units and correspond to cases in which  $u_3$  is equal to 0.25 or 0.75. In the most slowly converging sum, which involves  $u_3$  values of approximately 0.05 and 0.95, only two

#### EFG Lattice Summations

significant figures have been obtained at M = 38, illustrating the inefficiency of the de Wette method when  $u_3$  is close to 0 or 1.

#### Comparison of Results

In order to compare the results of the direct summation and de Wette methods, four of the EFG components have been selected. These components include examples of fast and slow convergence for the direct summation technique, cases in which the de Wette method produces rapid and poor convergence, and illustrations of the use of a direct summation over the plane containing the origin as an adjunct to the latter method.

# Table 4. Comparison of four point-charge EFG components at ionic sites in GdFeO<sub>3</sub> obtained by each method

For each EFG component the upper line refers to the direct summation method, the lower line to the de Wette method. All entries are in units of  $10^{-2}$  mm s<sup>-1</sup>

EFG component	Value	Lorentz factor term	Total	Nature of convergence
V <sub>33</sub> (O(1), Gd)	11 · 99469 - 8 · 287162	5·69936 25·981209	17·69405 17·694047	fast fast
$V_{13}(\text{Fe},\text{Gd})$	1 · 734666 1 · 734667	0 0	1 · 734666 1 · 734667	slow fast
$V_{11}(\text{Fe}, O(1))$	$-11 \cdot 81619 \\ -25 \cdot 83$	-14.01732	$-25 \cdot 83351 - 25 \cdot 83$	fast slow, oscillatory
$V_{33}(O(m), O(m))$	-0.263721 13.25741	-3.799570 -17.32081	-4.063291 -4.06340	slow slow, $N^{-1}$ extrapolation

Table 4 compares the values of the chosen EFG components at ionic sites in  $GdFeO_3$  obtained by the two different methods. When the EFG at an ionic site due to each group of ions of the same type is considered, the lattice sums depend on the cavity shape, and appropriate Lorentz factors  $\beta_{ij}$  have to be included to render them invariant (as described in Section 3). For a rectangular cavity

$$\beta_{ii} = 8 \arctan[a_j a_k / \{a_i (a_i^2 + a_j^2 + a_k^2)^{\frac{1}{2}}\}], \quad i, j, k = 1, 2, 3, \quad i \neq j \neq k,$$

 $\beta_{ij}=0\,,\quad i\neq j\,;$ 

whereas for the de Wette slab-shaped cavity  $\beta_{33} = 4\pi$  is the only nonzero factor. In Table 4 it may be seen how the inclusion of these Lorentz factors gives equivalent values for the EFG components and hence the lattice sums, obtained by the direct summation and de Wette methods.

Because the rate of convergence of EFG lattice sums calculated by means of both the direct summation and de Wette methods can vary considerably, it is useful to have a criterion for determining the most efficient technique. Although a direct summation over all ions within a cavity, whose side contains N unit cells, followed by extrapolation by means of a Neville table generally produces a more accurate result than a summation in two-dimensional reciprocal space over planes containing N basis vectors in their sides, it must be remembered that the former method involves



**Fig. 2.** Comparison of the convergence of (a)  $V_{33}(O(1), Gd)$ , (b)  $V_{13}(Fe, Gd)$ , (c)  $V_{11}(Fe, O(1))$  and (d)  $V_{33}(O(m), O(m))$  by direct summation (squares) and de Wette (circles) calculations. The appropriate Lorentz factors are included so that both sums converge to the same values, here normalized to unity.

a three-dimensional summation whereas the latter involves a summation in only two dimensions. The relative efficiency of the two techniques, as determined by the computer times required to evaluate the same sum to a given accuracy, depends on the relative number of lattice points which need to be included in the summations.

When all the ions included in a summation have  $u_3$  values relative to that at the origin between 0.2 and 0.8, the de Wette method uses less computer time to achieve any desired accuracy and is particularly favourable when six or seven significant figures are required in the result. For example, the EFG components  $V_{33}(O(1), Gd)$  and  $V_{13}(Fe, Gd)$  given in Table 4 (see also Figs 2a and 2b) are both more efficiently calculated by the de Wette method. However, when one or more ions have relative values of  $u_3$  which are close to 0 or 1, the de Wette method becomes less efficient than the direct summation technique which is particularly advantageous if not more than five significant figures are sufficient. The EFG component  $V_{11}(Fe, O(1))$  given in Table 4 is an example of this situation and its oscillatory behaviour is clearly seen in Fig. 2c.

It should be noted that a far greater variation is observed in the rate of convergence of lattice sums calculated by the de Wette method compared with those evaluated using a direct summation. This larger variation can be a drawback, especially in the determination of the EFG at a given site due to all surrounding ions, because a single ion with a relative  $u_3$  value close to 0 or 1 can seriously reduce the convergence rate of the total EFG components. As shown by Massidda (1976), this difficulty can often be overcome by making a different choice of axes for ions with such  $u_3$  values. However, in compounds such as cubic sesquioxides with the bixbyite structure (Barton and Cashion 1979), whose unit cells contain large numbers of ions, all three relative atomic parameters of some ionic sites may be sufficiently close to either 0 or 1 to significantly reduce the usefulness of such a transformation of coordinates.

The de Wette method also suffers from the disadvantage of requiring a separate summation for the plane containing the origin. Unless an auxiliary convergence function is employed, this summation has to be performed directly and then extrapolated, e.g. by means of a Neville table. The component  $V_{33}(O(m), O(m))$  is such an example where the  $N^{-1}$  convergence property was used and its slow approach is shown in Fig. 2d.

In the direct summation technique the rate of convergence of the total EFG components at a given site is not greatly reduced by the contribution from one particular type of ion. Although an extrapolation procedure is required to improve the accuracy of the lattice sums, no special functions are used and the total EFG can be computed by a single summation.

#### 5. Conclusions

A comparison has been made of the direct summation and de Wette methods for the evaluation of EFG lattice sums according to a point charge model of an ionic crystal. The calculation of EFGs at ionic sites in  $GdFeO_3$  has been used to illustrate these two techniques and particularly their convergence properties.

For simple arrays the de Wette method often has the advantage of producing more rapid convergence. But the regular convergence of direct summations over unit cell-shaped cavities enables this more versatile method to have greater efficiency in certain cases, especially where the unit cell contains a large number of ions. When the direct summation technique is used, the components of the EFG tensor converge, in general, as  $N^{-2}$  to their values for an infinite lattice even when summing over ions whose total charge is nonzero. We believe that the criterion for this convergence is a constant ratio of charge to summed volume.

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