ELECTRIC FIELD GRADIENT IN STANNUM-II

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Abstract

Electric field gradient at nuclear site in the lattice of tetragonal close packed (TCP) system of metallic stannum (Sn) at nuclear site are computed at several temperatures using a model developedonthe pattern similar to the charge shift model initiated for hexagonal close packed lattice. Numerical results are obtained using FORTRAN programs developed by us.

Keywords: Lattice sum,TCP lattice, electric field gradient, stannum, charge shift, nuclear site.

Introduction

Electric field gradient (EFG) is defined as spatial rate of variation in electric field intensity and is, thus, a nine component tensor defined ata space point. It isan important structural property of crystalline solids like metals and alloys through its well-known interaction with nuclear quadrupole moment. Local symmetry, co-ordination and valence of defects in solids, electronic and magnetic properties are extracted from quadrupole–field gradient relations.Several research articles appear in literature for its calculation using methods such as band structure, OPW[1],APW,tight binding, pseudopotential model [2], etc. Though these provide elegant theoretical footing, surely these pose formidable problems in terms of actual calculation of exact wavefunctions. The non-cubic ionic lattice and the electronic environment that is not spherically symmetric, produce EFG at a nuclear site, and are only approximately known. Despite numerous publications, the complete theory of EFG seems open. Such approaches as semi classical have gained momentum. Charge shift model of Bodenstedt [3] was initiated in this perspective for hexagonal close packed (hcp) *sp*-metal.Verma et al extended it to include transition metals of hcpsystem [4,5]. The validity region of the charge shift model was investigated [6]. The method was recently used to calculate cohesive energy[7,8,9,10]. We developed similar model for the tetragonal close packed crystals for the first time. Calculation for EFG in Indium agreed well[11].Here we have taken metallic stannum as our system(Sn-II) and used

a different approach to lattice sum as compared to previous work minimizing time and giving quick convergence.

Theory

Theelectric field gradient (*eq*) at nuclear site in crystalline materials plays a dominant role in nuclear quadrupole splitting, ΔE. For a nucleus in the state$\langle I, m_I |$,it **is** given by

$$\Delta E = eq\; eQ\; \frac{3m_I^2 - I(I+1)}{4I(I+1)}(1+\eta)^{1/2}$$

The asymmetry parameter η is set zero in tetragonal lattice by choosing the four fold symmetry axis, the c-axis, as the axis of quantization. The nuclear transition frequency in such a case may be given(in unit of MHz) by

$$\nu_{|m|\to|m|+1} = \frac{3(2|m|+1)}{4I(2I-1)}\frac{e^2}{h}Q$$

The experimental value of EFG is extracted from the measurement of the frequency and the quadrupole moment. It known that the experimental techniques are not free of error bars. Hence electronic contribution to EFG has always been open to question as ionic contribution comes from lattice summation and electronic one is obtained by a subtraction. In the model we are going to consider, both the ionic and the electronic EFG are calculable using lattice summations. We take up here the case of tetragonal close packed lattices.

Anideal unit cell of tetragonal close packed (tcp or bct) lattice is characterized by interfacial right angles, lattice parameters *a=b≠c,* and anaxial ratio (c/ a)equal to$\sqrt{2}$, that in actual crystals depends upon the particular motif and temperature.In our model, ions of tcpmetal are located at the four corners and the body center of the unit cell. Conduction electrons are assumed as tiny spheres located midway betweenthe ions forming the *first co-ordination cell* of the origin occupying ion. In this procedure, we get two non-equivalent electronic sites forming two non-equivalent planes perpendicular to the c-axis:*mixed plane*that is composed of ions andone type of conduction electron spheres,and*pure plane*that consists *purely*of the remaining type of conduction electron spheres. We determine the charge distribution as follows.

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 charge on a conduction electron sphere in the mixed planes is denoted by Q_t, and that in the pure plane by Q_e. 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,Q_e, isoccupying a total of eight sites in the unit cell, four above and four below the body-centered ion. The electrical neutrality for the unit cell, thus, gives us

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

To start with, a charge equal to negative of the ionic charge is equally distributed among the twelve electronic sites in the co-ordination cell. To realize actual axial

ratio, there is now affected a *shift* of charge from Q_t-sitesto Q_e-sites, parameterized by an algebraic quantityδ.

The charge transfer parameter δ is obtained by using the elasticity data and electrostatics of the unit cell on the following basis. The charges resulting after the shift produce an electrostatic*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 δ is expressed in terms of compliance co-efficient$S_{ij}$for tcpstructure as has been reported earlier by us [11]. We get

$$\delta = \frac{\frac{c}{a}-\sqrt{2}}{\sqrt{2}} \frac{54\,\varepsilon_0 a^4}{(Z\text{eff }e)^2(2S_{33}-S_{12}-S_{11})} \quad (2)$$

This,along with the neutrality Eq (1) of cell, is used to find the charges as:

$$Q_t = -\frac{1}{6}Z_{\text{eff}}e\,(1+2\delta) \quad (3)$$

$$Q_e = -\frac{1}{6}\,Z_{\text{eff}}e\,(1-\delta) \quad (4)$$

Thus, 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 Gradientusing the Nonequivalent Charges

A charge q at position $\boldsymbol{r}$relative to an ionic sitetaken as origin of co-ordinates in the crystal produces electric field intensity at the origin whose space rate of variation along c-axistaken as Z-axis is given by

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

Using thetcp lattice with a-axis and b-axis taken along X-axis and Y-axis respectively, and crystallo-physical co-ordinates in units of lattice parameters a, a, and c are denoted byreal number tripletsn_1, n_2andn_3.

Taking (000) at the interstitial ion in the unit cell,co-ordinates for the nonequivalent sites aregiven in Table1.

Using these, the position of a sitein any other unit cell may be written.

Notations:

$N_i = n_i + t_{ij_k}$ denotes the$i$-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. The multiplicity per unit cell for a j-th non-equivalent site is denoted byM_j. In this notation system, the position vectors may be written as

$\boldsymbol{r} = \sum N_i \boldsymbol{u}_i$ ($i =1$ for x-component, 2 for y-component and 3 for z-component). The vectors $\boldsymbol{u}_i$ are the unit vector $\boldsymbol{i}, \boldsymbol{j}$ and $\boldsymbol{k}$.The position vector of a site in TCP system is, thus, given by

$\boldsymbol{r} = (n_1 + t_{1j_k})\,\boldsymbol{i} + (n_2 + t_{2j_k})\,\boldsymbol{j} + (\frac{c}{a})\,(n_3 + t_{3j_k})\,\boldsymbol{k}.$

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 $Z_{eff}e$ 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).

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	$\{000\}$ $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}\{-\frac{1}{2}\frac{1}{2}\frac{1}{2}\}\{-\frac{1}{2}\ -\frac{1}{2}\frac{1}{2}\}\ \{\frac{1}{2}\ -\frac{1}{2}\frac{1}{2}\}$ $\{\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\}\{-\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\}\{-\frac{1}{2}\ -\frac{1}{2}\ -\frac{1}{2}\}\{\frac{1}{2}\ -\frac{1}{2}\ -\frac{1}{2}\}$
Q_t	0,c/2,-c/2	$\{0\ \ \frac{1}{2}\ \ 0\}\{-\frac{1}{2}\ \ 0\ \ 0\}\{0\ \ -\frac{1}{2}\ \ 0\}\{\frac{1}{2}\ \ 0\ \ 0\}$ $\{0\ \ \frac{1}{2}\frac{1}{2}\}\{-\frac{1}{2}\ \ 0\ \ \frac{1}{2}\}\{0\ \ -\frac{1}{2}\frac{1}{2}\}\{\frac{1}{2}\ \ 0\ \ \frac{1}{2}\}$ $\{0\ \ \frac{1}{2}\ -\frac{1}{2}\}\{-\frac{1}{2}\ \ 0\ -\frac{1}{2}\}\{0\ \ -\frac{1}{2}\ -\frac{1}{2}\}\{\frac{1}{2}\ \ 0\ -\frac{1}{2}\}$
Q_e	c/4,-c/4	$\{\frac{1}{4}\frac{1}{4}\frac{1}{4}\}\{-\frac{1}{4}\frac{1}{4}\frac{1}{4}\}\{-\frac{1}{4}\ -\frac{1}{4}\frac{1}{4}\}\{\frac{1}{4}\ -\frac{1}{4}\frac{1}{4}\}$ $\{\frac{1}{4}\frac{1}{4}\ -\frac{1}{4}\}\{-\frac{1}{4}\frac{1}{4}\ -\frac{1}{4}\}\{-\frac{1}{4}\ -\frac{1}{4}\ -\frac{1}{4}\}\{\frac{1}{4}\ -\frac{1}{4}\frac{1}{4}\}$

The coefficients B_j are obtained by the lattice summations consistent with *counting of sites,* implied in LHS of equation (1), and *convergence of the lattice sum.*
The notorious lattice sums for evaluation of EFG pose problem in terms of convergence as also encountered in problems of Lorentz field of dipoles, normal modes of oscillator lattice, and spin wave theory of ferromagnetism. 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 andParseval formula[12], and Euler-Meclaurin series[13,14]. We have used hereaplane wise summation procedure; we consider a particular plane normal to c-axis, that bears the fourfold symmetry 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. 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 wave function deviation from Free State. To account for this, one usesSternheimer'sfactor $(1 - \gamma_\infty)$ for ions and electrons [15]. Thus we use

$eq = (\sum_{j=1}^{3} Q_j B_j) (1 - \gamma_\infty) \frac{e}{4\pi\epsilon_0 a^3}$ (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°. The charges Q_j and anti-shielding factor [16] are dependent on element in question.

Result of EFG for Stannum

Stannum(II) crystallizes in a tetragonal close packed structure with lattice parameter a=3.81angstrom (=b) and c= 3.48 angstrom at 300 K of temperature. Its compliances [17]are

$$S_{11} = 16.3 \times 10^{-12} \text{m}^2\text{N}^{-1}$$
$$S_{12} = -3.6 \times 10^{-12} \text{m}^2\text{N}^{-1}$$
$$S_{33} = 14.1 \times 10^{-12} \text{m}^2\text{N}^{-1}$$

Using these in equation (2) for doubly ionized stannum, we get δ= - 0.5895. Equations (3) and (4) give electronic charges $Q_e = -0.5298\ e$ and $Q_t = -0.0597\ e$. The lattice sums are obtained using equation (6) and EFG using equation (7). We have used γ_∞ = -22.34 and get an EFG of $1.043 \times 10^{21} \text{Vm}^{-2}$.

Temperature dependence of EFG

Pure Snis D_{4h}^{19} structuredtcp(sp-band) metal. Itoffers time differential perturbed angular distribution (TDPAD) and Mössbauer measurement of EFG at different temperatures within a relative error of 0.3.We have taken data for c/a at various temperatures of Sn (II) and computed the lattice sums. Lattice sums clearly indicate the decrement of EFG with rise in temperature. This is consistent at least qualitatively with experiments and expectations of Nishiyama and Christiansen[18]. Following is the table of lattice sum for (c/a) at several temperatures in Sn (II).

Table2: **Temperature and computed EFG of Sn-II**

Temperature (K)	Axial ratio	Ionic lattice sum(B_1)	Electronic lattice sum B_2B_3	EFG (computed) ($\times 10^{21}$Vm^{-2})

33	0.54557	15.1412	-10.4836	-12.4122	4.646
106	0.54634	15.0504	-10.4651	-12.3794	4.590
148	0.54675	15.0019	-10.4553	-12.3611	4.558
166	0.54706	14.9653	-10.4478	-12.3477	4.536
178	0.54715	14.9558	-10.4459	- 12.3441	4.529
180	0.54721	14.9479	-10.4440	-12.3411	4.525
186	0.54733	14.9347	-10.4410	-12.3360	4.458
194	0.54746	14.9185	-10.4380	-12.3300	4.449
200	0.54745	14.9202	-10.4388	-12.3309	4.447
212	0.54768	14.8920	-10.4331	-12.3208	4.430
300	0.913	0.64218	-0.62183	-1.56437	1.043

These data may be plotted to directly view main features. Plots of EFG in units of 10^{21}V m^{-2}against the temperature in kelvin up to 212 K are as in the diagram.
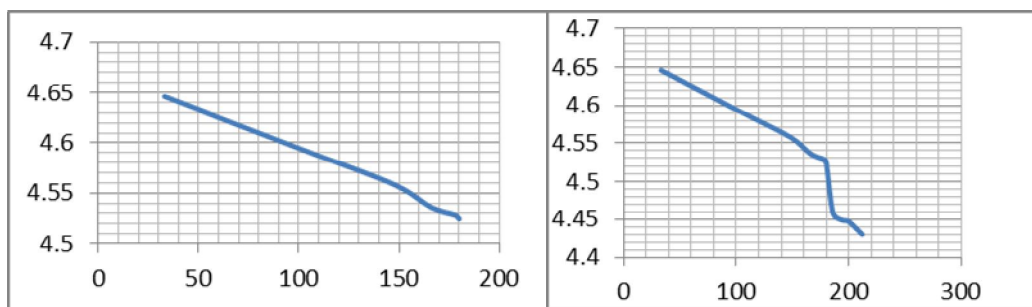

Figure 1 : Plot of *eq* (T)

The left plot uses data from 33 K to 178 K; deviations in curvature are observed after 148 K. These are more pronounced (right side plot) at higher temperatures.

Conclusion
The value of electric field gradient at nuclear site belonging to doubly ionized stannum in metallic environment of tcp lattice is calculated and temperature effect isobserved consistent with experimental behavior.

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