CHAPTER 4

Systematics of the Electric Field Gradient at Impurities in Non-cubic Metals

4.1 Introduction

The nuclear quadrupole interaction in non-cubic metals is a result of the presence of electric field gradient (EFG). How exactly the EFG originates is yet to be understood well. Experimental data on EFG reported in recent years [1,2] have enabled reaching some conclusions on the origin of EFGs. In this chapter we present a brief account of the earlier works on the calculation of EFG in metals with hexagonal close packed (hcp) structure. We also present a systematic behaviour exhibited by the electronic contribution \( \text{eq}^{el} \) to the EFG observed by us and a relation for calculating \( \text{eq}^{el} \)

4.2 The EFG Tensor

The electric field gradient tensor \( V_{ij} \) at the nuclear site due to a point charge \( Ze \) is given by,

\[
V_{ij} = Ze/r^5 [3x_i x_j - r^2 \delta_{ij}]
\]  

(4.1)
where \( r^2 = \sum_{i} x_i^2 \) and \( x_i \) are the cartesian coordinates of the charge. \( V_{ij} \) is a traceless tensor and hence only five of the nine components are independent. A unique axis system called the principal axis of the EFG tensor can be defined such that the off-diagonal elements vanish and the diagonal elements are so chosen as

\[
|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|
\]

The EFG tensor is usually described by only two independent parameters, \( V_{zz} = \text{eq} \) and the asymmetry parameter

\[
\eta = \frac{V_{\infty} - V_{yy}}{|V_{zz}|}
\]

With the above ordering \( \eta \) is restricted to \( 0 \leq \eta \leq 1 \).

The field gradient is mainly contributed by two sources [3]. They are (i) fixed positive ions of the crystal surrounding the Mössbauer atom, called the lattice contribution (eq_{\text{latt}}) and (ii) the non-cubic electron distribution in partially filled valence orbitals of the Mössbauer atom, called the electronic contribution (eq_{\text{el}}).

The resultant EFG is written as

\[
\text{eq} = (1-\gamma_{\infty}) \text{eq}_{\text{latt}} + \text{eq}_{\text{el}}
\]  

(4.2)

where \((1-\gamma_{\infty})\) is the Sternheimer antishielding factor. \( \text{eq}_{\text{latt}} \) can be calculated by the lattice sum method. For hcp
structure the value of $e_{\text{latt}}$ was calculated by Das and Pomerantz [4], in terms of $c/a$ ratio as

$$e_{\text{latt}} = \frac{Ze}{4\pi\varepsilon_0} a^3 \left[ 0.0085 - 4.3584 (c/a - 1.633) \right] \quad (4.3)$$

For calculating the value of $e_{\text{el}}$, a detailed knowledge of the wavefunctions of the conduction electrons in the impurity-host system is required. Hence, no successful method for calculating $e_{\text{el}}$ has emerged so far. $e_{\text{el}}$ would naturally depend upon the anisotropy of the Fermi surface. Watson et al., (ref.3) assumed that the spatial distribution of conduction electrons near the impurity should follow the symmetry of the host matrix, in computing $e_{\text{el}}$ for pure metals and ordered alloys.

4.3 Systematic Behaviour of the EFG in Materials

4.3.1 Correlation between $e_{\text{ion}}$ and $e_{\text{el}}$

Detailed study of the experimental results on the EFG in non-cubic metals by Raghavan et al., [5] resulted in the observation of a linear relationship between $e_{\text{ion}}$ and $e_{\text{el}}$ given by,

$$e_{\text{el}} = -K e_{\text{ion}} \quad (4.4)$$

where $e_{\text{ion}} = (1 - \chi^\infty) e_{\text{latt}}$ and $K$ lies between 2 and 5.
In systems for which both the magnitude and sign of EFG are known experimentally, \( e^{el} \) was determined from the total EFG and the theoretically calculated value of \( e^{ion} \) and a correlation, known at Raghavan's universal correlation was arrived at between the two contributions to the EFG. Some earlier data on non-cubic metals were represented graphically by Kaufmann and Vianden (ref.1) and the same is reproduced in section 3.3, in Fig.3.2. It can be seen from the plot that most of the data support the Raghavan's correlation.

However, recent experimental data in several systems show deviation from the correlation. It is remarkable that in all these cases either the host or the probe belongs to a transition element series. The experimental results for EFGs in several transition metals also show this trend of deviating from the correlation. Also considerable variation has been noticed in the same system, when done as a source experiment and as an absorber experiment. Ernst et al., [6] determined the value of \( K \) in equation \((4.4)\) for elements belonging to various groups in the periodic table and observed deviation from that proposed by the universal correlation. They found the value of \( K \) to be of the order of \(-2\) for the groups IIIb and IVb where the outermost d-shell is less than half filled, and \( K \sim +3 \) for groups VIIb, VIIIb
and IIb, where the d-shell is half-filled, more than half-filled or completely filled respectively. The ion correlation graph obtained by them is reproduced in section 3.3, in Fig.3.3. Deviation in sign and magnitude of the proportionality constant was also observed by Krusch and Forker [7] in several transition metals. These suggest that in transition element systems the electronic part of EFG may be dominated by contributions which do not arise in sp metals. In a theoretical study Piecuch and Janot [8,9] have shown that the magnitude of the local contribution to the EFG at transition element impurities should be proportional to the occupation of the d-states of the impurity, which depends upon the density of states of the host.

4.3.2 Probe Dependence of the EFG

The experimental data on the EFG in non-cubic metals show that the EFG is dependent on the probe in the form of valence difference between the impurity and the host. In addition to the host electronic contribution, a local electronic contribution may also be present due to the valence electrons of the probe atom which remain spatially correlated to the host atom. An expression which reveals the possible influence of impurity on the resulting EFG is the
ratio of this EFG at an impurity site $P$ in a host $H$ to the EFG in a pure system ($P=H$),

$$\frac{V_{zz}(P,H)}{V_{zz}(H,H)} \quad (4.5)$$

The EFG at an impurity site would, naturally, be sensitive to changes in the conduction electron wave functions around this site. A metal can be viewed as an electron gas and hence the mobile electrons will partially screen the impurity charge and in doing so redistribute themselves near the impurity site in such a way as to influence the field gradient. To show that this charge screening manifests in the EFG, a plot of set of ratios (4.5) for different probes $P$ in each matrix $H$ as a function of the difference in valence between the impurity and the host have been plotted by Leitz et al., [10]. Collins [11] also made similar plots and they bring out the fact that in sp metals the electronic part of the EFG is approximately proportional to the valence of the impurity atom, which in turn is related to the number of conduction electrons around the impurity in the lattice.

4.3.3 Temperature Dependence of EFG

The variation of quadrupole interaction frequency with temperature has been reported for various systems. In
majority of the systems reported earlier, consisting of pure systems and dilute impurity alloys, the EFG is found to obey a simple empirical relation proposed by Christiansen et al., [12],

\[ eq(T) = eq(0)(1 - BT^{3/2}) \]  

(4.8)

where \( T \) is the temperature of the system and \( B \) is a parameter which depends on the system. Various other expressions have also been suggested by Verma and Rao [13]. But recent data show marked deviation from the above relation. A detailed account of these and new observations are given in chapter 5.

4.4 Theoretical Calculation of Electric Field Gradient

4.4.1 The Lattice Contribution

The lattice contribution to the field gradient is

\[ eq^{\text{latt}} = \sum_{N} Z e^{2}(3 \cos^{2} \theta_{N} - 1)/r_{N}^{3} \]  

(4.7)

where \( r_{N} \) and \( \theta_{N} \) are the polar position coordinates of the \( N^{th} \) ion with respect to the EFG principal axis and summation has to be carried out over all the ions in the lattice except the one at the origin.
In calculating the lattice contribution to the EFG, the crystalline solid is regarded as an array of point ionic charges \(Ze\) situated at the lattice sites. The electrons are assumed to be uniformly distributed so that they do not contribute to the field gradient, and summation of the individual contribution of each point ion is done using equation (4.7). The direct lattice sum is found to be slowly converging. Simmons and Slichter [14] devised an alternative direct sum procedure by dividing the lattice into Wigner-Seitz polyhedra, each of which is electrically neutral consisting of a point positive ion and a uniform electron density. Other methods of summation were also suggested by Ewald [15] and Nijboer and deWette [16,17].

Assuming that for a given lattice structure the dependence of the lattice part of the EFG on lattice constants is fairly smooth, Das and Pomerants (ref.4) obtained an expression for hcp lattice which was earlier given in equation (4.3). Equation (4.3) is valid over a wide range of \(c/a\) as can be seen from Fig.3.1.

### 4.4.2 The Electronic Contribution

The electronics contribution to the EFG is written as,
\[ \text{eq}^{el} = -e \int \rho_e (\mathbf{r}) \left( 3 \cos^2 \theta - 1 \right) / r^3 \, dr \]  
(4.8)

where \( \rho_e (\mathbf{r}) \) is the conduction electron density the calculation of which is very difficult for want of exact wavefunctions [18]. \( \rho_e (\mathbf{r}) \) is, in general, given by,

\[ \rho_e (\mathbf{r}) = 2 \sum_{nk} \phi_n (\mathbf{r})^2 \]

where the summation over \( n \) refers to bands and that over \( \mathbf{k} \), to the states in each occupied band below the Fermi surface. The factor 2 is introduced to incorporate the two spin states of each electron. Putting the above expression for \( \rho_e (\mathbf{r}) \) in equation (4.8) the equation becomes,

\[ \text{eq}^{el} = -2e \sum_{nk} \left< \phi_n (\mathbf{r}) \right| \left( 3 \cos^2 \theta - 1 \right) / r^3 \left| \phi_n (\mathbf{r}) \right> \]  
(4.9)

\( \phi_n (\mathbf{r}) \) can be obtained using appropriate crystal potential and OPW method.

Thompson et al., [19] have given a first principles analysis of the contributions from the isotropic, anisotropic and anharmonic lattice vibrations to the lattice and electronic parts of the EFG. The temperature dependence of the EFG was accounted for by incorporating the temperature dependent pseudo-potential. It is found that the lattice contribution to the EFG is affected primarily by anisotropic phonons whereas the isotropic component almost

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entirely accounts for the variation of the electronic part of the EFG with temperature.

4.4.3 Pseudopotential Approach and Charge Screening Effects

The difficulties encountered in calculating the exact crystal potentials can be avoided by adopting the pseudopotential approach by constructing explicit electron wavefunctions which may be used to evaluate the EFGs. The basic method in these calculations is to find the electronic charge distortions which cause a new charge distribution. An impurity ion in a metal having an impurity - host valence difference results in a redistribution of the conduction electrons around the impurity atom to screen the effective charge differences.

A basically different model for EFG was suggested by Nishiyama et al. [20,21] based on the simultaneous treatment of electronic screening along with the lattice vibrations. The effect of conduction electrons is to shield the valence ions so that their effective charge becomes,

\[ Z e \delta (r - \mathbf{R}) - e \rho_{sc} (r - \mathbf{R}) \]

where \( \rho_{sc} \) is the screening charge distribution. The EFG at the origin due to a single ion at a position \( \mathbf{R} \) with respect
to the probe is given by,

\[ F_C(\mathbf{R}) = \int \delta(\mathbf{r} - \mathbf{R}) - e \rho_{\text{sc}}(\mathbf{r} - \mathbf{R})r^{-3} \times 2 \rho_2 \cos \theta_\mathbf{r} d^3r \]

The net EFG at the probe nucleus is evaluated by taking into account the contributions from all the screened ions which are antishielded by the probe ion. The time dependent EFG at a temperature \( T \) is given as

\[ \text{eq}(T, t) = (1 - \gamma_{\text{eff}}) \int \sum \delta(\mathbf{R} - \mathbf{R}_i(t)) F_C(\mathbf{R}) d^3R \]

where \( \gamma_{\text{eff}} \) is an enhancement factor and \( R_i(t) \) is the instantaneous position of the \( i \)th ion. Since the frequency of lattice vibrations is large compared to the quadrupole interaction frequency, we have to take the time average over the ionic vibrations which are regarded as uncorrelated and isotropic \[22\] and hence we get

\[ \text{eq}(T) = \text{eq}(t, T) = (1 - \gamma_{\text{eff}}) \int \sum \delta(\mathbf{R} - \mathbf{R}_i(t)) F_C(\mathbf{R}) d^3R \quad (4.11) \]

and the Fourier transform of this equation leads to

\[ \text{eq}(T) = (1 - \gamma_{\text{eff}}) \int S_0(\mathbf{k}) - 1 \exp[-(\mathbf{k} \cdot \mathbf{r})^2/2] F_C(\mathbf{k}) d^3k \quad (4.12) \]

where \( F_C(\mathbf{k}) \) is the Fourier transform of \( F_C(\mathbf{R}) \) and \( S_0(\mathbf{k}) \), the structure factor of the non-vibrating lattice. The influence
of the lattice vibrations on the EFG at the probe ion is described by the Debye-Waller factor with $\langle x^2 \rangle$ being the isotropic mean square displacement. By using a pseudopotential $V(\mathbf{r})$ derived from a Coulomb potential $V_C(R)$, screened by a free electron gas

$$V_C(R) = \frac{1}{2\pi^2} \int_0^\infty \frac{V_C(k)}{0\varepsilon(k)} \frac{\sin(kR)}{kR} k^2 dk,$$

equation (4.12) can be rewritten as

$$\text{eq}(T) = (1-\gamma_{\text{eff}}) \text{eq}_{\text{sc}}(T) \exp(-\frac{4k_f^2\langle u^2 \rangle}{3f}),$$

where $\text{eq}_{\text{sc}} = \sum_{i=1}^n 2p_2 (\cos \theta_i)$ over the screened ions, and $k_f$ is the Fermi radius. $\varepsilon(k)$ is the dielectric function [23].

This model due to Nishiyama et al. could not give results consistent with experimental data for the magnitude of the EFG but could explain, to some extent, the temperature dependence of the EFG.

4.4.4 Conduction Electron Charge Shift Model

The conduction electron charge shift model developed by Bodenstedt and Perscheid [24] provides a method of calculating the EFG in hcp metals in terms of the charge
shift of conduction electrons. The charge shift is related to the deviation of $c/a$ from the ideal value of $(8/3)^{1/2}$ for a hcp lattice. They assumed that the conduction electrons fill the space between ions in the lattice. For easiness of calculation the conduction electron distribution is separated into charge clouds, the centres of which are situated in between the nearest neighbour ions, as shown in Fig.4.1. Thus, each positive ion is surrounded by six negative charge clouds in its own hexagonal plane with three clouds above and three below. The charge clouds in hexagonal planes are on equivalent sites and must, therefore, bear the same charge $Q_{hp}$. The same argument holds for the charge clouds between the hexagonal planes. Let this charge be called $Q_{el}$. Since the lattice as a whole is neutral,

$$Q_{hp} + Q_{el} = -1/3 Z_{eff}$$

where $Z_{eff}$ is the effective charge of the ion. The conduction electron charge shift $\delta$ is defined by

$$Q_{hp} = -1/6 Z_{eff} (1+\delta) \quad \text{and}$$

$$Q_{el} = -1/6 Z_{eff} (1-\delta)$$

By using the approximation that each of the conduction
Fig. 4.1 Charge distribution in an hcp metal idealized for the Charge Shift Model (reproduced from ref. 24)
electron charge cloud and the ionic charge distribution has spherical symmetry, a lattice sum calculation can be done for each of them yielding

\[ e_{q} = e_{q}^{\text{ion}} - \frac{1}{6} e_{q}^{\text{hp}} (1+\delta) - \frac{1}{6} e_{q}^{\text{el}} (1-\delta) \]  

(4.14)

For a hexagonal close packed lattice the value of \( \delta \) is calculated using the formula,

\[ \delta = \frac{1}{Z_{\text{eff}}^{2}} \left( \frac{c/a - (8/3)^{1/2}}{36 \varepsilon_{0} a^{4}} \right) \left( \frac{1}{6} \left( -2S_{13} + S_{12} + S_{11} \right) + \frac{S_{33}}{3} - \frac{S_{13}}{13} \right) \]  

(4.15)

where \( S_{ik} \) are the elastic coefficients of the host lattice.

The value of \( e_{q}^{\text{total}} \) is calculated by multiplying \( e_{q} \) by Sternheimer correction factor \((1-\gamma)\), since all charges contributing to \( e_{q} \) are outside the probe ion sphere.

The effect of the vibrations of the probe nucleus is incorporated by calculating the average value of \( e_{q}(r) \), \( r \) representing the instantaneous position of the probe ion.

Then one gets

\[ e_{q}(r) = e_{q}^{0} + \frac{1}{2!} \frac{\delta^{2} e_{q}}{\delta x_3^2} \langle x_{\parallel}^2 \rangle (1-\varepsilon) \]

where \( \varepsilon = \frac{\langle x_{\perp}^2 \rangle}{\langle x_{\parallel}^2 \rangle} \) and \( \frac{\delta^{2} e_{q}}{\delta x_3^2} = \sum_{i} \frac{\delta e_{q}}{\delta x_3^2} \)

\[ \frac{\delta^{2} e_{q}}{\delta x_3^2} = \frac{1}{4\pi\varepsilon_{0}} \sum_{i} \frac{Q_{i}}{R_{i}^{2}} 24 P_{4} (\cos \theta_{i}) \text{ for the positive} \]

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ions and conduction electron charge clouds.

This model also enables us to estimate the probe dependence of the EFG for probe ions both with an ionic radius not larger than that of the lattice ion. To incorporate the probe dependence first the total lattice sum in pure metal $eq$ is determined and the EFG due to the twelve surrounding charge clouds carrying the effective charge of the probe $eq^P (Z_{eff}^p)$ is added. The resulting quantity is multiplied by $(1-\gamma_\infty)$ of the probe to get the total EFG.

$$eq_{\text{total}}^{\text{probe}} = (1-\gamma_\infty) \left[ eq - eq^P (Z_{eff}^p) + eq^P \right].$$

(4.16)

$eq^P$ is calculated using the formula

$$eq^P = \frac{1}{4\pi\varepsilon_0} \frac{Z_{eff}^p}{a^3} 4 \left( (1+\delta)-(1-\delta) \frac{1/2(c/a)^2}{1/3+1/4(c/a)^2} - \frac{1/3}{1/3+1/4(c/a)^2} \right)^{5/2}.$$

(4.17)

obtained using the lattice sum method.

All the models discussed above have only limited success in predicting the EFG in metals and explaining its systematic behaviour and temperature dependence. In this chapter we discuss a new systematic behaviour observed on the electronic contribution to the EFG and also propose a formula for calculating $eq^{el}$.
4.5 Observed Systematic Deviations of the EFG in Transition-Metal Hosts

As explained in section 4.3.1 recent experimental observations on the EFG in transition metals show considerable deviation from the universal correlation due to Raghavan et al. Investigations made on the basis of the available data [25] have revealed an interesting systematic behaviour exhibited by the electronic contribution to the EFG.

From the available data on the quadrupole interaction frequency, the EFG at the probe sites in these materials is calculated using the relation,

\[ e_{\text{eq}}^{\text{total}} = \nu \]  

(4.18)

where \( \nu \) is the quadrupole interaction frequency, \( e \) is the electronic charge and \( Q \) is the electric quadrupole moment. The value of \( e_{\text{eq}}^{\text{latt}} \) for the hcp hosts have been computed using the Das-Pomerantz formula (equation 4.3), knowing the lattice constants \( a \) and \( c \). The ionic part of the EFG is

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obtained by multiplying the value of $eq^{\text{latt}}$ by the factor $(1-\gamma_\omega)$ of the probe. From the above, the electronic part of the EFG is computed using the basic equation,

$$ eq^{\text{total}} = eq^{\text{ion}} + eq^{el} $$(4.19)

The values of $eq^{el}$ so computed, for various transition-metal hosts at different probe sites are given in Table 4.1, along with the electron configuration of the host material. The data are taken from ref. 25. From the above, the dependence of $eq^{el}$ on the number of d-electrons is investigated. It is observed that when the number of d-electrons is less than two, the sign of $eq^{el}$ is positive and when it is greater than two, the sign of $eq^{el}$ is negative. When the number of d-electrons is two, $eq^{el}$ is found to be either positive or negative, and in some cases like $^{111}\text{CdTl}$ it is even zero.

Also it is observed that there is a wide variation in the reported value of EFG for metals with two d-electrons. This means that even small changes in the environment caused during the preparation of the experimental sample can result in marked variation in the distribution of the two d-electrons which may be lying near the Fermi level of the host as virtually bound d-states. In such systems the EFG should be strongly temperature dependent and the sign of $eq^{el}$ can change from positive to negative. This has been
### Table 4.1: Electronic contribution to the EFG at different probes in various host materials

<table>
<thead>
<tr>
<th>Host Configuration</th>
<th>Electron Configuration</th>
<th>$^{57}$Fe</th>
<th>$^{99}$Ru</th>
<th>$^{111}$Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>eq</td>
<td>ion</td>
<td>el</td>
</tr>
<tr>
<td>Sc</td>
<td>$3d^14s^2$</td>
<td>±1.3</td>
<td>+0.22</td>
<td>1.08</td>
</tr>
<tr>
<td>Y</td>
<td>$4d^15s^2$</td>
<td>±1.51</td>
<td>+0.25</td>
<td>1.26</td>
</tr>
<tr>
<td>Ti</td>
<td>$3d^24s^2$</td>
<td>-0.49</td>
<td>+0.47</td>
<td>-0.96</td>
</tr>
<tr>
<td>Zr</td>
<td>$4d^25s^2$</td>
<td>±3.29</td>
<td>+0.31</td>
<td>2.98</td>
</tr>
<tr>
<td>Hf</td>
<td>$5d^26s^2$</td>
<td>±1.66</td>
<td>+0.42</td>
<td>1.24</td>
</tr>
<tr>
<td>Re</td>
<td>$5d^56s^2$</td>
<td>-0.49</td>
<td>+0.41</td>
<td>-0.90</td>
</tr>
<tr>
<td>Os</td>
<td>$5d^86s^2$</td>
<td>-0.75</td>
<td>+0.69</td>
<td>-1.44</td>
</tr>
<tr>
<td>Co</td>
<td>$3d^74s^2$</td>
<td>-0.16</td>
<td>+0.22</td>
<td>-0.38</td>
</tr>
<tr>
<td>Ru</td>
<td>$4d^75s^1$</td>
<td>-0.71</td>
<td>+0.67</td>
<td>-1.38</td>
</tr>
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(Contd...)
<table>
<thead>
<tr>
<th>Host Configuration</th>
<th>178(_{\text{Hf}})</th>
<th>181(_{\text{Ta}})</th>
<th>193(_{\text{Ir}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>eq(_{\text{exp}})</td>
<td>eq(_{\text{ion}})</td>
<td>eq(_{\text{el}})</td>
<td>eq(_{\text{exp}})</td>
</tr>
<tr>
<td>Sc 3d(^1)4s(^2)</td>
<td>±5.18</td>
<td>+1.31</td>
<td>3.85</td>
</tr>
<tr>
<td>Y 4d(^1)5s(^2)</td>
<td>±5.9</td>
<td>+1.52</td>
<td>4.38</td>
</tr>
<tr>
<td>Ti 3d(^2)4s(^2)</td>
<td>±5.88</td>
<td>+2.86</td>
<td>-8.54</td>
</tr>
<tr>
<td>Zr 4d(^2)5s(^2)</td>
<td>±4.61</td>
<td>+1.9</td>
<td>-6.51</td>
</tr>
<tr>
<td>Hf 5d(^2)6s(^2)</td>
<td>±5.83</td>
<td>+2.56</td>
<td>-8.39</td>
</tr>
<tr>
<td>Re 5d(^5)6s(^2)</td>
<td>±6.23</td>
<td>+2.52</td>
<td>-8.75</td>
</tr>
<tr>
<td>Os 5d(^6)6s(^2)</td>
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<td>+4.22</td>
<td>-10.63</td>
</tr>
<tr>
<td>Co 3d(^7)4s(^2)</td>
<td>±1.91</td>
<td>+0.95</td>
<td>-2.86</td>
</tr>
<tr>
<td>Ru 4d(^7)5s(^1)</td>
<td>±4.48</td>
<td>+4.57</td>
<td>-9.37</td>
</tr>
</tbody>
</table>

eq values in \(10^{17}\) V/cm\(^2\)
observed by Forker and Trzcinski \cite{28} experimentally for ruthenium as probe in scandium lattice.

The systematic behaviour exhibited by $\text{eq}^{\text{el}}$ is shown in Fig. 4.2. The systematics is used to predict the sign of $\text{eq}^{\text{el}}$ for transition metal systems for which sign of the total EFG is not known. The value of $\text{eq}^{\text{ion}}$ for various systems are calculated using the Das-Pomerantz formula and the value of $\text{eq}^{\text{el}}$ for such systems are computed assuming Raghavan's correlation to be valid for the systems. The sign of $\text{eq}^{\text{el}}$ is assigned from the systematics explained above. Then the total EFG is calculated using equation (4.19). The values of total EFG so predicted are given in Table 4.2.

4.6 Theoretical Calculation of the Electronic contribution to the Electric Field Gradient

As mentioned in section 4.2, so far no successful expression has emerged, which can be used to get a theoretical estimate of $\text{eq}^{\text{el}}$. The practice has been to subtract the ionic part of the EFG calculated using the Das-Pomerantz formula from

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Fig. 4.2 Systematic behaviour of eq^{el} with the number of d-electrons in the host. Open circles refer to data with unknown signs, their locations are predicted.
Table 4.2 Values of EFG ($10^{17}$ V/cm$^2$) in different systems predicted on the basis of the systematics reported in section 4.5.

<table>
<thead>
<tr>
<th>System</th>
<th>$e_{\mathrm{eq}}$</th>
<th>$e_{\mathrm{ion}}$</th>
<th>$e_{\mathrm{el}}$</th>
<th>$e_{\mathrm{tot}}$</th>
<th>System</th>
<th>$e_{\mathrm{eq}}$</th>
<th>$e_{\mathrm{ion}}$</th>
<th>$e_{\mathrm{el}}$</th>
<th>$e_{\mathrm{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSc</td>
<td>+0.215</td>
<td>+0.645</td>
<td>+0.86</td>
<td>CdRu</td>
<td>+2.0</td>
<td>-6.0</td>
<td>-4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeY</td>
<td>0.249</td>
<td>+0.747</td>
<td>+0.996</td>
<td>HfZr</td>
<td>+2.12</td>
<td>+6.36</td>
<td>+8.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeTi</td>
<td>+0.488</td>
<td>-1.404</td>
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the total EFG obtained experimentally, to get the value of \( \text{eq}^{el} \). In this section a simple relation for calculating \( \text{eq}^{el} \) in dilute alloys of transition metals is reported.

4.6.1 Expression for \( \text{eq}^{el} \)

Total electronic contribution to the EFG in metals is contributed by the electrons of the probe atoms in the host lattice and the electrons in the lattice. Hence it depends on the electron configuration of both the probe and the host atoms. In addition, it would also depend on the nature of the host lattice. The distribution of electrons in the probe atom will be controlled by the distribution of ions and electrons of the host in the lattice, which wholly depends on the type of the lattice and the electronic structure of both the probe and the host atoms. The electrons of the probe, therefore, tend to occupy low potential energy sites in the lattice. Hence it is assumed that the non-spherical distribution of electrons of a particular kind which produces EFG at the probe nucleus depends on the difference between the number of electrons of that kind in the probe and the host atoms and their distribution in the lattice.

The difference in size between the two atoms (probe and host) produces a strain in the lattice during implantation.
This results in a small distortion of the lattice from its natural structure. This also contributes to deviation from spherical symmetry, thereby resulting in an enhancement of the EFG.

In transition metals eq^{el} is due to the d-electrons, the s-electrons and the size difference between the probe and the host atoms. The d-electron contribution is written as

$$K_1(Z_{dh} - Z_{dp})$$

where $Z_{dh}$ and $Z_{dp}$ are the number of d-electrons in the host and the probe atoms respectively and $K_1$ is a constant. Taking the number of s-electrons in the host and the probe respectively as $Z_{sh}$ and $Z_{sp}$, the s-electron contribution to eq^{el} is written as

$$K_2(Z_{sh} - Z_{sp})$$

$K_2$ being a constant. The contribution due to distortion of the host lattice caused by the difference in size between host and probe atoms is taken

$$K_3(r_h - r_p)$$

where $r_h$ and $r_p$ being the radii of the host and the probe atoms respectively and $K_3$, a constant. The constants $K_1$, $K_2$ and $K_3$ are characteristic of the lattice. Thus the effective electronic contribution to the EFG is written as,

$$eq^{el} = K_1(Z_{dh} - Z_{dp}) + K_2(Z_{sh} - Z_{sp}) + K_3(r_h - r_p)$$

The values of $K_1$, $K_2$ and $K_3$ calculated from available experimental data are respectively 3.5, 10 and 0.5. eq^{el} for various systems have been calculated using equation (4.20)
and they are given in Table 4.3. The theoretical values so obtained are found to be in agreement with the experimental data available in the literature (ref. 25). The values are also in agreement with the systematic variation in the sign of eq\textsuperscript{el} with the number of d-electrons reported in section 4.5.

4.7 Discussion

The electric field gradient in materials is yet to be understood well. It is considered to be composed of two parts, viz, the electronic part and ionic part. We have the lattice sum method of calculating the ionic contribution, that too only in the case of hcp materials. In other non-cubic systems theoretical calculations of eq\textsuperscript{ion} are yet to be attempted. As regards eq\textsuperscript{el} it is more complicated and theoretical calculation can be done only if the wavefunctions of all the electrons contributing to eq\textsuperscript{el} are known. We have made an attempt to calculate the same using the relation reported (equation 4.20), taking into account the difference in s-electrons in the host and the probe, the difference in d-electrons in them and the difference in the atomic radii of the host and the probe. The size difference between the atoms should be a strong contributor to eq\textsuperscript{el}
Table 4.3  Values of $\text{eq}^\text{el}$ calculated using equation (4.20)

<table>
<thead>
<tr>
<th>System</th>
<th>$\text{eq}^\text{el}_{\text{cal}}$ (10$^{17}$ V/cm$^2$)</th>
<th>$\text{eq}^\text{el}_{\text{exp}}$ (10$^{17}$ V/cm$^2$)</th>
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<tr>
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because the size difference results in the reorientation of the electronic distribution in the lattice around the probe. In the above relation we come across constants $K_1$, $K_2$ and $K_3$, the exact theoretical evaluation of which is possible only by knowing the electronic wavefunctions.

The systematics that is proposed reveals the behaviour of d-electrons lying near the fermi surface and over the fermi surface. It is observed that the two d-electrons lying on the fermi surface behave in a peculiar way contributing to positive and negative values of $eq^{el}$ and in some cases like CdTi, no $eq^{el}$ at all. The distribution of these electrons should be highly dependent on the environment and also should be highly temperature dependent. In such systems, as the temperature changes the electron distribution also changes and at low temperatures localization of such electrons may take place at low potential sites, as in the case of superconductors and semiconductors, where there are only few free electrons, resulting in an increase in electronic contribution to the EFG. As the temperature increases this localization also increases and a stage will be reached when a large number of electrons are raised through a band gap to a conducting state, when localization effect decreases as the electron distribution becomes more and more uniform. This results in a decrease in $eq^{el}$ and
hence in the total EFG. This behaviour of electrons has been discussed in detail in chapter 5 and has been used to account for the observed temperature dependence of EFG in many systems. From this temperature dependence it is possible to estimate the superconducting band gap, which is also discussed in chapter 5.
References