

## Point Asymmetry in Charge Shift Model for Electric Field Gradient in TCP Metals

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### Abstract

Electric field gradient at nuclear site in the lattice of tetragonal close packed (TCP) metals such as Indium is computed using the theory developed on the pattern of the Charge Shift Model initiated for hexagonal close packed (hcp) lattice. Numerical results are obtained using FORTRAN programs developed by us for electric field gradient in Indium. A tabulation of lattice sums for electric gradient in this metal suggests that all the three nonequivalent sites under the charge shift ansatz do not simultaneously pass through null electric field gradient for the case when the tcp lattice of the element transforms to body centered cubic lattice with axial ratio unity. At least one non-equivalent electronic site in the frame work of the charge shift model lacks the point symmetry of tetragonal system and contributes an extra electric field gradient.

**Keywords:** Lattice sum, TCP lattice, electric field gradient, Indium, charge shift, body centered cubic lattice.

### Introduction

Electric field gradient (EFG) is an important structural property of crystalline solids like metal and alloys. Local symmetry, co-ordination and valence of defects in solids, electronic and magnetic properties are extracted from quadrupole-field gradient relations. The non-cubic ionic lattice and spherically asymmetric electronic environment produce EFG at a nuclear site, and are only approximately known. Several approaches appear in literature for calculation using methods such as band structure, OPW [1], APW, tight binding, pseudo potential model [2], etc. Though these provide elegant theoretical footing, surely these pose formidable problems in terms of actual calculation of exact

wave functions. And, as such, semi classical approaches have surfaced with some momentum. *Charge shift model* of Bodenstedt [3] was initiated in this perspective for hcp (*sp*) metal. Verma et al extended it to include transition metals with hcp lattices [4, 5]. The validity region of the charge shift model was investigated by Gupta et al [6]. The method was recently used to calculate cohesive energy[7, 8, 9]. We developed similar model for the tetragonal close packed crystals for the first time. Calculation for EFG in Indium agreed well [10]. Here we use a plane wise lattice summation to our lattice minimizing computation time by quick convergence. We observe by graphical analysis of lattice sums in the framework of the charge shift model the presence of asymmetry in one of the non-equivalent conduction electronic sites, which may be a possible source of some extra electric field gradient in the frame work of charge shift model for tetragonal system.

### Theory

An ideal unit cell of tetragonal close packed (tcp or bct) lattice is characterized by interfacial right angles, and lattice parameters  $a=b \neq c$ . In crystals, the axial ratio ( $c/a$ ) differs from the ideal value of  $\sqrt{2}$ . In crystal, ions of tcp metal are located at the four corners and the body center of the unit cell. The conduction electrons are smeared in lattice according to amplitude square of their wave functions. The exact wave functions are, however, not available, and approximate methods are in use for the computation of electronic properties up to significant degree of justifications. In charge shift model, conduction electrons are assumed as tiny spheres located midway between the ions forming the first co-ordination cell of the origin occupying ion.

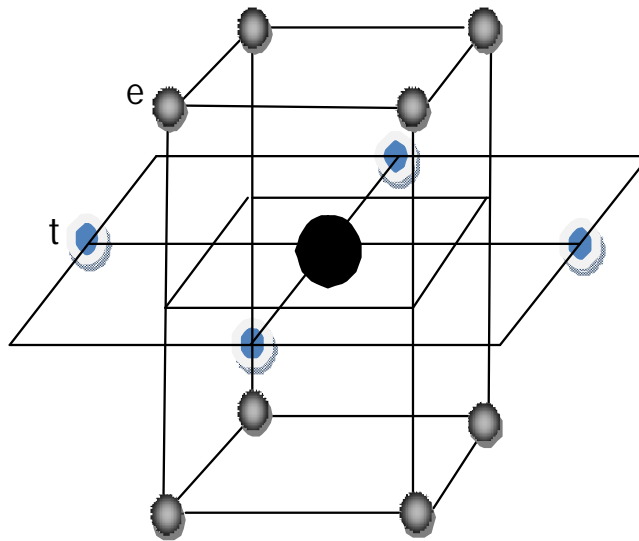


Fig. 1: Conduction electron cabinet around the ion

Metallic bonding arises due to their gluing action. Using the crystal symmetry, we get two non-equivalent electronic sites ( $e$  and  $t$ ) forming two non-equivalent planes perpendicular to the  $c$ -axis: *mixed plane*(A) that is composed of ions *and* one type of conduction electron spheres, while *pure plane*(B) that consists *purely* of the remaining type of conduction electron spheres.

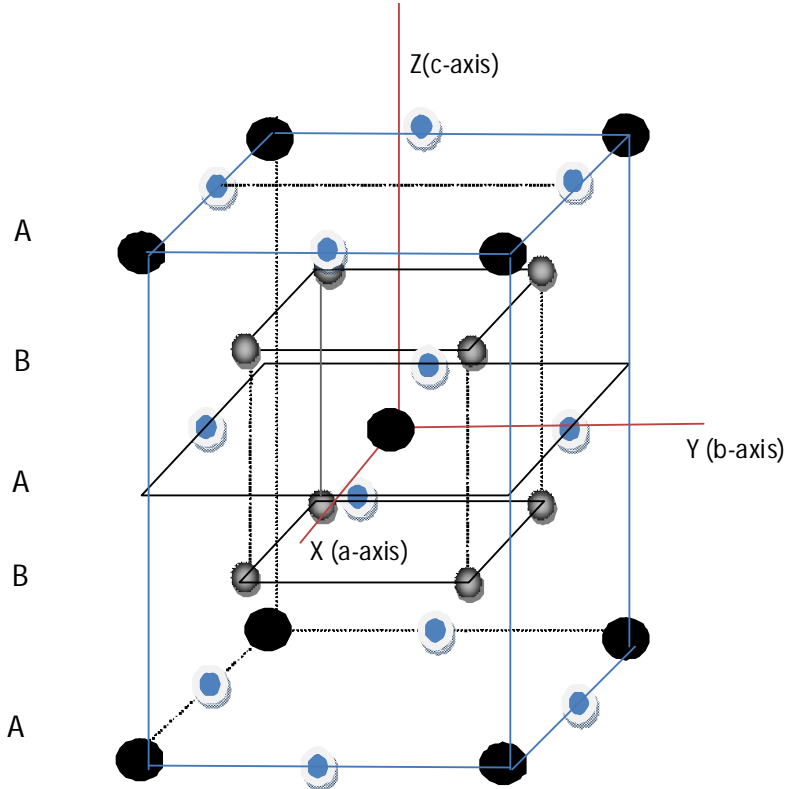


Fig. 2: TCP unit cell: non- equivalent sites and planes

The ionic charge, consistent with electronic wave function overlap with nucleus, is denoted by  $Z_{eff}e$ , where  $e$  is modulus of electronic charge. The total conduction electronic charge per ion ( $-Z_{eff}e$ ) is equally distributed among the twelve electronic sites in the co-ordination cell (figure-1), to start with, forming half of the total charge at a site as the other half is supposed to come from the other partner ion. The ions lie in the mixed planes. The charge on a conduction electron sphere in these planes is denoted by  $Q_t$ . In a unit cell, the eight  $Q_t$  lie at midpoints of edges and four at middle of each faces parallel to  $c$ -axis. The other type of electronic site that lies in the pure plane is charged by  $Q_e$ , occupying a total of eight sites in the unit cell, four above and four below the ion at the body center of the unit cell (figure-2). The electrical neutrality for the unit cell is, thus, written as

$$\frac{1}{4}[8Q_t] + \frac{1}{2}[4Q_t] + 8Q_e + 2Z_{eff}e = 0 \quad (1)$$

There is now affected a *shift* of charge from  $Q_t$  to  $Q_e$ -sites, parameterized by an algebraic factor  $\delta$ . This and the neutrality of cell are used to find the charges as:

$$Q_t = -\frac{1}{6} Z_{\text{eff}} e (1+2\delta) \quad (2)$$

$$Q_e = -\frac{1}{6} Z_{\text{eff}} e (1-\delta) \quad (3)$$

The factor  $\delta$  is obtained by considering the elasticity and the electrostatics of the unit cell as follows. The charges resulting due to the shift produce a stress that brings the ideal unit cell to the actual shape and size. The same can be affected by mechanical stress also. The two approaches are made consistent and  $\delta$  is expressed in terms of compliance co-efficient  $S_{ij}$  for the element with tcp structure. Depending upon the sign and magnitude of  $\delta$ , the departure of axial ratio from ideal value is fairly explained. The derivation and work concerned is the same as we have reported earlier [10]. We get

$$\delta = \frac{c-\sqrt{2}}{\sqrt{2}} \frac{54 \epsilon_0 a^4}{(Z_{\text{eff}} e)^2 (2S_{33} - S_{12} - S_{11})} \quad (4)$$

Thus, using equation (4), the charge distribution in the whole crystal is obtained under the framework of the model. The value of  $Z_{\text{eff}} e$  is obtained for suitable overlap of electron wave function with the nucleus.

### The electric field gradient

Once a charge distribution is known, numerical computation of electronic properties such as electric field gradient is a natural step for a justified model in a system such as TCP.

Let us take a charge  $q$  at position  $\vec{r}$  relative to an ionic site as origin of co-ordinates in the crystal. It produces electric field intensity at the origin whose space rate of variation along  $c$ -axis as  $Z$ -axis (the electric field gradient along  $c$ -axis) is given by

$$V_{zz} = \frac{q}{4\pi\epsilon_0} \frac{3z^2 - r^2}{r^5} \quad (5)$$

Taking in the tcp lattice  $a$ -axis,  $b$ -axis and  $c$ -axis as X-axis, Y-axis and Z-axis respectively, the crystallo-physical co-ordinates of lattice sites are denoted by real number triplets  $n_1$ ,  $n_2$  and  $n_3$  in units of lattice parameters  $a$ ,  $a$ , and  $c$ . To find the EFG in equation (5), we must take contributions from all the sites in the lattice. For this a lattice summation is required.

### Notations:

$N_i = n_i + t_{ijk}$  : An  $i$ -th component of position vector of nonequivalent charge located at  $k$ -th position of  $j$ -th nonequivalent type site in the  $n$ -th unit cell

$M_j$  = Multiplicity per unit cell for a  $j$ -th non-equivalent site.

In this notation system, the position vectors may be written as  $\mathbf{r} = \sum N_i \hat{\mathbf{e}}_i$  ( $i = 1$  for x-component, 2 for y-component and 3 for z-component).

The vectors  $\hat{\mathbf{e}}_i$  are the unit vector  $i, j$  and  $k$ . The position vector of a site in TCP system is, thus, given by

$$\mathbf{r} = (n_1 + t_{1jk}) \mathbf{i} + (n_2 + t_{2jk}) \mathbf{j} + \left(\frac{c}{a}\right)(n_3 + t_{3jk}) \mathbf{k}.$$

With these notations, the EFG may be written as

$$V_{zz} = \sum_{j=1}^3 Q_j b_j$$

Here  $Q_j$  are charges given in equations (2) and (3) with  $Q_j$  equal to  $Z_{\text{eff}}e$  for  $j=1$ ,  $Q_t$  for  $j=2$  and  $Q_e$  for  $j=3$ . The lattice sum is contained in  $b_j$ , where

$$b_j = \frac{e}{4\pi\epsilon_0 a^3} B_j$$

With

$$B_j = \sum_{n_3} \sum_{n_2} \sum_{n_1} \sum_{j_k=1}^{M_j} \frac{3N_3^2 - (N_1^2 + N_2^2 + N_3^2)}{(N_1^2 + N_2^2 + N_3^2)^{2.5}} \quad (6)$$

It may be seen that the lattice sums given by equation (6) depend only upon axial ratio ( $c/a$ ).

Lattice sum for evaluation of EFG poses problem in terms of convergence. Much care has been taken in this direction by using various lattice sum methods like plane wise summation, summation in spherical region, summation using Fourier transform and Parseval formula[11], and Euler-Meclaurin series[12, 13]. We have used here a less straining yet working method, the first. In plane wise summation procedure, we consider a particular plane normal to c-axis, the fourfold symmetry axis here, sum over all the sites and then do the same for the next plane, and so on. All these sums are added together to give the lattice sum.

The net EFG at nuclear site due to ionic and electronic sites can, thus, be calculated.

However, the nucleus that is put now in the crystal environment at the origin interacts with the field gradient splitting its energy levels that is strongly dependent on the degree of deviation of wave function from Free State. A correction to account for this is to multiply the distant sum by Sternheimer factor  $(1 - \gamma_{\infty})$  for ions and electrons [14]. Thus, we write for EFG ( $eq$ ) at nuclear site in crystalline environment as

$$eq = [Z_{\text{eff}} B_1 + Q_t B_2 + Q_e B_3] (1 - \gamma_{\infty}) \frac{e}{4\pi\epsilon_0 a^3} \quad (7)$$

The three dimensionless lattice sums  $B_j$  in the above equation are

independent of the lattice parameter  $a$ , and depend only on the axial ratio  $c/a$  of the crystals with interfacial angles  $90^\circ$ . The charges  $Q_j$  and anti-shielding factor are dependent on element in question.

### The numerical computation of the lattice sums for EFG

For numerical computations, co-ordinates of TCP lattice points and electronic sites within unit cell are obtained.

Table 1: Crystallo-physical co-ordinates used in TCP unit cell

Non-eq charges( $Q_j$ )	z-coordinates of the planes	Co-ordinates in units of $a$ , $a$ and $c$
$Z_{eff} e$	$0, c/2, -c/2$	$\{0\ 0\ 0\}$ $\{\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\} \{-\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\} \{-\frac{1}{2}\ -\frac{1}{2}\ \frac{1}{2}\} \{\frac{1}{2}\ -\frac{1}{2}\ \frac{1}{2}\}$ $\{\frac{1}{2}\ \frac{1}{2}\ -\frac{1}{2}\} \{-\frac{1}{2}\ \frac{1}{2}\ -\frac{1}{2}\} \{-\frac{1}{2}\ -\frac{1}{2}\ -\frac{1}{2}\}$
$Q_t$	$0, c/2, -c/2$	$\{0\ \frac{1}{2}\ 0\} \{-\frac{1}{2}\ 0\ 0\} \{0\ -\frac{1}{2}\ 0\} \{\frac{1}{2}\ 0\ 0\}$ $\{0\ \frac{1}{2}\ \frac{1}{2}\} \{-\frac{1}{2}\ 0\ \frac{1}{2}\} \{0\ -\frac{1}{2}\ \frac{1}{2}\} \{\frac{1}{2}\ 0\ \frac{1}{2}\}$ $\{0\ \frac{1}{2}\ -\frac{1}{2}\} \{-\frac{1}{2}\ 0\ -\frac{1}{2}\} \{0\ -\frac{1}{2}\ -\frac{1}{2}\}$
$Q_e$	$c/4, -c/4$	$\{\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}\} \{-\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}\} \{-\frac{1}{4}\ -\frac{1}{4}\ \frac{1}{4}\}$ $\{\frac{1}{4}\ -\frac{1}{4}\ \frac{1}{4}\}$ $\{\frac{1}{4}\ \frac{1}{4}\ -\frac{1}{4}\} \{-\frac{1}{4}\ \frac{1}{4}\ -\frac{1}{4}\} \{-\frac{1}{4}\ -\frac{1}{4}\ -\frac{1}{4}\}$

We prepared the Table 1 using body centered ion as origin of orthogonal axes with X-, Y- and Z-axes parallel to  $a$ -,  $b$ - and  $c$ -axes respectively. The lattice sums of equation (6) were evaluated for a large number of  $c/a$ -values and graphs were plotted.

The lattice sum over all the ions in  $z=0$  plane turns out to be -9.03316 for the standard axial ratio of 1.414 for which the charge shift parameter  $\delta = 0$ . This compares well with the corresponding value -9.03362 obtained by de Wette [11].

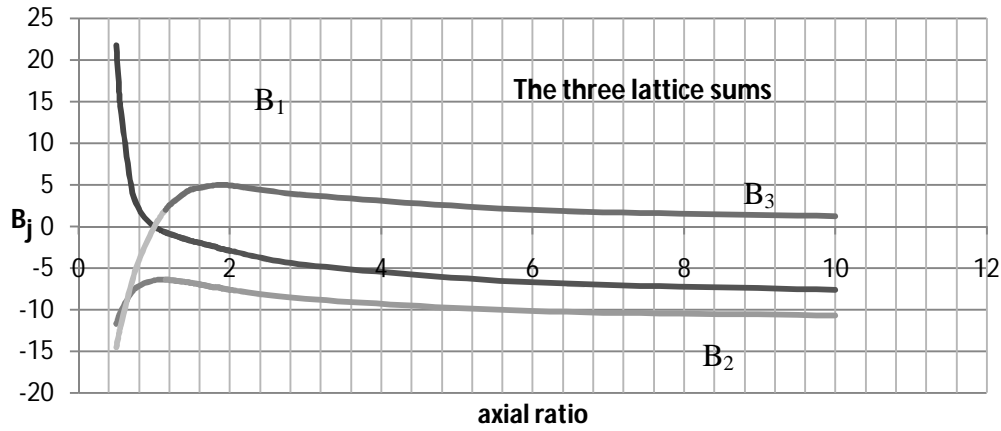


Fig. 3 : The three lattice sums and axial ratio

For the axial ratio equal to 1, the TCP lattice goes bcc for which case EFG along c-axis is expected to be zero due to cubic symmetry. For this case, our calculation of ionic sum,  $B_1$ , turns out to be 0.0001, and is encouraging up to three decimal places of magnitude. The total EFG turns out to be  $0.035 \cdot 10^{21} \text{Vm}^{-2}$ . This small deviation from zero may be attributed to some non-cubic degree in conduction electron packets as detected in the graphical treatment.

To see inside features, we plot these  $B_j$  against axial ratio and analyze. The plot indicates that ionic lattice sum ( $B_1$ ) and electronic lattice sum ( $B_3$ ) pass to zero for an axial equal to that of bcc crystal. The sum  $B_3$  shows peak at axial ratio 1.88 with a value +4.9855, and, thereafter, decrease slowly to meet abscissa. This is very interesting as TCP goes to bcc at  $c/a = 1$ . However, the sum  $B_2$  shows slight deviation from this behavior.

The sum  $B_2$  also tries to reach closer to zero near bcc axial ratio (axial ratio 1.1) but remains negative. The lattice of sites for this sum may be slightly non-cubic at the position of peak and suggest asymmetry in this sub-lattice.

### Result of EFG for Indium

Metallic Indium (In) crystallizes in a tetragonal close packed structure with lattice parameter  $a=3.253$  angstrom and  $c= 4.947$  angstrom at 300 K of temperature. The value of electric field gradient in Indium may be obtained using the lattice sums appearing in equation (6). It turns out to be  $1.50 \cdot 10^{21} \text{Vm}^{-2}$  for lattice parameter  $a=3.25\text{\AA}$  and the data for elastic constants, axial ratio (1.076) and Sternheimer factor  $\gamma_{\infty}$  used previously by Verma et al [10].

Table 2: EFG in nucleus of In metal

Sternheimer factor ( $1-\gamma_{\infty}$ )	EFG calculated ( $\times 10^{21} \text{ Vm}^{-2}$ )	EFG quoted in ref[10] ( $\times 10^{21} \text{ Vm}^{-2}$ )
24 (ion)	1.394	1.45
25 (mean)	1.452	
25.9(neutral atom)	1.504	

The experimental value quoted there, is  $1.45 \times 10^{21} \text{ Vm}^{-2}$ . However, in the above reference [10], the Sternheimer factor  $\gamma_{\infty}$  used is -24.9 which is for a neutral atom, and which, for ionized Indium in crystal, should be divided by 1.1 [15]. We effected this change, and the value of EFG turns out to be  $1.394 \times 10^{21} \text{ Vm}^{-2}$  (Table-2)

## Conclusion

The electric field gradient in tetragonal system of Indium is calculated successfully by charge shift model. The charge shift model for EFG in tetragonal system presents the crystal as composed of three lattices: one made of ions only, giving the lattice sum  $B_1$ , and two lattices made of two non-equivalent electronic charges, giving lattice sums  $B_2$  and  $B_3$ . The lattice of conduction electron packets lying in the ionic planes slightly lacks the point symmetry possessed by ionic crystal and introduces an extra EFG contribution to electronic electric field gradient.

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