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Electric field gradient in cubic and other ionic crystals

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Abstract. A method is developed for an accurate evaluation of the electric field gradient (EFG) tensor in the cubic lattices of point charges. It is shown that only two values of the geometrical factors similar to the Madelung constants are necessary for calculation of all EFG components at all sites in all standard cubic crystals. The EFG tensor at all carbon atoms in the different phases of alkali-doped fullerene crystals is presented as an example. It is demonstrated that a cubic network of zero potential lines with halved lattice constant exists in perovskite crystals and some fullerites. A numerical procedure is proposed for calculation of EFG at any point of the unit cell for the arbitrary cloud of point charges. The method is based on the presentation of crystal sums by means of the McDonald functions.

1. Introduction

The calculation of the electric field gradient (EFG) in ionic lattices is of some interest in connection with the application of nuclear quadrupole resonance (NQR) methods to crystals with mainly ionic bonding, such as copper oxide ceramics, etc [1-3]. The expansion of the crystal potential over spherical harmonics in the vicinity of the node considered is usually used for this purpose [1]. The modified Evjen method [2-4] is also applicable.

The present paper extends the method of Madelung constant calculation developed in [5, 6] on EFG. It is useful to cast gradient components $q_{\mu\nu}$ in a form similar to the electrostatic potential $V = (e/R)\xi$

$$q_{\mu\nu} = (e/R^3)\xi_{\mu\nu} \quad (1)$$

where $\xi_{\mu\nu}$ is a geometrical factor similar to the Madelung constant ξ . The proposed technique ensures the exact calculation of the geometrical constants $\xi_{\mu\nu}$ and accurate comparison of the data for different crystals. Moreover, this representation allows one to express all EFG components at the nuclei for all the usual ionic cubic crystals in terms of two constants only.

In the more complicated crystal $\text{YBa}_2\text{Cu}_3\text{O}_7$ the geometrical factors of EFG components will be presented as linear forms with known coefficients of effective charges on two types of inequivalent oxygen and copper atoms. Thus the possibility arises of finding the charge redistribution between these atoms directly from NQR measurements. It may be recalled that the properties of high-temperature superconducting ceramics are often discussed in terms of charges on Cu and O.

2. Geometrical factors of model systems

We shall use decomposition of the cubic crystal potential into contributions from two model systems, L and M, already used for calculation of Madelung constants and potential geometrical factors for an arbitrary point [5, 6]. The charge distribution of the first one (L) consists of the point charges of identical sign in the whole plane, and the charge signs in parallel planes alternate. The second system (M) consists of parallel lines of identical charges whose signs alternate in the perpendicular plane. The potential for these has been expressed in terms of the zeroth-order McDonald function [6]. It only remains to differentiate these expressions for the present purpose. The technique proposed is rather universal and applicable independently of the existence of non-zero net dipole moment of the unit cell in contrast to the method of [4].

The expressions for the EFG components follow directly from equations (5) and (12) of [6]. For the L system these are

$$\begin{aligned}
 \xi_{zz} &= - \sum'_{s,t=-\infty}^{\infty} C_0(u\rho_{st}, z) \\
 \xi_0 &= (1/u^2) \sum'_{s,t=-\infty}^{\infty} [(x-s)^2 - (z-t)^2] C_2(u\rho_{st}, z) / \rho_{st}^2 \\
 \xi_{xx} &= (\xi_0 - \xi_{zz})/2 \quad \xi_{yy} = -(\xi_0 + \xi_{zz})/2 \\
 \xi_{xz} &= \sum'_{s,t=-\infty}^{\infty} [(x-s)/\rho_{st}] C_1(u\rho_{st}, z) \\
 \xi_{xy} &= \sum'_{s,t=-\infty}^{\infty} [(x-s)(y-t)/\rho_{st}^2] C_2(u\rho_{st}, z) \\
 \xi_{yz} &= \sum'_{s,t=-\infty}^{\infty} [(y-t)/\rho_{st}] C_1(u\rho_{st}, z)
 \end{aligned} \tag{2}$$

where the following notation is used:

$$\begin{aligned}
 C_i(v, z) &= 4\pi^2 \sum_{\ell=1}^{\infty} (2\ell-1)^2 K_i(\pi(2\ell-1)v) \cos[\pi(2\ell-1)z] \quad i = 0, 2 \\
 C(v, z) &= 4 \sum_{\ell=1}^{\infty} K_0(\pi(2\ell-1)v) \cos[\pi(2\ell-1)z] \\
 C_i(v, z) &= 4\pi^2 \sum_{\ell=1}^{\infty} (2\ell-1)^2 K_i(\pi(2\ell-1)v) \sin[\pi(2\ell-1)z] \quad i = 1
 \end{aligned} \tag{3}$$

and K_i is the i th McDonald function.

Similar expressions hold for the M system, where the geometrical factors are denoted by $\zeta_{\mu\nu}$:

$$\begin{aligned}
 \zeta_{yy} &= -(1/u^3) \sum_{s,t=-\infty}^{\infty} (-1)^s C_0(\tau_{st}, y) \\
 \zeta &= (1/u^2) \sum_{s,t=-\infty}^{\infty} (-1)^s [(x-s)^2 - (z-t)^2/u^2] C_2(\tau_{st}, y)/\tau_{st}^2 \\
 \zeta_{xx} &= (\zeta - \zeta_{yy})/2 \quad \zeta_{zz} = -(\zeta + \zeta_{yy})/2 \\
 \zeta_{xy} &= (1/u^3) \sum_{s,t=-\infty}^{\infty} (-1)^s (x-s) C_1(\tau_{st}, y)/\tau_{st} \\
 \zeta_{xz} &= (1/u^4) \sum_{s,t=-\infty}^{\infty} (-1)^s (x-s)(z-t) C_2(\tau_{st}, y)/\tau_{st}^2 \\
 \zeta_{yz} &= (1/u^4) \sum_{s,t=-\infty}^{\infty} (-1)^s (z-t) C_1(\tau_{st}, y)/\tau_{st}.
 \end{aligned}
 \tag{4}$$

Here

$$\rho_{st}^2 = (x-s)^2 + (y-t)^2 \quad \tau_s^2 = (x-s)^2 + (z-t)^2/u^2 \tag{5}$$

z is measured in units of d , the distance between opposite charges, and x and y similarly are measured in units of ud , the distance in the xy plane. The prime on the sum denotes missing out the term $s = t = 0$ for $x = y = 0$. It should be replaced by the constant

$$-4 \sum_{k=1}^{\infty} (-1)^k / k^3 = 3.6001707 \tag{6}$$

for $z = 0$ and by

$$\beta''(-z) + \beta''(z) + 2/z^3 \tag{7}$$

for $z \neq 0$ where $\beta(z)$ is the known function [7] connected with the logarithmic derivative of the Euler Γ -function. These series converge much more rapidly than $1/\rho^3$ except in the vicinity of $x = y = 0$.

For instance, we have for the points A and F (figure 1) for $u = 2$

$$\xi_{xx}(A) \equiv \alpha = 1.880136 \quad \xi_{xx}(F) \equiv \beta = 0.54174. \tag{8}$$

The accuracy may be controlled by means of symmetry conditions, which hold for the M system on substitution of x by y and vice versa in consequence of some latent identities between sums of the McDonald functions.

The number of independent EFG factors for the main points may be significantly reduced on account of the symmetry requirements for the potential geometric factors. These are expressed by equation (6) from [6] (we use this occasion to correct a misprint in sign in this equation)

$$f(x, y, z) = f(-x, y, z) = f(x, -y, z) = f(x, y, -z) = f(y, x, z) \tag{9}$$

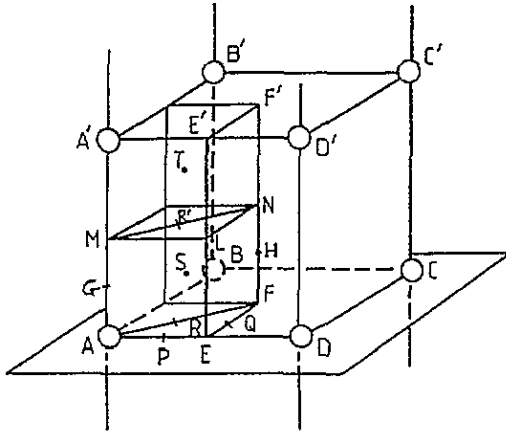


Figure 1. The main points of the cubic cell.

which is identical for both systems. The periodicity condition looks like

$$\begin{aligned}
 f(x - 1/2, y, z) &= f(x + 1/2, y, z) \\
 f(x, y - 1/2, z) &= f(x, y + 1/2, z) \\
 -f(x, y, z - 1/2) &= f(x, y, z + 1/2)
 \end{aligned}
 \tag{10}$$

for the L system. Signs should be changed for the M system in equations (10). Differentiation of equations (9) shows that mixed EFG components with the subscript of the perpendicular to some face vanish on this face. Therefore the EFG tensor is diagonal on edges. The same conditions hold in 'vertical' planes that pass through the cell centre N (figure 1). Thus, the EFG tensor is diagonal along the perimeter LEFN in the L system, and only the xz component is non-zero on the line LN. Since the potential vanishes in the horizontal plane NML, the components ξ_{xx} , ξ_{yy} and ξ_{xy} also vanish there, as well as $\xi_{zz} = -\xi_{xx} - \xi_{yy}$, and since the EFG tensor is diagonal at L, M and N it completely vanishes at these points.

The roles of the central vertical and horizontal planes in the M system are interchanged as a result of the change of sign in equation (10). Therefore the EFG tensor is diagonal on lines ML and AE, and by similar reasoning it vanishes at L and E. Thus on the three lines of the square perimeter LNFE only ζ_{xy} is non-zero, and on LE only ζ_{yz} is non-zero.

The additional restrictions follow from the connections between potential factors of L and M systems (equations (10) and (11) in [6]):

$$\xi_{xx}(x, y, z, u) = \xi_{yy}(y, x, z, u) \quad \xi_{xz}(x, y, z, u) = \xi_{yz}(y, x, z, u) \tag{11}$$

etc, and similarly for ζ :

$$\begin{aligned}
 \zeta_{xx}(x, y, z) &= 8[\xi_{xx}(x/2, z, y) - \xi_{xx}((x-1)/2, z, y)] \\
 \zeta_{zz}(x, y, z) &= 8[\xi_{yy}(x/2, z, y) - \xi_{yy}((x-1)/2, z, y)] \\
 \zeta_{yy}(x, y, z) &= 8[\xi_{zz}(x/2, z, y) - \xi_{zz}((x-1)/2, z, y)] \\
 \zeta_{xy}(x, y, z) &= 8[\xi_{xz}(x/2, z, y) - \xi_{xz}((x-1)/2, z, y)].
 \end{aligned}
 \tag{12}$$

The values of u if not indicated explicitly are $1/2$ for ζ , $1/\sqrt{2}$ for ζ' , 2 for ξ . In particular, for the vertical line passing through A we have

$$\zeta_{xx}(0, 0, z) = 8[\xi_{xx}(0, z, 0) - \xi_{xx}(1/2, z, 0)] \quad (13)$$

$$\zeta_{yy}(0, 0, z) = 8[-\xi_{xx}(0, z, 0) - \xi_{yy}(0, z, 0) + \xi_{xx}(1/2, z, 0) + \xi_{yy}(1/2, z, 0)].$$

Taking into account the symmetry of the M system to this axis $\zeta_{xx} = \zeta_{yy}$, we obtain a relation between EFG components of the L system at the horizontal edge and the parallel line passing through the centre

$$2\xi_{yy}(x, 0, 0) + \xi_{xx}(x, 0, 0) = 2\xi_{yy}(x, 1/2, 0) + \xi_{xx}(x, 1/2, 0). \quad (14)$$

From this it follows for $x = 0$ and $x = 1/2$ on account of notation (8) that

$$3\alpha = 2\xi_{\parallel}(E) + \xi_{\perp}(E) \quad 3\beta = 2\xi_{\perp}(E) + \xi_{\parallel}(E)$$

where the subscripts denote orthogonal and parallel to the edge AD components. Then

$$\xi_{\perp}(E) = 2\beta - \alpha \quad \xi_{\parallel}(E) = 2\alpha - \beta. \quad (15)$$

In the same way from equations (13) and (12) we have

$$\zeta_{xx}(G) = \zeta_{yy}(G) = 8[\xi_{\perp}(P) - \xi_{\perp}(Q)] = 4[\xi_{\parallel}(Q) - \xi_{\parallel}(P)] \quad (16)$$

$$\zeta_{xy}(H) = 16\xi_{xz}(R') = 42.481894. \quad (17)$$

The EFG components for the atomic positions in the M system with $u = 1/\sqrt{2}$, which also enter compositions forming standard cubic lattices [5], are also expressed through the same constants α and β . From equation (9) in [5] presented in the form

$$g(x, y, z, 1/\sqrt{2}) + g(x - 1/2, y - 1/2, z, 1/\sqrt{2}) \\ = 2f(z, (x + y)/2, y - x, 2) + f(z, (x + y - 1)/2, y - x, 2) \quad (18)$$

we have

$$\zeta'_{xx}(x, y, z) + \zeta'_{xx}(x - 1/2, y - 1/2, z) \\ = 4[\phi(z, (x + y)/2, y - x) + \phi(z, (x + y - 1)/2, y - x)] \\ \zeta'_{yy}(x, y, z) + \zeta'_{yy}(x - 1/2, y - 1/2, z) \\ = 4[\vartheta(z, (x + y)/2, y - x) + \vartheta(z, (x + y - 1)/2, y - x)] \quad (19)$$

$$\zeta'_{xy}(x, y, z) + \zeta'_{xy}(x - 1/2, y - 1/2, z) \\ = 4[\chi(z, (x + y)/2, y - x) + \chi(z, (x + y - 1)/2, y - x)]$$

$$\phi = -\xi_{xx} - 2\xi_{yz} \quad \vartheta = -\xi_{xx} + 2\xi_{yz} \quad \chi = -\xi_{xx} - 2\xi_{zz}.$$

From these it immediately follows that

$$\zeta'_{xx}(A) = -8\beta \quad \zeta'_{xx}(M) = -8\alpha \quad \zeta'_{xy}(F) = 24\alpha \quad \zeta'_{xy}(N) = 24\beta. \quad (20)$$

In the same way from equation (12) the equation for the quartered points results:

$$\xi_{xy}(1/2, y, z) = 16\xi_{xz}(1/4, z, y) \\ \zeta'_{xx}(R) + \zeta'_{xy}(R) = 8\xi_{\perp}(P) \quad \zeta'_{xx}(R) - \zeta'_{xy}(R) = 8\xi_{zz}(P) \\ \zeta'_{xx}(G) = -4[\xi_{\parallel}(P) + \xi_{\parallel}(Q)] \quad \zeta'_{xy}(H) = 8[2\xi_{\perp}(P) + \xi_{\perp}(Q)] \quad (21)$$

where the values of ξ may be taken into account:

$$\xi_{\parallel}(P) = 16.685136 \quad \xi_{\parallel}(Q) = 0.125925 \\ \xi_{\perp}(P) = -6.72046 \quad \xi_{\perp}(Q) = 1.559118.$$

3. Lattice contributions to EFG of atomic positions in standard cubic crystals

The potential of the standard cubic lattices including alkali-doped fullerites has been expressed in terms of a similar quantity for the systems L and M [6]. Since this expression is valid for an arbitrary point of the crystal volume the EFG components can be immediately obtained by a proper differentiation. These are given in table 1 (by means of this table some misprints that slipped into table 1 of [6] may be corrected). The results are presented in terms of the tensor functions $\xi_{\mu\nu}$, $\zeta_{\mu\nu}$ and $\zeta'_{\mu\nu}$. It is convenient to use rotated (by 45°) tensor $\eta_{\mu\nu}$ instead of $\zeta'_{\mu\nu}$:

$$\begin{aligned} \eta_{xx} &= (\zeta'_{xx} + \zeta'_{yy} - 2\zeta'_{xy})/2 & \eta_{yy} &= (\zeta'_{xx} + \zeta'_{yy} + 2\zeta'_{xy})/2 & \eta_{xy} &= (\zeta'_{yy} - \zeta'_{xx})/2 \\ \eta_{xz} &= (\zeta'_{xz} - \zeta'_{yz})/\sqrt{2} & \eta_{yz} &= (\zeta'_{xz} + \zeta'_{yz})/\sqrt{2}. \end{aligned} \quad (22)$$

Then suitable EFG components of the crystals are presented in terms of $\xi_{\mu\nu}$, $\zeta_{\mu\nu}$ and $\eta_{\mu\nu}$ with the same subscripts by means of equations from table 1. (The similarity of subscripts gives the possibility to omit them for the sake of brevity.) The results for the other crystals are as simple as those from table 1 but are not given explicitly in order to avoid the cumbersome equations for each component separately. Instead, all these have been programmed.

Table 1. Gradient factors of cubic crystals.

Crystal	Gradient factor
NaCl	$\zeta(2x, 2y, z) - \zeta(2x, 2y, z + 1/2)$
CsCl	$\eta(x + y, y - x, z) + 8\xi(x - 1/2, y - 1/2, 2z)$
CaF ₂	$\zeta(2x, 2y, z) - \zeta(2x, 2y, z + 1/2) + 8\eta(2x + 2y, 2y - 2x, 2z) + 64\xi(2x - 1/2, 2y - 1/2, 4z)$
ZnS	$\zeta(2x, 2y, z) - \zeta(2x, 2y, z + 1/2) + 8\eta(2x + 2y, 2y - 2x, 2z) - \zeta(2x - 1/2, 2y - 1/2, z - 1/4) + \zeta(2x - 1/2, 2y - 1/2, z + 1/4) + 64\xi(2x - 1/2, 2y - 1/2, 4z)$
Cu ₂ O	$\{\zeta(2x - 1/2, 2y - 1/2, z - 1/4) - \zeta(2x, 2y, z) - \zeta(2x - 1/2, 2y - 1/2, z + 1/4)\}/2 - 4\eta(2x + 2y, 2y - 2x, 2z) - 32\xi(2x - 1/2, 2y - 1/2, 4z) - 8\xi(x, y, 2z) + 8\xi(x - 1/2, y - 1/2, 2z) - \zeta(2x, 2y, z + 1/2)/2$
BaBiO ₃	$16[\xi(x, y, 2z) - \xi(x - 1/2, y - 1/2, 2z)] + 2\zeta(2x, 2y, z)$
C ₆₀ ³⁻ A ₃ ⁺ FCC	$2[\zeta(2x, 2y, z + 1/2) - \zeta(2x, 2y, z) - 4\eta(2x + 2y, 2y - 2x, 2z) - 32\xi(2x - 1/2, 2y - 1/2, 4z)]$
C ₆₀ ³⁻ A ₃ ⁺ BCC	$16[\xi(x - 1/2, y - 1/2, 2z) - \xi(x, y, 2z)]\zeta(2x, 2y, z) - \zeta(2x, 2y, z + 1/2)$

In particular the values of EFG in the lattice sites can be obtained by means of table 1 and the values of ξ , ζ and ζ' mentioned in the preceding section. For instance, at the Bi atom in the perovskite crystal

$$q_{xx} = q_{yy} = (2/R^3)\{8[\xi_{xx}(A) - \xi_{xx}(F)] + \zeta_{xx}(A)\} = (2/R^3)[8\alpha - 8\beta + 8(\beta - \alpha)] = 0.$$

Similarly at the Ba atom

$$q_{xx} = q_{yy} = 2[8[-\xi_{xx}(F) + \xi_{xx}(A)] + \zeta_{xx}(M)]/R^3 = 2[8\alpha - 8\beta + 8(\beta - \alpha)] = 0.$$

And at the oxygen atom

$$q_{\perp} = (2/R^3)[\xi_{xx}(E) - \xi_{yy}(E) - \zeta_{xx}(A)] = (2/R^3)[8(2\beta - \alpha) - 8(2\alpha - \beta) - 8(\beta - \alpha)] \\ = 32(\beta - \alpha)/R^3 \quad (23)$$

$$q_{\parallel} = (2/R^3)[\xi_{yy}(E) - \xi_{xx}(E) - \zeta_{yy}(A)] = 64(\alpha - \beta)/R^3.$$

However, vanishing EFG at Bi and Ba as well as that $q_{\parallel} = -2q_{\perp}$ at O could be anticipated beforehand from the cubic symmetry and the condition $q_{xx} + q_{yy} + q_{zz} = 0$. By the same reasoning EFG is zero at all the atomic positions of the crystals mentioned in table 1 with the exception of cations in BCC symmetric crystal $C_{60}^{-}A_3^{+}$. There at the edge and face middles it will be, respectively,

$$q_{\parallel} = -2q_{\perp} = -(1/R^3)\{16[\xi_{yy}(E) - \xi_{xx}(E)] - \zeta_{yy}(A) - \zeta_{yy}(M)\} = 64(\beta - \alpha)/R^3 \\ q_{\perp} = -2q_{\parallel} = -(1/R^3)\{16[\xi_{zz}(F) - \xi_{zz}(A)] + \zeta_{zz}(A) + \zeta_{zz}(M)\} \quad (24) \\ = (1/R^3)[32\beta - 32\alpha + 32(\beta - \alpha)] = 64(\beta - \alpha)/R^3$$

and \perp denotes the perpendicular component to the edge in the first case and to the face in the second case. The remaining exception is the Cu atom in Cu_2O , for which all diagonal components are zero and non-diagonal are $-16\xi_{xz}(R')$. The latter means that the EFG tensor is diagonal in the axes directed along and perpendicular to the Cu-O line where

$$q_{\parallel} = -2q_{\perp} = -32\xi_{xz}(R'). \quad (25)$$

Thus owing to the cubic symmetry and the tensor nature of EFG, here only two constants $\alpha - \beta$ and $\xi_{xz}(R')$ are needed for a full description of all atomic positions in all cubic crystals. This is somewhat surprising since for the scalar potential three constants were necessary [5]. However, from the symmetry argument only it cannot be established, for example, that $-q(O)/q(Rb) = (R_{C_{60}A^+}/R_{BaBiO_3})^3$ and that $q_{\perp}(O) < 0$, $q_{\parallel} = -2q_{\perp}(O) > 0$ in the perovskite crystal. The latter inequalities are in accordance with the greater hardness of the longitudinal vibrations of the oxygen atom as compared to the transverse ones, as their amplitudes show, being equal to 0.12 Å and 0.26 Å [8], respectively. It could be recalled that EFG components contribute significantly to suitable atomic force constants [9]. Vanishing of EFG for Bi and Ba also agrees with the isotropic type of their vibrations [8].

Another interesting property may be noticed from table 1 for the perovskite crystal. This is the existence of a network with zero potential. The period of this cubic network is half the lattice constant: its vertices are situated at the points with quartered coordinates 1/4; 3/4, etc. Indeed, from equations (10) vanishing of the potential factors follows $\xi(x, y, 1/2) = \zeta(1/2, y, z) = \zeta(x, 1/2, z) = 0$. Then the sixth line of table 1 means that the potential turns to zero if any two of the three coordinates are equal to 1/4 or 3/4. A similar property holds also for the BCC $C_{60}A_3$ crystal.

Calculation of EFG at an arbitrary point of any crystal from table 1 and in some other crystals may be achieved by means of the mentioned program, which gives the necessary values to five decimal places in a few seconds even on a PC AT 286/287.

For instance, in $C_{60}A_3$ of symmetry A15, the non-zero gradient appears at the anion sites as a consequence of displacement of cations from their positions in the edge and face centres. Suitable geometrical factors are $\xi_{xx} = -3.84279$, $\xi_{yy} = -10.06029$ for the C_{60} centre. Since $C_{60}A_6$ is a superposition of the two above systems with opposite displacements, here

the EFG tensor has an axial symmetry and $-\xi_{zz} = \xi_{xx} + \xi_{yy} = -13.90308$. The same value remains in the exotic system $C_{60}A_9$ [10] since addition of the BCC $C_{60}A_3$ lattice to $C_{60}A_6$ gives no contribution to anion sites. EFG remains also axially symmetric in the $C_{60}A_4$ *Immm* system but here the anisotropy is larger: $\xi_{xx} = 19.97588$. For cations it is much greater, e.g. in $C_{60}A_3$ A15 the gradient components for these positions are $\xi_{xx} = 379.8635$, $\xi_{yy} = -20.8085$, etc.

A more complicated example is presented in table 2. There, the contributions of the crystal field to EFG components that are additional to the intraionic ones are given for three inequivalent carbon atoms of fullerene in the Rb-doped lattice [11]. A special orientation of the icosahedral axes relative to the cubic ones (orientation 'A' in terms of [6]) is used, which does not split the half-filled level t_{1u} .

Table 2. Crystal-field contribution to gradient ($e/\text{\AA}^3$) in $C_{60}^-A_x^+$.

Point number	xx	yy	xy	xz	yz
$C_{60}A_3$, FCC, $R = 14.436$					
1	-0.014 82	0.002 46	-0.043 13	-0.031 77	0.017 92
2	-0.016 84	-0.018 77	-0.344 53	-0.115 30	-0.132 40
3	-0.003 23	0.012 10	0	0	-0.007 60
$C_{60}A_3$, BCC, $R = 11.787$					
1	0.026 57	-0.009 31	-0.027 62	-0.022 92	-0.000 87
2	0.010 36	0.014 28	-0.024 86	-0.006 06	-0.008 33
3	-0.056 69	0.097 58	0	0	-0.044 50
$C_{60}A_6$, BCC, $R = 11.548$					
1	-0.039 09	0.024 54	-0.129 96	-0.037 54	-0.060 29
2	0.016 32	0.004 42	-0.159 67	-0.037 70	-0.027 71
3	-0.004 29	-0.111 87	0.042 34	0	-0.072 99
$C_{60}A_4$, BCC, $R = 11.657$					
1	-0.000 78	0.011 97	-0.048 94	-0.012 08	-0.030 52
2	0.025 83	0.025 69	-0.061 61	-0.015 93	-0.006 89
3	-0.011 05	-0.039 35	0.038 70	0	-0.067 78

4. Necessary generalizations

The first notation concerns the use of the skew angle coordinate system defined by the absolute values a_1, a_2, a_3 of the lattice vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ and the angles between them, $\vartheta_{12}, \vartheta_{13}, \vartheta_{23}$. These are connected with the Cartesian coordinate system by

$$\mathbf{a}_n = a_n^k \mathbf{i}_k \quad \mathbf{i}_1 = \mathbf{i}, \mathbf{i}_2 = \mathbf{j}, \mathbf{i}_3 = \mathbf{k} \quad (26)$$

where the tensor algebra notation is used with the standard summation over similar upper and lower indices. Without loss of generality it may be assumed that

$$\begin{aligned} a_1^1 &= a_1 \sin \vartheta_{13} & a_1^2 &= 0 & a_1^3 &= a_1 \cos \vartheta_{13} & a_2^1 &= a_2^2 = 0 & a_2^3 &= a_2 \\ a_3^1 &= a_2 (\cos \vartheta_{12} - \cos \vartheta_{13} \cos \vartheta_{23}) / \sin \vartheta_{13} & a_3^2 &= a_2 \sqrt{T} / \sin \vartheta_{13} & a_3^3 &= a_2 \cos \vartheta_{23} \end{aligned} \quad (27)$$

where \sqrt{T} is defined below. The elements b_k^n of the matrix of the inverse transformation

$$b_k^n a_n^l = \delta_k^l \quad (28)$$

define a set of contravariant vectors

$$b^n = b_k^n i_k \quad (29)$$

which obey

$$b^n \cdot a_k = b_s^n a_k^s (i_s \cdot i_r) = b_s^n a_k^s \delta_r^s = b_s^n a_k^s = \delta_k^n. \quad (30)$$

We see from equation (30) that b^n are nothing other than the vectors of the reciprocal lattice

$$b^1 = [a_2 a_3]/V \quad b^2 = [a_3 a_1]/V \quad b^3 = [a_1 a_2]/V \quad V = a_1[a_2 a_3]. \quad (31)$$

The covariant metric tensor is

$$g_{ik} = (a_i \cdot a_k) = a_i a_k \cos \vartheta_{ik} \quad (32)$$

while equations (31) allow one to find its contravariant coordinates

$$g^{ik} = (b^i \cdot b^k) = (\cos \vartheta_{ij} \cos \vartheta_{jk} - \cos \vartheta_{ik})/(a_i a_k T) \quad g^{ii} = \sin^2 \vartheta_{jk}/a_i^2 T \quad (33)$$

and equations (30) guarantee that the necessary condition

$$g_{ik} g^{kj} = \delta_i^j \quad (34)$$

is fulfilled. The determinant of g equals V^2 since $g_{ik} = a_i^n a_k^n$, where

$$V^2 = a_1^2 a_2^2 a_3^2 (1 - \cos^2 \vartheta_{12} - \cos^2 \vartheta_{13} - \cos^2 \vartheta_{23} + 2 \cos \vartheta_{12} \cos \vartheta_{13} \cos \vartheta_{23}) \quad (35)$$

which determines the value of T as

$$T = V^2/(a_1 a_2 a_3)^2 = 1 - \cos^2 \vartheta_{12} - \cos^2 \vartheta_{13} - \cos^2 \vartheta_{23} + 2 \cos \vartheta_{12} \cos \vartheta_{13} \cos \vartheta_{23}. \quad (36)$$

The radius vector of an arbitrary crystal point will be determined by its contravariant coordinates:

$$r = b^i x_i = a_i x^i \quad x^1 = x \quad x^2 = y \quad x^3 = z \quad x_i = g_{ik} x^k. \quad (37)$$

Then the field, i.e. the potential gradient, is expanded over the vectors of the reciprocal lattice

$$\partial V/\partial r = (\partial V/\partial X)i + (\partial V/\partial Y)j + (\partial V/\partial Z)k = (\partial V/\partial X^i)b_s^i i_s = (\partial V/\partial x^i)b^i. \quad (38)$$

Similarly EFG $\xi_{ik} = \partial^2 V/\partial x^i \partial x^k$ is a covariant tensor and Laplacian vanishing looks like

$$\Delta = g^{ik} \xi_{ik} = 0. \quad (39)$$

By the same reasoning calculation of the NQR coupling constant q requires inclusion of the inverse transformation (28) since the nuclear quadrupole tensor is usually known in Cartesian coordinates: $q = Q_{ij}q_{ij}$ where

$$q_{ij} = e\xi_{k\ell}b_i^k b_j^\ell. \quad (40)$$

The values of b_i^k corresponding to equations (27) may be found from

$$\begin{aligned} b^1 &= [i + j(\cos \vartheta_{13} \cos \vartheta_{23} - \cos \vartheta_{12})/\sqrt{T}]/\sin \vartheta_{13} & b^2 &= j \sin \vartheta_{13}/(a_2\sqrt{T}) \\ b^3 &= [-(\cot \vartheta_{13})i + (\cos \vartheta_{12} \cos \vartheta_{13} - \cos \vartheta_{23})j/(\sqrt{T} \sin \vartheta_{13}) + \bar{k}]/a_3. \end{aligned} \quad (41)$$

Now we can generalize the definition of the L system to an arbitrary lattice formed by a_1, a_2, a_3 . It will be a periodic set of parallel straight lines directed along a_3 with a longitudinal period a_3 : charges $+q$ are situated at the origin and at the end of a_3 and $-q$ at the middle between them. Thus, $d = a_3/2$ in the previous notation. (The further necessary generalization when $-q$ is situated in an arbitrary point between two $+q$ charges will be considered below.) The origin of one of these straight lines is its intersection point with the (a_1, a_2) plane

$$N = ma_1 + na_2 \quad (42)$$

where m, n are integers. The potential at the observation point r in the zero cell is determined by the lengths of two segments that describe the position of this point relative to the line creating the potential: the length $\rho_{m,n}$ of the perpendicular from this point to the line and the distance $p_{m,n}$ from the base of the perpendicular to the line origin. It is evident that

$$\bar{p}_{mn} = a_3(a_3 \cdot r_n) = p_{mn}a_3/2 \quad p_{mn} = x_mu_1 + y_nu_2 + 2z \quad (43)$$

and

$$\bar{\rho}_{mn}^2 = \rho_{mn}^2 a_3^2/4 \quad \rho_{mn}^2 = x_m^2 u_{11} + y_n^2 u_{22} - 2x_m y_n u_{12} \quad (44)$$

where

$$\begin{aligned} u_1 &= 2a_1 \cos \vartheta_{12}/a_3 & u_2 &= 2a_2 \cos \vartheta_{23}/a_3 & u_{11} &= 4a_1^2 \sin^2 \vartheta_{13}/a_3^2 \\ u_{22} &= 4a_2^2 \sin^2 \vartheta_{23}/a_3^2 & x_m &= x - m & y_n &= y - n. \end{aligned} \quad (45)$$

Then according to equation (1) we obtain the desired generalization

$$V(r) = 2q \sum_{m,n=-\infty}^{\infty} C(\rho_{mn}, p_{mn})/a_3. \quad (46)$$

The function $C(\rho, z)$ has already been defined in equation (3). The EFG components are obtained by a proper differentiation of equation (46) and will not be given explicitly. The condition (39) may be used for checking.

The second generalization is connected with the method of description of arbitrary charge distribution within a cell. Instead of the L system we consider a similar set of lines but with the negative charge at an arbitrary distance d (in units of the cell edge length) rather

than in the middle between positive ones: $L_i(d)$ where $i = 1, 2, 3$ denote the direction of the charge line. The former system L in new notation is $L = L_3(1/2)$. The corresponding potential is obtained by means of the function $S(\rho, z)$:

$$S(\rho, z) = [F(\rho, z) - F(\rho, z - d)]/a_3 \quad (47)$$

where $F(\rho, z)$ describes the potential of two sets of opposite charges equidistantly distributed along two parallel lines on a distance ρ between them and mutually shifted by z . According to [7, equation (8.526.1)]

$$F(\rho, z) = 4 \sum_{\ell=1}^{\infty} K_0(2\pi \ell \rho) \cos(2\pi \ell z) \quad (48)$$

$$F(\rho, z) - 2(C + \ln \rho/2) = \sum_{\ell=-\infty}^{\infty} [\rho^2 + (z + \ell)^2]^{-1/2} - 2 \sum_{\ell=1}^{\infty} \ell^{-1}.$$

In the limit case $\rho = 0$ the potential is described by the logarithmic derivative of Γ -function (C is the Euler constant)

$$F(0, z) = 2C + \Psi(z) + \Psi(1 - z) = 1/z(1 - z) + 2z^2 \sum_{k=1}^{\infty} [k(k^2 - z^2)]^{-1}. \quad (49)$$

The former function in this notation is

$$C(\rho, z) = \frac{1}{2}[F(\rho/2, z/2) - F(\rho/2, (z - 1)/2)]. \quad (50)$$

The systems $L_i(d)$ allow one to obtain the potential of an arbitrary cloud of periodically distributed point charges. If a charge Q_s is situated at a point x, y, z in the unit cell, adding subsequently to it three systems $L_3(z), L_2(y), L_1(x)$ with the origins at $(x, y, 0), (x, 0, 0), (0, 0, 0)$, respectively, we place it at the cell origin where it annihilates the other charges similarly displaced since the net cell charge is zero. Finally the decomposition looks like

$$L = \sum_{i=1}^s Q_i [L_1(x_i)|_{000} + L_2(y_i)|_{x,00} + L_3(z_i)|_{x,y,0}] \quad (51)$$

and by means of subsequent application of equation (47) the problem is solved completely. If in some cases the net charge is non-zero we can place a suitable compensating charge at the cell origin. The programming of equation (51) is as easy as that of the cubic crystal case, and the corresponding program works as fast as the one mentioned.

As a simple example we present the value of the Madelung constant ξ and EFG geometrical factors for the hexagonal close packing of layers of opposite charges: $\xi = 1.23557$, $\xi_{xx} = \xi_{yy} = -5.10932$, $\xi_{xy} = 2.55462$, $\xi_{zz} = 27.24927$, $\xi_{xz} = \xi_{yz} = 0$. This follows from equation (51) where $a_1 = a_2$, $a_3 = a_1 2\sqrt{2/3}$, $\vartheta_{12} = 120^\circ$, $\vartheta_{13} = \vartheta_{23} = 90^\circ$. The comparison with a suitable value for the cubic close packing of similar layers, i.e. with the L system itself for which $\xi = 1.37068$ [5], is quite reasonable: the mutual repulsion is stronger in the first case.

A more complicated calculation illustrates the application of the present technique to the 'idealized' Y-Ba-Cu-O model [5]. The potential constants in the equation $V = e\xi/R$ and geometrical EFG factors from equation (1) for non-equivalent atomic sites are given in table 3

Table 3. The geometrical factors of potential and EFG in $YBa_2Cu_3O_7$.

Atom	Charge	ξ	ξ_{xx}	ξ_{yy}
Cu1	$3 - q - 2q_0$	$-8.1748 - 0.5613q + 5.7494q_0$	$-25.0485 - 9.3616q + 9.5564q_0$	$64.0173 - 9.3616q - 34.9764q_0$
Cu2	$2 + q/2$	$-7.9784 + 0.2806q + 1.2373q_0$	$-17.5578 + 4.6808q - 4.7782q_0$	$-16.9676 + 4.6808q - 5.0733q_0$
O1	$-2 + q_0$	$6.9867 - 6.0936q - 5.7681q_0$	$67.5928 - 67.5669q - 88.8114q_0$	$-15.2055 + 20.9085q + 31.8110q_0$
O2	-2	$5.0040 + 3.0468q + 1.0118q_0$	$-21.7966 - 10.4543q - 1.7157q_0$	$23.2263 + 33.7835q + 3.9125q_0$
O3	-2	$4.9740 + 3.0468q + 1.0268q_0$	$23.8183 + 33.7835q + 3.6165q_0$	$-21.2046 - 10.4543q - 2.0117q_0$
O4	$-2 + q_0$	$5.2403 - 2.3072q - 3.5152q_0$	$-31.2063 + 5.4063q + 24.8662q_0$	$-18.2302 + 5.4063q + 18.3782q_0$
Ba	2	$-5.5582 - 1.9562q - 0.1883q_0$	$2.3201 - 2.0758q - 0.1072q_0$	$-10.6560 - 2.0758q + 6.3808q_0$
Y	3	$-6.2029 + 3.9124q + 1.0349q_0$	$12.6951 + 4.1517q + 0.2145q_0$	$12.6441 + 4.1517q + 0.2400q_0$
L1	0	$2.4172 - 6.0936q - 3.4834q_0$	$-22.6891 + 20.9085q + 35.5528q_0$	$60.1089 - 67.5669q - 85.0696q_0$
L2	0	$1.9447 + 4.6145q + 1.0610q_0$	$-3.8697 - 10.8129q - 0.2756q_0$	$-3.8188 - 10.8129q - 0.3011q_0$

($\xi_{zz} = -\xi_{xx} - \xi_{yy}$), where R is the transverse size of the unit cell and $c = 3R$. The notation of atomic positions is taken from [12]. The corresponding potentials for $R = 3.87 \text{ \AA}$ differ from those reported in [12] by no more than a few tenths of an eV except for the data for Y, where the difference reaches 10 eV, and for O1, where it is 4 eV for the case (a) of [12]. The influence of the orthorhombic distortion is small. For $a = R = 3.89 \text{ \AA}$, $b = 3.82 \text{ \AA}$, $c = 3R$ the constant terms in ξ are: -8.1325 (Cu1), -8.0561 (Cu2), 5.2576 (O1), 5.0317 (O2), 4.9786 (O3), 7.0426 (O4), -5.6177 (Ba), -6.2044 (Y). The differences with those in table 3 are less than 0.07.

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