CHAPTER II

A. HYPERFINE MAGNETIC FIELDS

The hyperfine fields (hff) in ferromagnetic metals were first observed by Khutsishvili [1]. The measurement of hff at nonmagnetic atoms in iron by Samoilov et al. [2] created theoretical and experimental interests in this field. Hanna et al. [3] discovered that the hff at iron atom in iron is opposite to the direction of the ionic spin moment. It increased the theoretical activity and as a result of which, the role of 'core polarization' came into light. Since then, the hff have been studied at different solute atoms in different types of ferromagnetic metals and alloys (dilute and concentrated). A systematic has emerged for the hff with respect to the atomic number of solute atoms, and the external parameters like concentration, temperature and pressure. It has increased the understanding about the origin of the hff and the electronic structure of the impurity in different ferromagnetic host matrices.

2.1 Origin:

There are three major contributions to the hff at any solute atom: (1) orbital hyperfine field, (2) spin-dipolar hyperfine field, and (3) Fermi contact hyperfine field.

2.1.1 The Orbital Hyperfine Field:

It is associated with the circular motion of the electron of the atom. The magnetic field due to the equivalent
current of this circular motion (in the classical picture) interacts with the nuclear magnetic moment. A quantum mechanical treatment \cite{4} gives the total field at the nucleus

\[ B_{\text{orb}} = - \frac{J_{\text{orb}}}{4\pi} + 2J_B \sum_{l} r_{l}^{-3} \]

for the electrons in the shells with quantum numbers \( n, l \) and the respective radial distributions \( \langle r_{l}^{-3} \rangle \). The non-\( s \)-electrons in unfilled shells give this type of contribution. In \( d \)-transition metals, the angular momentum of the outer unpaired \( d \)-electrons get quenched (expectation value of \( L \) is zero due to the crystalline fields), and this part becomes vanishingly small. However, there are evidences that in cobalt, the angular momentum of the outer \( d \)-electrons is not completely quenched. In the rare earths, the major contribution, comes from the partially filled \( f \)-shell electrons and is of the order of \( 10^6 \) to \( 10^7 \) Gauss. When embedded in metals the rare earth ions are defined by the quantum number \( J \) \cite{5}, because the \( f \)-shell electrons are shielded by the outer \( 5s \) and \( 5p \) closed shell electrons from the crystalline fields.

2.1.2. The Spin-dipolar Hyperfine Field

This field originates both from the spin moment at the ion itself and from the outer ionic moments. The spin-dipolar field is associated with the spin-angular momentum of the electron and is expressed by
This field contribution comes from the unfilled non-$s$-shells and also depends on the host symmetry. In the cubic symmetry the field contribution due to the outer ionic moments is zero. For other systems, this contribution is of the order of $10^4$ Gauss.

2.1.3 Fermi contact Hyperfine Field:

The $s$-electrons have finite spin density at the nucleus and contributes to the total hyperfine field at the nucleus through Fermi contact interaction. This contribution is known as Fermi contact field ($B_{\text{con}}$), and is expressed as

$$B_{\text{con}} = -\frac{\mu_e}{4\pi} \cdot \frac{\mu}{3} \cdot 2\mu_B \cdot \sum_{l} \langle \hat{S}_l \rangle \cdot <r^{-3}_1 <r^{-3}_sd>_1>$$

This field is of the order of $10^5$ Gauss and results from a single electron in an unfilled $s$-shell and from the conduction electrons which have $s$-character. The conduction electron polarization at the diamagnetic impurity in the ferromagnetic host produces hff through the Fermi contact interaction.

There is another important mechanism known as the core-polarization effect, by which $s$-electrons produce hff at the nucleus. The half-filled shell $s$-states ions, e.g. Mn$^{2+}$ (3$d^5$) and Eu$^{2+}$ (4$f^7$) etc., should have zero valued hff but experimentally large hyperfine fields have been
observed. In these ions the core polarization of the closed \( s \)-shells creates net \( s \)-spin density at the nucleus. In the first transition series, the parallel spins from the \( 1s \) and \( 2s \) shells are effectively attracted towards the \( 3d \) shell, leaving a net antiparallel spin density at the nucleus. The \( 4s \) shell, in contrast, has its parallel spin effectively attracted inwards and therefore produces a more dominant parallel spin density at the nucleus. The total \( s \)-electron spin density at the nucleus, caused by exchange polarization, is written as

\[
\rho_s(0) = \sum_{ns} \left( |\Psi_{ns}^{(0, \uparrow)}|^2 - |\Psi_{ns}^{(0, \downarrow)}|^2 \right)_{\downarrow}
\]

where the summation is overall the partially and completely filled \( ns \) shells. A small imbalance at the nuclear site between parallel and antiparallel spins, from filled shells, leads to a significant contribution to \( B_{hf} \) through the Fermi contact interaction, which can be large for the inner core electrons. An exhaustive discussion of the core polarization effect in the transition metals and the rare earths has been given by Watson and Freeman.

The total hyperfine field at the solute atoms, neglecting the 'local' field contributions, can be written as

\[
\vec{B}_{hf} = - \frac{\mu_B}{4\pi} \sum_{i} \frac{1}{\vec{r}_{i}} \left[ \vec{r}_{i} \cdot < \vec{r}_{i}^{-3} > - < \vec{r}_{i}^{-3} > \right] \vec{r}_{sd i} + \frac{\alpha_m}{3} \sum_{i} \sum_{ns} \left( |\Psi_{ns}^{(0, \uparrow)}|^2 - |\Psi_{ns}^{(0, \downarrow)}|^2 \right)_{\downarrow}
\]
where $\hbar/2m_e$ is the Bohr magneton.

In addition to this field, the nucleus will experience the externally applied field (if any) plus a local field. The measured effective field ($B_{\text{eff}}$) in a domain is represented as \[ B_{\text{eff}} = B^c_{\text{hf}} + B_{\text{L}} + B_{-\mathcal{M}}. \]

Here $B^c_{\text{hf}}$ and $B_{\text{L}}$ represent the corrected hyperfine field and the applied field respectively. $D$ is the demagnetising factor, and $B_{\text{L}}$, is the Lorentz field (\( \frac{4}{3} \pi M \)) plus the field arising from dipoles in the Lorentz cavity. In the literature $B^c_{\text{hf}} (= B^c_{\text{hf}} + B_{\text{L}})$ has been reported as the hyperfine field.

2.2 Systematics of Impurity Hyperfine Fields

A vast body of data is available for the impurity hf in the ferromagnetic metals Fe, Co, Ni and $d$-d. The hyperfine field trend with atomic number have been discussed by different authors \([7,9] \). The magnitudes of hf for a particular impurity (when the localized moment contributions are small) are approximately proportional to the magnetic moments of the respective host matrices \([7] \). The characteristics of the impurity hf with atomic number in ferromagnetic metals can be summarized as follows:

2.2.1 Transition Impurities:

The 3d, 4d and 5d dilute impurities in Fe, Co and Ni have negative fields (with the exception of Y$^{2+}$Fe$^2$).
The 3d-impurity hff in Fe is shown in fig. 2.1, where the dotted line corresponds to the contribution from conduction electron polarization. In the beginning of each d series, the field is negative and increases with increasing d-electrons and gets maximum value when the d-shell is approximately half filled. This systematic variation is explained in terms of the extra field due to the local moment through core polarization. There develops a negative d-moment on the impurities of the first half of the series and a positive d-moment on the impurities in the second half of the transition series. The trend in Gd metal is just reverse of that observed in Fe metal.

2.2.2 Rare Earth Impurities:

For the rare earth impurities in Fe, Ni and Co, with the increase in the number of electrons in the 4f shells, the hyperfine field changes from a negative value to a large positive value somewhere between Ce and Pr and then crosses zero again somewhere between Eu and Gd and reaches a large negative value.

2.2.3 sp Impurities:

The fields at 3p, 4p and 5p impurities are comparatively large than the hff seen by the corresponding 3d, 4d and 5d impurities in the respective hosts. The fields are negative for elements in the first half of the sp series and positive for elements in the second half (fig. 2.1).
Fig. 2.1 THE MAGNETIC HYPERFINE FIELDS IN Fe

(a) THE hff AT 3d IMPURITIES IN Fe

(b) THE hff AT 5p IMPURITIES IN Fe
There is another class of ferromagnetic materials, known as the Heusler alloys ($X_2YZ$ and $XYZ$) \cite{10}, which have been extensively used to study the systematics at $X$, $Y$, and $Z$-sites for different impurities. In general, $X$ site atom is from the 3d, 4d or 5d series with an almost full outer d shell, $Y$ atom is also the transition atom but with fewer outer d electrons than $X$, and $Z$ is a non-transition metal atom. Except in the case when $X$ is Co, $Y$ site carries whole of the magnetic moment ($4\mu_B$ on Mn). The 5sp impurities at $Z$ site have shown the same trend as that in Fe \cite{11}, showing the same mechanism of the conduction electron polarization. It has prompted many semi-empirical approaches to explain the systematic variation of the impurity hyperfine magnetic fields \cite{12}.

2.3 Theories:

The observed similarity in the trends of hff at impurities in the pure ferromagnetic metals and alloys ($Fe_3Si$ and Heusler alloys) indicates the similar mechanism(s) operating in all the systems to produce the hff at impurities. The origin of the hyperfine field in metals is much more complicated than in free atoms or ions. This is because of the non-localized nature of the outer electrons, whose polarization plays an important role but is not well understood. In the various theoretical models (treating generally non-magnetic impurity in the ferromagnetic host or dilute...
magnetic impurities in transition and noble metals) various mechanisms are envisaged for producing conduction electron spin polarization, e.g., s-d exchange interaction, s-d hybridization etc. The local electronic effects of the impurity are treated in two ways and there is a strong controversy over the local electronic effects. According to Stearns [13], it is the atomic volume of the impurity, which is the dominating factor in determining the hyperfine field, while Campbell and Vincze [14] have given importance to the valence of the impurity. Watson et al. [15] have discussed these claims and suggested that the atomic volume, valence, electronegativity and a number of other quantities are intimately related. These models have been discussed by Price et al. [11] and Stearns and Norbeck [12], and are briefly described below.

The very first approach is by Daniel and Friedel [16] to explain the dilute non-magnetic impurities in the ferromagnetic metals. This model is based on the concept of Friedel's scattering theory where the field is created due to the conduction electron polarization by the host moment. The host moment acts on the free electron like conduction band giving uniform conduction electron polarization proportional to the host d moment. The impurity is represented by the spin dependent square well potential perturbing the conduction electron polarization in the vicinity
of the impurity. The conduction electrons screen the charge difference ($\Delta z$) which is equal to the difference between the outer valence electrons of the impurity and the conduction electron per host atom. This charge difference determines the phase shift at the Fermi energy. After several approximations, it was shown that host conduction electron polarization is positive. The field may be positive or negative depending on the potential due to the screening charge ($\Delta z$) and the s-d exchange energy. This model could not explain CuFe results. Campbell [17] modified the Daniel-Friedel model by introducing s-d hybridization and showed that this mechanism leads to the negative spin polarization. He further explained the systematics of hff at transition and sp impurities in Fe and the impurity fields in Gd [18].

Caroli and Blandin proposed their virtual bound state model [19] and predicted accurately the sign and fairly the order of magnitude of hff at the Sn site in Pd$_2$MnSn and at Cu site in Cu$_2$MnAl. However, the sign of Sn fields in Cu$_2$MnSn and Ni$_2$MnSn are opposite to those of experimental observations. In this model the localized moments give rise to phase shifts in the scattered waves, which in turn through interference effects with the incoming waves leads to the spin polarization of the conduction band. Blandin and Campbell [20] extended this model by taking into account the pre-asymptotic correction in the expression,
describing conduction electron spin polarization by adding an extra phase shift term \( \phi \approx \pi/2 \). But this model is still far from the field values at higher \( \Delta z \) region.

Jena and Geldart [21] have shown that instead of independent ion approximation in the Blandin-Campbell model the interference between different ions should be considered. Both the models by Blandin and Campbell [19] and by Jena and Geldart [21] explain the sp-impurity hff qualitatively in the Heusler alloys but the Jena and Geldart model can be used for the concentrated magnetic materials.

Steams [22] has explained hff at impurities by assuming three types of contributions

\[
H_z = H_{cp} + H_{ce} + H_{v}
\]

where \( H_{cp} \) is due to the polarization of inner core 1s, 2s and 3s electrons by the magnetic electrons. \( H_{ce} \) is due to the polarization of the 4s-like conduction electrons by the moment on the transition metal atoms. All these terms give negative fields. \( H_{v} \) is the volume overlap term proportional to the impurity volume and gives positive field contribution to the nucleus. This model could not explain the temperature and pressure dependence of hff at nonmagnetic impurities in iron. Kolk [23] has considered the local lattice distortion effect instead of direct volume overlap term in the model of Steams.
Different from these charge perturbation theories and the volume-misfit theories, there is another purely phenomenological approach by Balabanov and Delyagin [24] based on the negative $H(r)$ and the positive $H^+(r)$ contributions to the resultant field. The negative contribution which is the local contribution, depends on $r$ to a greater degree than the positive contribution $H^+(r)$, defining collective contribution. After proper parameterization it explains the hff systematics in iron, nickel and cobalt and the pressure dependence of the hyperfine fields.

All the above theoretical approaches are based on certain approximations and are used to explain the systematics of the hff by using certain adjustable parameters. Recently, Kanamori et al. [25] have calculated the hff at the nonmagnetic impurities in iron and nickel from first principles. The results are in good agreement with the experimentally observed values. In this theory the perturbation due to the impurity is confined to a muffin-tin sphere centred at the nuclear position of the impurity and local density of s like states at the impurity atom is calculated by using realistic band calculations for the host matrix.

A rigorous test of various approaches is provided by the temperature and pressure dependence of the hff.
2.4 Temperature Dependence:

The temperature dependence of the hff, especially the knowledge whether it follows the host magnetization or not, have given the valuable information about the local electronic structure and the relative role of the various mechanisms producing the hff. A large deviation was observed in the variation of hff at Mn from the corresponding magnetization of Fe [26] at different temperatures. The anomalous temperature dependence has also been observed for other impurity-host combinations [27,28,29]. This anomalous behaviour occurs once in each α-series for each of the host ferromagnets and approximately in the middle of the temperature range (T/Tc).

Jaccarino et al. [30] proposed the molecular field model to explain the MnFe results. He assumed weaker coupling between the impurity-host moments than that between the host-host moments. A good fit could not be obtained in other cases in terms of the variable parameter \( g \), the relative reduction in the exchange interaction between the host-host moments. Also this model does not consider the effect of the conduction electron polarization at the impurity. Loo [31] extended this model by adding another term taking into account the conduction electron polarization. But the various parameters, used to get the experimental fit, have no physical base and the magnetic moment values
assumed in this model did not agree with the neutron diffraction data.

Campbell [32] following the Friedel scattering theory and based on the observation of the peak in the residual resistivity measurements, explained and predicted these anomalies by his critical screening charge theory. Although he made ad hoc assumption to define the splitting of the virtual bound state at the Fermi level, even it could signify the importance of the charge screening of the impurity and hence the anomalous behaviour due to the special electronic structure around the impurity. This view is supported by the pressure dependence measurements [33].

The anomalous behaviour in the temperature dependence of hff have been observed for sp impurities in ferromagnets [29,34]. There have been various attempts to explain these deviations in terms of the local demagnetization effect [35,36], but the pronounced deviations observed in case of SnCo, AsCo, GeCo, etc., could not be explained on this basis and there appears a trend that such anomalous behaviour is observed for the impurities in the vicinity of the zero cross-over transition (with respect to $\Delta z$), e.g. Ge (in 4sp series) and Sn (in 5sp series). Raghavan et al. [34] have shown that the temperature dependence of hff at 4sp impurity in the fcc phase of Co is similar to that observed in Fe and Ni for the same impurity, but in the hcp phase of Co there is a substantial temperature dependence.
The contribution due to the hcp phase is negative and sensitive to the distance and symmetry of the neighbouring magnetic host atoms from a nonmagnetic impurity atom. This lattice part has given a large pressure dependence in the hcp Co structure [37]. Reid et al. [33] have shown the importance of the constant volume correction to get the explicit temperature dependence of hff. The hff at constant volume seems to follow the host magnetization. Lindgren and Vijay [38] have shown that in case of CdFe and GdCd, the deviation is opposite to that expected from the volume expansion.

2.5 Pressure Dependence:

Now enough data of the pressure derivative of hff exists to test the predictions of the different models and it has also helped to understand the temperature dependence of hyperfine fields [33,38,39]. Some characteristics of the pressure dependence of the hff are as follows:

1. For the non-magnetic impurities, the quantity \( \frac{1}{B_{hf}} \cdot \frac{d\ln B_{hf}}{dp} \) seems to be positive if \( B_{hf} < 0 \) and negative if \( B_{hf} > 0 \). It indicates a decrease in positive contribution or an increase in negative contribution to the total hyperfine field.

2. The explicit pressure derivative (the effect of the host magnetization subtracted from the experimental pressure derivative) seems to be about the same and negative
for different 5 sp elements in Fe, Co and Ni (with the exception of CdFe) and is independent of the value of $B_{hf}(0)$ [38].

3. The sign of $\frac{dB_{hf}(0)}{d\rho}$ is negative for a number of impurities in different ferromagnetic hosts with exceptions for Al, Cu and Au dilute impurities in Fe [33, 40, 41].

The theories based on the Daniel-Friedel scattering theory [4, 19, 21] do not make it possible to know the pressure effect directly due to the unknown effect of the pressure on the screening charge of the impurity and on other assumed parameters. Similarly, Steams model [12] does not explain pressure dependence explicitly. The semi-empirical approaches by Dolgogin [42] (based on the Balabonov model) and Kolk [23], predicting the negative $\frac{dB_{hf}}{d\rho}$, came out to be wrong in case of CdFe, AlFe and AuFe. Janak [43] has done a full-consistent band calculation for the host magnetization, the hff and their derivatives for Fe and Ni. Their results are in good agreement with the experimental values. Kanamori et al. [25] have indicated that it is possible to calculate the pressure dependencies for the nonmagnetic impurities in Fe, Co and Ni with their model, and qualitatively both negative and positive values can be expected for $\frac{dB_{hf}}{d\rho}$, depending on the local electronic structure at the impurity atom and its variation with the local volume. The value of $\frac{dlnB_{hf}}{dlnV}$ can be of the order of one.
In the light of above theoretical approaches it is clear that the complete impurity-host band calculations are required to understand the role of the various sources and the mechanism in producing the hff at the nucleus.
B. ELECTRIC FIELD GRADIENTS

The hyperfine magnetic field at the nucleus is sensitive to the outer electronic spin distributions, while the EFG (electric field gradient) at the nucleus gives the information about the charge distribution around the nucleus. The electric quadrupole interaction, between the nuclear quadrupole moment and the EFG at the nucleus, have been treated mathematically by Frauenfelder and Steffen [44] and Steffen and Alder [46]. In metals the EFG at the nucleus arises due to the outer electronic charges (both inside and outside the ion). It is difficult to know the mechanism and the relative contributions from different sources quantitatively, as it requires the many-body treatment of both the bound and free charges simultaneously. The impurity other than the host atoms again makes the problem complex. These fields may be induced due to the defects associated with the radiation damage or impurities in the cubic metals or alloys. Here only the noncubic metals (especially with hop structure) are discussed. Inspite of the complex behaviour, a vast data is available for the EFG in noncubic metals [46], which have helped to understand the nature of EFGs qualitatively. The various theoretical approaches and the experimental informations concerning the EFG in different impurity-host systems with respect to the external parameters (like concentration, temperature and pressure) have been reviewed by Das [47], Raghavan [48]
and Kaufmann and Vianden [49]. A brief account of the efg systematics, relevant to the present work, is given below:

2.6 Origin:

In noncubic metals the efg can be thought of arising from the lattice ions \( q_{\text{latt}} \), conduction electrons \( q_{\text{con.}} \) and the localized shell electrons \( q_{\text{loc.}} \). Instead of considering all these sources self consistently, the total efg \([50]\) is conventionally defined as

\[
q = q_{\text{ext}} (1 - \gamma_{\infty}) + q_{\text{loc.}} (1 - R)
\]

where \( q_{\text{ext}} = q_{\text{latt}} + q_{\text{con}} \).

The \( \gamma_{\infty} \) and \( R \) are the Sternheimer factors \([51]\) having values \(-7 < \gamma_{\infty} < -100\) and \(|R| < 0.2\) respectively. The Sternheimer factors are considered for the deformation induced in the closed shells of the ion due to the external and the localized charge (e.g. 4f shell electrons in rare earths) distributions. The calculated Sternheimer factors, using the relativistic Hartree-Fock-Slater theory, have been tabulated by Peick et al. \([52]\).

Early theoretical attempts were to calculate the lattice contribution and the conduction electron contribution separately and then multiply with the corresponding Sternheimer factors before summing up to compare with the experimental values. In the light of the recent experimental observations (universal correlation), a selfconsistent and
the simultaneous treatment is required for all the sources. The efg representation by eq.(2.1) may be true for the insulators but for the metals it is not adequate [48].

The lattice contribution is obtained by using the point-ion lattice summation method [53,54], by assuming spherical ion cores at the lattice sites with uniform background of electrons (to ensure charge neutrality) and performing the summation

$$q_{latt} = \sum_i e_n \sum_j \frac{(3z_{ij}^2 - r_{ij}^2)}{r_{ij}^5}.$$  

Das et al. [53] obtained the following expression for the hcp metals.

$$q_{latt} = \frac{a}{a^3} \left[0.0065 - 4.3584 \left(\frac{c}{a} - 1.633\right)\right]$$  (2.2)

where a and c are lattice constants. This lattice contribution vanishes for an ideal hcp structure ($c/a = 1.633$).

To calculate the electronic contribution $q_{con}$, there have been mainly two approaches; one is model-potential approach [55], and another one is based on the OPW and tight binding methods [89]. Both are discussed in the succeeding section of 'theories'. Until the sign of the efg was not available, only the magnitude was used to compare with the experimental values. A comparison of the lattice contribution ($1 - V_0$) $q_{latt}$ with the experimental values [53] brought into existence a substantial contribution from the conduction electrons. Watson et al. [56] discussed the details.
of the different contributions to $q_{\text{loc}}$. The importance of the electronic contribution was reinforced later on by the measurement of sign, temperature dependence and pressure dependence of efg. We will discuss below the significance of these studies and their theoretical understanding.

2.7 Systematics of Electric Field Gradients

Experimental investigations of efg in different impurity-host systems have revealed broadly the following three types of characteristics [49].

2.7.1 Correlation Between the Lattice and the Electronic Contribution:

The determination of the sign of efg, yielded approximate proportionality between the calculated lattice contribution $(1-\gamma_{\infty})q_{\text{latt}}$ and the electronic contribution (the difference between the experimental efg value and the calculated lattice contribution) [57]. Raghavan et al. [57] plotted these values for the non-rare earth systems, and proposed a relation, known as 'universal correlation',

$$q = q_{\text{latt}} (1-\gamma_{\infty}) (1-k) \quad K \approx 2 \text{ to } 4 . \quad (2.3)$$

For most of impurity-host systems, the sign of both the contributions is opposite to each other and the correlation curve passes through the II.. and IV quadrants. Although it is an approximate relationship, but it shows that the conduction electrons of the host adjust around the impurity atom according to the deformation of its shells, defined by
the Sternheimer factor. The deviations from this universal curve are obvious; as it involves the simplified picture of the lattice contribution (assuming integral charge on ion, \( z_e \)), and the anti-shielding factor \( Y_{\infty} \) for free atoms. In some cases the specific electronic structure (e.g. density of states at the Fermi level \( \epsilon_F \)) connected with impurity and host systems may also cause the deviation. Generally, the efg in hosts of groups IIB, VIIB, and VIIIB follow the Raghavan's correlation. Ernst [59] found that there exists an additional branch in the first quadrant where both the contributions have same sign for the host elements in groups IIB and IVB of the periodic table. Some of the impurity-host efg do not follow any of the above correlation, e.g. CdTi and CdHf [60].

Another probe related characteristic effecting the correlation between the ionic and the electronic contribution is the valence. Leitz [61] observed the increasing trend of the efg in sp-metals with the effective charge of impurity. Collins [62] plotted the efg in sp metals with respect to the number of conduction electrons and found the proportional variation.

2.7.2 Temperature Dependence:

The temperature dependence studies of the efg in metals have shown the strong dependence, unexplainable on the basis of the thermal expansion of the lattice (calculated
from the eq. 2.2). In analogy with the temperature dependence of the efg in the ionic and molecular solids \cite{63}, one could think of the effect of lattice vibrations here also. Christiansen et al. \cite{64} discovered the $T^{3/2}$ dependence of the efg, and for the investigated sp host metals, described the temperature dependence as
\[ q(t) = q(0) (1-BT^{3/2}) . \]

They proposed the quadrupole-quadrupole coupling model to reproduce the $T^{3/2}$ dependence through the collective excitations of the spin system. The parameter $B$, defining the slope of the temperature dependence, was found in later experiments to depend on both the host and the impurity. However, the predictions of the quadrupole-quadrupole coupling model are not followed for the impurity Cd$^{111}$ in Hg \cite{65}. At present, the thermal lattice vibrations are responsible for the $T^{3/2}$ dependence and the local vibration modes at the specific impurity for the strength (slope) of the temperature dependence. However, systematic deviations from the $T^{3/2}$ temperature dependence have been observed for several impurity-host systems, e.g., FeBe \cite{66} and Ta in rare earth metals \cite{67}. In FeBe system, a quadratic dependence is observed at low temperatures, but at higher temperatures it shows the linear dependence. In rare earths, the temperature dependence appears to be better described by the linear dependence. It is difficult to explain this linear dependence.
only on the basis of the crystal-field induced quadrupolar distortion of rare-earth ions [68]. These exceptions involving transition/or rare-earth metal hosts or impurities, indicate the significance of the density of states at the Fermi level for the host and the local electronic structure of the impurity.

2.7.3 Pressure Dependence:

The hydrostatic and the uniaxial pressure dependence experiments have been carried out to study the dependence of the efg on the average conduction electron density and the crystal structure [69]. The efg varies linearly with pressure in most of the systems and depends on the unit cell volume (V) as
\[ q \propto V^{-\alpha}, \quad \alpha \approx 3 \text{ to } 6 \]

while from the point-ion lattice sum model, it should be proportional to \( V^{-1} \) for the isotropic reduction of the volume. Such a strong pressure dependence can arise due to the conduction electron charge distribution. The combined uniaxial and the hydrostatic pressure measurements [70] has shown the linear proportionality between the efg and the deviation of c/a from the ideal close packing value (c/a)\(_{0}\). The value of (c/a)\(_{0}\) so obtained for TaHf is 1.78. There are evidences that the efg vanishes at the value of c/a=1.633 for hcp systems. A linear extrapolation approximation may
be responsible for this difference in $(c/a)_0$ value. The logarithmic derivatives (defined in the Oh, III), $(\delta \ln q / \delta p)_T$ and $(\delta \ln a / \delta t)_P$ are used to express the pressure dependence and the explicit temperature dependence of the efg respectively. In this way the knowledge of the sign of efg and the nuclear quadrupole moment is not required. The observed pressure derivatives $(\delta \ln q / \delta p)$ lie in the range from $10^{-3}$ to $10^{-2}$ per k bar [69] and have positive value except for the Cd [71] and Zn [72] metals, which may be due to the highly elongated unit cell of Zn and Cd. The magnitude of the pressure derivative is the same for all the systems studied except few exceptions (reflecting the specific impurity-host electronic structure). The explicit temperature dependence of the efg is found stronger in sp metals [71,73] than in transition metals [73,70] and this behaviour may be attributed to the thermally induced repopulation of conduction electron states. It unambiguously shows the role of conduction or localized electrons. The lattice vibrations also affect the volume dependence through the lattice volume. A dynamic-Hartree-screened lattice sum approach predicts more closely the charge of the pressure derivative at different temperatures [74].

Whereas the above efg systematics have shown some common features, there were some deviations for the host metals which have either the higher d-spin density at the
surface or the well localized 4f-electrons. Another ant observation is that the antishielding factor e ionic contribution is reflected in the electronic bution also. These observations require the theoretical ent of the conduction electrons with respect to the and structure and the impurity electronic structure. ent, the true non-transition metals are considered a theoretical treatment of the efg. Some of the principle based and the phenomenological theoretical ches are discussed below.

Theories:

As pointed out earlier, the experimentally observed lue was more than the ionic contribution, obtained he point ion lattice sum calculations [53]. This ence is due to the conduction electron charge distr and is a major contribution to the efg. Very few tical calculations are available using the first ple and the problem lies in the fact that one is ed to know the wavefunctions for electrons throughout tire occupied region of k-space. One of the app is due to Das and coworkers using the first principle ation, where electronic contribution is obtained by ing the sum of efg from the conduction electrons of occupied energy band;

$$e_{\text{eq,el}} = e \int f(r) \left(3 \cos^2 \theta - 1\right)/r^3 \, dr.$$
\[ \rho(\mathbf{r}) \] is the total conduction electron charge at \( \mathbf{r} \).

\[ \rho(\mathbf{r}) = 2 \sum_{\mathbf{k}, \alpha} |\psi_{\mathbf{k} \alpha}(\mathbf{r})|^2. \]

Summation is over the occupied states \( \mathbf{k} \) and the \( \alpha \) is due to the electron spin (a state is occupied by \( \alpha \) electrons with spin up and down).

Hygh and Das [75] calculated the efg for antimony, noting that all the bands bounded by a Fermi surface are occupied. By using the tight-binding Wannier functions, obtained from the orthogonalized atomic orbitals (OPW), a method of summing contributions over all of \( \mathbf{k} \) space was satisfied. Their results agreed with the experimentally deduced values [76], but in real metals one cannot assume the bands as fully occupied. Mohapatra et al. [77] and it al. [78] have used the OPW functions in tight approximation to calculate the efg in Be and Mg respectively. This approach could not be followed in other cases where the real crystal potentials are not available. In Zn and Cd metals, Mohapatra et al. [79] used the potentials and explained the sign, the magnitude and pressure dependence (even neglecting the effect of \( d \) vibrations) of the efg. In the recent calculations Das et al. have taken more realistic shielding effects
e electronic contribution together with pseudopotentials fine their predictions and to explain the temperature dependence in Cd and Zn. But their results of the temperature dependence are not in good agreement. Jena [81] introduced electron-phonon interaction in the QPW approach and included the temperature dependence.

Another theoretical approach have been to use the ical pseudopotential to each ion and taking the effective conduction electrons through the screening response is potential. The efg at the nucleus is obtained by the contribution of each screened ion potential. In an approach the explicit use of the electron wave-ion is avoided. The anti-shielding factor is taken into account as the sources producing the efg are outside the origin. Sholl [82] used this approach for In. In these calculations another factor \( \alpha \) (effective relaxation) is introduced, taking into account the fact that the anti-shielding factor for the neutral ion in the metal is different from the anti-shielding factor \( \gamma_{\infty} \) for atoms. This implies that the screening charge around the origin is distorted and contributes to efg.

Following the above approach Mishiyama et al. [83], a phenomenological model, explained the \( T^{3/2} \) temperature dependence and the pressure dependence of the efg. He treated
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taneously the electronic screening of the ions along lattice vibration s, assuming that screening charge...
electron charge shift model. They have assumed conduction electrons concentrated primarily at the faces of the Wigner-Seitz polyhedra and calculated their contribution to the total efg by the point-charge summation method. This model not only provides the way to calculate the zero order efg, but it can work as basis to understand the reverse sign relationship between the ionic and the electronic contributions to the efg.

All the above approaches have been limited only to pure non-transition metals, where the localized electron states are assumed to be vanishingly small. In the case of transition metals it is not true, as their d-electron states are at the Fermi level. There are experimental evidences on the importance of these states in affecting the efg, but definite relationship is established till now. Watson et al. treated the effect of electronic states in the vicinity of Fermi level, in the tight-binding APW (Augmented Plane Wave) approximation. They concluded that redistribution of the electronic states of the various 7 symmetry, under the effect of the noncubic crystal lattice contribution, at the Fermi level will cause extra field, proportional to the density of these states at the Fermi level. Fiscus and Janot reconsidered model of Watson et al. and got an extra factor (density-of-
states factor) for the electronic Coulomb and exchange interactions. This factor, in a first approximation, is proportional to the density of d-electron states at the Fermi level but is not directly proportional to the lattice field gradient. Their predicted values of the sign and the magnitude are in poor agreement with the available measurements in the pure hcp transition metals. They have predicted the correct sign in Hf metal but the wrong sign in case of Re. The predictions about the temperature dependence in the pure 5d-, 4d- and 5d- metals (hcp) cannot be justified until the temperature dependence measurements are carried out in these metals.

It is clear from the present status of the theoretical approaches that there is a considerable progress to understand the efg in the pure hcp normal metals quantitatively by both the first-principle based formulations and the sophisticated charge-screening formulations. But in case of pure transition metals the theory is still in the beginning even to understand the efg systematics qualitatively. The progress in understanding the pure systems can be to understand the efg in the impurity-host systems quantitatively.
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