CHAPTER 3
TRANSITION METAL MODEL POTENTIAL THEORY FOR EFG IN DILUTE ALLOYS OF COPPER

The problem of impurity in metals involves two aspects: a precise description of the electronic structure of the host metal and the self-consistent solution of the scattering problem including a Hamiltonian for the host metal and the impurity atom. Two limiting solutions in the free electron and tight-binding approximations for the host metal have been extensively discussed (Friedel 1958, Friedel and Guinier 1963). d-band metals have often been described within the tight-binding limit using a phenomenological impurity potential which is determined self-consistently (Friedel 1967). Da Silva et al. (1971a,b) discussed the pseudopotential approach for simple, noble and transition metal dilute alloys. The explicit calculations of this approach are still awaited.

Kohn and Vosko (1960) developed the general theory for scattering of Bloch electrons from an impurity to calculate EFG as discussed in chapter 2. However, in the final calculations, these authors replace the Bloch functions by single orthogonalized plane wave (OPW) functions to include the core structure of the host metal, therefore their results remain valid only for simple metals. In transition metals the core structure is different from simple metals. The separation between core and conduction electrons is not clear and the conduction electrons have both the s- and d-characters. Although the problem of how...
to deal with the core and conduction electrons in transition metals is characteristically involved. Lots of data exist on impurities in transition metals and this encouraged us to utilize the model potential theory of transition metals (Animalu 1973) to study the perturbed charge distribution in a transition metal due to an impurity and to utilize it to evaluate EFG and $\eta$.

The plan of this chapter is as follows: Shaw and Harrison (1967) model wavefunction transformation is used in section 3.1 to evaluate the excess charge density and its space variation. The specific results are presented for CuZn and CuSn alloys. The formalism of section 3.1 is used in section 3.2 to evaluate the valence effect contribution to EFG and $\eta$. One contribution is found due to free electron part and other due to depletion hole part of the excess charge density. The size effect contribution is added in the same manner as in chapter 2. The calculations and results for Cu alloys are presented in section 3.3 and these are discussed in section 3.4.

3.1 The Excess Charge Density and its Space Variation

Shaw and Harrison showed that the Hartree wave equation for the perfect crystal can be transformed into a model wave equation

$$\left\{ -\left(\frac{\hbar^2}{2m}\right) \nabla_k^2 + \psi(E_k) \right\} |\chi_k\rangle = E_k |\chi_k\rangle, \quad (3.1)$$

where $|\chi_k\rangle$ is the model wave function and $\psi(E_k)$ is the non-local model potential operator defined as
\( w(E) = v - \sum L_i A_i(E) |1\rangle \langle 1| \). \hspace{1cm} (3.2)

The two terms on the right hand side are diagonal and non-diagonal respectively in \( r \) representation. The second term is known as the non-local part of the model potential. \( A_i(E) \) are the potential well depth corresponding to state \( |1\rangle \) and energy \( E \). \( w(E) \) in Eq. (3.2) is sufficiently general to include both the Hien-Aabarenkov model potential and Harrison transition metal pseudopotential. The model wave Eq. (3.1) gives the model wavefunction transformation

\[
|\psi_k^E\rangle = \left[ 1 - \frac{\partial w(E_k)}{\partial E_k} \right] |X_k\rangle,
\]

(3.3)

where \( \frac{\partial w(E_k)}{\partial E_k} \) has the same properties as the projection operator of CPT\# pseudopotential theory, therefore formally

\[
\left[ 1 - \frac{\partial w(E_k)}{\partial E_k} \right]^2 = \left( 1 - \frac{\partial w(E_k)}{\partial E_k} \right).
\]

(3.4)

The use of Eq. (3.3) in Eq. (2.43) gives the impurity scattered wavefunction as

\[
\Psi_k^E(r) = \left[ 1 - \frac{\partial w(E_k)}{\partial E_k} \right] |X_k\rangle + \frac{f_k(r,k')}{r} \left[ 1 - \frac{\partial w(E_{k'})}{\partial E_{k'}} \right] |X_{k'}\rangle.
\]

(3.5)

Using Eqs. (3.3) to (3.5) in Eq. (2.40) we get the impurity induced excess charge density for the \( k \)th state as

\[
\delta n_k(r) = \frac{1}{r} \left[ \chi_k^*(r) f_k^\phi(r) \chi_k(r) + c.c. \right] + \frac{1}{r^2} \left[ |f_k^\phi(r)|^2 \chi_k^*(r) \right] - \frac{1}{r^2} \left[ |f_k^\phi(r)|^2 \chi_k^*(r) \right] - \frac{1}{r^2} \left[ |f_k^\phi(r)|^2 \chi_k^*(r) \right].
\]

(3.6)
Here we use the sphericity of the energy surface and treat $\frac{\partial \omega}{\partial \mathbf{k}}$ as the first-order term. The first two terms correspond to scattering of a model wave of wavevector $\mathbf{k}$ into another model wave of wavevector $\mathbf{k}'$. The last two terms represent the scattering of a model wave into another augmented model wave due to the non-local character of the model potential and these terms include the deformation of core wavefunctions in the scattering process. It is evident that for the local model potential, the last two terms vanish and therefore the charge distribution defined through the non-model part of the wavefunction will only take part in the scattering process.

To have a more transparent picture of Eq.(3.6), we use the plane wave expansion of model wavefunction and rearrange the terms as follows:

$$\delta n_k^m (\mathbf{r}) = \delta n^f_k (\mathbf{r}) + \delta n^{\text{dep}}_k (\mathbf{r}), \quad (3.7)$$

where

$$\delta n^f_k (\mathbf{r}) = \frac{1}{r} \langle k | r \rangle \Sigma q f_k (\mathbf{r}) \frac{1}{q' q} f_{k'}^* \langle k' | r \rangle + c. c. + \frac{1}{r^2} \langle k' | r \rangle \left( \frac{\partial}{\partial k} \right) \langle k' | r \rangle$$

$$+ \Sigma q q' f_k (\mathbf{r}) \frac{1}{q' q} f_{k'}^* \langle k' | q' \rangle \langle k | q' \rangle + c. c.$$
and

\[ \delta n_{\text{dep}}(r) = -(1/r) \left[ \langle \vec{k}| \vec{r} \rangle f^{*}_{\text{kc}}(\theta) \left( \frac{\partial w(E_{k'})}{\partial E_{k'}} \right) \langle \vec{r}| \vec{k'} \rangle + \text{c.c.} \right] \]

\[ - \left( \frac{1}{r^2} \right) \left[ \langle \vec{k'}| \vec{r} \rangle \left| f^{*}_{\text{kc}}(\theta) \right|^2 \left( \frac{\partial w(E_{k'})}{\partial E_{k'}} \right) \langle \vec{r}| \vec{k'} \rangle \right] \]

\[ - \left( \frac{1}{r} \right) \left[ \langle \vec{k'}| \vec{r} \rangle f^{*}_{\text{kc}}(\theta) \left( \frac{\partial w(E_{k'})}{\partial E_{k'}} \right) \sum_{q'} a_{q'}^{*}(k') \langle \vec{r}| \vec{k'}+q' \rangle + \text{c.c.} \right] \]

\[ \left( \frac{\partial w(E_{k'})}{\partial E_{k'}} \right) \langle \vec{r}| \vec{k'} \rangle + \text{c.c.} \right] \]

\[ - \left( \frac{1}{r^2} \right) \left[ \langle \vec{k'}| \vec{r} \rangle f^{*}_{\text{kc}}(\theta) \left| f^{*}_{\text{kc}}(\theta) \right|^2 \left( \frac{\partial w(E_{k'})}{\partial E_{k'}} \right) \sum_{q'} a_{q'}^{*}(k') \langle \vec{r}| \vec{k'}+q' \rangle + \text{c.c.} \right] \]

\[ \langle \vec{r}| \vec{k'} \rangle \right]. \quad (3.9) \]

Here \( \langle \vec{r}| \vec{k} \rangle = (1/\Omega) \exp(ikr) \), \( \Omega \) is the crystal volume, \( \vec{q'} \) is the reciprocal vector and \( a_{q'}^{*}(k) \) are the expansion coefficients which can be determined with the help of the perturbation theory and the normalising condition of the Bloch function. Evidently from Eq. (3.7) the excess electronic charge density is separated into two parts \( \delta n_{\text{e}}(r) \) and \( \delta n_{\text{dep}}(r) \) for every state \( k \). \( \delta n_{\text{e}}(r) \) is the change in uniform charge density for the \( k \)th state and is produced by scattering of free electrons by a potential which is defined through the transition amplitude \( f(k,k') \). \( \delta n_{\text{dep}}(r) \) is the change in depletion hole charge density for the \( k \)th state and may be regarded as produced by scattering of free electrons by a potential defined through the effective scattering amplitude \( f_{\text{kc}}(\theta) \left( \frac{\partial w(E_{k'})}{\partial E_{k'}} \right) \).

Now we investigate the variations of \( \delta n_{\text{e}}(r) \) and
\( \delta n^\text{dep}(\mathbf{r}) \) as a function of \( r \). The first two terms of Eq. (3.8) are easily integrated over \( k \) using Eq. (2.45) and this gives the usual Friedel oscillation.

\[
\delta n^\text{f}(\mathbf{r}) = (1/2\pi^2 r^3) \sum (2l + 1) \left[ -\sin \gamma \cos (2k_F r \gamma) \right] ,
\]

(3.10)

The remaining terms in Eq. (3.8) are of the higher order and give rise to the bandstructure effects. These terms are of only quantitative importance and introduce nothing new in the behaviour of \( \delta n^\text{f}(\mathbf{r}) \). This has been discussed in detail by Herrison (1966).

To find the space variation of \( \delta n^\text{dep}(\mathbf{r}) \), we consider only the first two terms of Eq. (3.9) presuming that the other terms are of higher order. Replacing sum over \( k \) by integration we get

\[
\delta n^\text{dep}(\mathbf{r}) = -\left( 2/\pi^2 \right) \int \frac{dk}{k} \left\{ -\frac{1}{r} \exp(-i \mathbf{k} \cdot \mathbf{r}) \left| f^0_k(\mathbf{r}) \right|^2 \left( \frac{\partial w(\mathbf{E}_k)}{\partial E_k} \right) \right\} ,
\]

(3.11)

Using the Heine-Abarenkov type model potential extended by Animalu for transition metals, we get

\[
\frac{\partial w(\mathbf{E}_k)}{\partial E_k} = -\frac{1}{N} \frac{dA}{dE} \delta \Theta(R_m - r')
\]

(3.12)

where \( \delta \Theta \) is the projection operator which picks up the \( l \)th component of the wavefunction on which it projects, and \( \Theta(R_m - r') \) is the step function such that \( d\Theta/dE \) is non-zero only in the effective core radius \( R_m \) of the host ion. We evaluate Eq. (3.11)
using Eq. (3.12) and the same approximations as discussed in chapter 2. Leaving the terms for which the integration in the crystal volume cancels, we are left with the leading term of Eq. (3.11) as

\[
\delta n_{\text{dep}}(\vec{r}'+\vec{r}_n) = \frac{1}{2\pi^2} \int \frac{dk}{k} \left[ \frac{k f_k(r)}{i} \right] \exp(ik|\vec{r}'+\vec{r}_n|) 
\]

\[
+ \sum \left( \frac{\partial A_i}{\partial \omega} \right) \exp \left( i k |\vec{r}'+\vec{r}_n| \right) + \text{c.c.} \right] \Theta(R - r') \quad (3.13)
\]

Here \( \vec{r} \) is replaced by \( \vec{r}'+\vec{r}_n \), where \( \vec{r}_n \) is the distance of the \( n \)th host atom from the impurity and \( \vec{r}' \) is the distance from the \( n \)th atom to the point \( \vec{r} \) measured from impurity (Fig. 2.1).

Oli and Animalu (1976) used \( \frac{\partial A}{\partial \omega} = (A_{\text{a}}/A_{\text{m}}) \) and \( \frac{\partial A}{\partial \omega} = (A_{\text{d}}/A_{\text{d}}) \) where \( E_0 \) and \( E_1 \) are the differences in spectroscopic term values for a given \( \lambda \) and \( \Delta A_0 \) and \( \Delta A_1 \) are the differences in corresponding model potential well depths. However for the \( \lambda = 2 \) resonant state in a transition metal, the spectroscopic term values do not provide complete information near the resonance energy \( E = E_d \), therefore \( A_2(E) \) is replaced by the real part of the T matrix model well depth. Therefore at \( E = E_d \) one can write approximately

\[
\frac{\partial A_2}{\partial \omega} = \frac{A_2(E_0)(E_0 - E_d)}{(E_0 - E_d')^2 + (1/4) \omega_d^2}, \quad (3.14)
\]

where \( E_d = \hbar k_d^2/2m \) is the electronic mass, \( k_d \) is the Fermi momentum for the \( d \) band, \( \omega_d \) is \( d \) band width, \( E_F \) is the Fermi energy for the spherical Fermi surface and \( E' = \hbar k^2/2m \).

Using these simplifications and Eq. (2.45) in Eq. (3.13) we get
To simplify further it is assumed that the phase shifts are slowly varying function of $k$ and therefore $\eta_{1}^{k}$ is replaced by $\eta_{1}^{k}$ approximately. This enables one to integrate exactly the first two terms of Eq. (3.15). An exact evaluation of the third term is not possible as it involves a term which does not form the closed contour, therefore, it is integrated by parts and only the leading terms in the $r$ dependence are retained. The final expression is arranged as follows:

$$
\delta n_{\text{dep}}(r' + r) = (1/\pi^{3/2}) \sum_{l=0}^{\infty} (2l + 1) P_{l}(\cos\theta)(\frac{1}{|r' + r|})^{2}
$$

$$
\left[ -\left(\frac{\Delta \eta_{l}}{\Delta \omega_{0}}\right) \left( \int_{0}^{k_{p}} \cos(\eta_{l}^{k} k|k|^{r' + r}) \right) j_{0}(k|k|^{r' + r}) dk
\right.
$$

$$
\left. + \left( \int_{0}^{k_{p}} \sin(\eta_{l}^{k} k|k|^{r' + r}) j_{1}(k|k|^{r' + r}) dk \right) \right] \left( \frac{\Delta \eta_{l}}{\Delta \omega_{0}} \right)
$$

$$
\left( \frac{1}{\Delta \omega_{0}} \right) \delta n(\theta) \left( \frac{1}{\Delta \omega_{0}} \right)
$$

$$
\left[ -\left(\frac{5 \Delta \eta_{l}}{\Delta \omega_{0}}\right) \delta n(\theta) \left( \frac{1}{\Delta \omega_{0}} \right)
\right]
$$

$$
\Theta(\frac{R - r}{R'})
$$

(3.16)
where
\begin{equation}
\delta n_n(r' + r_n) = S_1(k_p) \sin(2k_p|r' + r_n|) / |r' + r_n|^3 - C_1(k_p) \sin(2k_p|r' + r_n|) / |r' + r_n|^3,
\end{equation}
\begin{equation}
\delta n_p(r' + r_n) = S_1(k_p) \left[ \frac{2}{|r' + r_n|^3} - \frac{\sin(2k_p|r' + r_n|)}{|r' + r_n|^3} \right] + C_1(k_p) \frac{\sin(2k_p|r' + r_n|)}{|r' + r_n|^3},
\end{equation}
and
\begin{equation}
\delta n_d(r' + r_n) = S_1(k_p) \left[ - \frac{2k_p}{|r' + r_n|^3} \right] + A' \frac{\sin(2k_p|r' + r_n|)}{|r' + r_n|^3}.
\end{equation}

Here \( C \) is the Euler constant, and
\begin{align}
S_1(k_p) &= \left( \frac{1}{2} \right) \sin \left( 2 \gamma_1 \right) k_p, \\
C_1(k_p) &= \left( \frac{1}{2} \right) \left[ -1 - \cos 2 \gamma_1 \right], \\
\sin(x) &= \int_0^x (\sin t/t) dt, \\
\cos(x) &= \int_0^x ((1 - \cos t)/t) dt, \\
B &= 2 \int_0^{k_p} \left[ P(k)/k \right] dk, \\
P(k) &= \int \frac{k(B - k^2)}{(E_d - k^2)^2 + (1/4) w_d^2} dk.
\end{align}
and

$$A' = \frac{\mathcal{E}_d}{\left( \mathcal{E}_d - \mathcal{E}_p \right)^2 + (1/4)} \frac{\nu^2}{\partial_d} \left( -4\mathcal{F}(k_F) \right).$$

(3.20g)

The parameters $E_d$ and $\mathcal{E}_d$ can be obtained from the bandstructure calculations and $A_2(\mathcal{E}_p)$ can be obtained by extrapolating the tabulated well depths $\mathcal{A}_2(\mathcal{E})$ to $\mathcal{E}_p$ (Oli and Anandu 1976). The phase shifts can be determined with the help of the friedel sum and experimental data on residual resistivity, thermoelectric power, and specific heat etc. of the dilute alloys.

In Eq.(3.16) $n_{s}$, $n_{p}$ and $n_{d}$ may be regarded as changes in depletion hole charge density due to s, p and d characters of the Bloch function in the effective core region. We notice two important features of $\Delta n_{d}(r)$.

(1) $\Delta n_{s}$, $\Delta n_{p}$ and $\Delta n_{d}$ consists of oscillatory parts decaying as $1/r^3$. For $\Delta n_{d}$, this part is weighted by a constant $A'$ which depends upon the d bandwidth, the d band resonance energy and the distribution of free electrons in the metal. $\Delta n_{s}$ and $\Delta n_{p}$ depend only on the Fermi momentum of free electrons. The oscillations found in this part are not similar to Friedel oscillations, these vary like the $\sin$ and $\cos$ functions defined in Eq.(3.20) and $d$ upon the distance from the impurity and upon the Fermi momentum $k_F$. The total oscillations of $\Delta n_{d}(r)$ are superimposed oscillations of $\Delta n_{s}$, $\Delta n_{p}$ and $\Delta n_{d}$.

(ii) $\Delta n_{p}$ and $\Delta n_{d}$ also consist of a part which decreases smoothly as $1/r^3$. It was pointed out by Sagalyn et al. (1961) that $1/r^3$ variation of the potential and hence of charge density at large
distance from the impurity arises due to the lattice distortion. In the present theory, the lattice distortion has not been included explicitly, therefore the $1/r^3$ term may be thought due to the effective displacement of the ion core which arises due to the displacement of the charge centre in the effective core region from the nuclei. This term is $\delta n_d$ is also weighted by a constant $A'$ which depends upon the characteristics of d bands.

The EFG is due to oscillatory nature of charge perturbation, therefore it is interesting to compare $\delta n_f(r)$ and $\delta n_{dep}(r)$ explicitly at least for few alloys. There was an omission of square in the denominator in the expression for $F(k)$ given by Prakash (1978) and the correct expression is given in Eq.(3.20f). The quantities $(\Delta A_1 / \Delta E_1)$ are evaluated in the same manner as described by Oli and Animalu (1976).

We calculate $\delta n_f(r)$ and $\delta n_{dep}(r)$ explicitly for typical alloys of CuZn and CuSn in which the impurity is nearest and far away from Cu in the periodic table. The necessary potential parameters and other constants for copper are given in Table 3.1. Hurd-Gordon (1968) phase shifts are used. The results for CuZn alloys are shown in Fig. 3.1. $\delta n_f(r)$ exhibits the usual Friedel oscillations. $\delta n_{dep}(r)$ vanishes for $|r'| > R$, therefore it is shown only in the effective core region of first nearest neighbour (1NN). The contribution to $\delta n_{dep}(r)$, i.e., $\delta n_s(r)$, $\delta n_p(r)$ and $\delta n_d(r)$ are also shown separately in Fig. 3.1. The contributions $\delta n_s(r)$ and $\delta n_d(r)$ are negative and positive respectively and
are varying slowly with $r$. However $\delta n_p(r)$ is large and positive at small value of $r$ and decreases rapidly and finally attains large negative value at larger $r$. As compared to $\delta n_f(r)$, the magnitude of $\delta n_{\text{dep}}(r)$ is quite large and oscillatory in the effective core region, therefore the large contribution to BFG is expected. The results for $\delta n_f(r)$ and $\delta n_{\text{dep}}(r)$ for CuSn alloy are shown in Fig. 3.2. We find that the change in depletion hole charge density is positive and larger as compared to CuZn alloy. Similar characteristics of $\delta n_f(r)$ and $\delta n_{\text{dep}}(r)$ are found in the vicinity of 2NN also (not in the figure). Therefore, we conclude that the characteristics of $\delta n_f(r)$ and $\delta n_{\text{dep}}(r)$ are impurity dependent. The conclusion is consistent with the charge transfer calculations of Visnov et al. (1979).

### 3.2 Valence Effect Contribution to BFG

The general expression for valence effect contribution to BFG is given by Eq.(2.41). In transition metal model potential theory discussed in section 3.1 the charge perturbation due to impurity is written as

$$\delta n(r) = \delta n_f(r) + \delta n_{\text{dep}}(r),$$

where the explicit expression for $\delta n_f(r)$ and $\delta n_{\text{dep}}(r)$ are given by (3.10) and (3.16) respectively. Substituting Eq.(3.21) in Eq.(2.41) we find

$$\begin{align*}
q_{||} \left( \vec{r}_n \right) &= q_{||} \left( \vec{r}_n \right) + q_{||} \left( \vec{r}_n \right), \\
v_{||} \left( \vec{r}_n \right) &= v_{||} \left( \vec{r}_n \right) + v_{||} \left( \vec{r}_n \right),
\end{align*}$$

(3.22)
where

\[ V_{f}^{s}(r_{n}) = - \int \frac{\delta n_{f}(r_{n}^{s} + r')}{r'} \left[ 1 - \gamma(r') \right] (3 \cos^2 \theta' - 1) \, dr' \quad (3.23) \]

and

\[ V_{\text{dep}}^{s}(r_{n}) = - \int \frac{\delta n_{\text{dep}}(r_{n}^{s} + r')}{r'} \left[ 1 - \gamma(r') \right] (3 \cos^2 \theta' - 1) \, dr' \quad (3.24) \]

The explicit evaluation of Eqs. (3.23) and (3.24) is carried out in the following two models for the impurity perturbed region.

3.2.1 The Kohn-Vosko model

KV evaluated the integral over \( r' \) in atomic sphere volume where \( \gamma(r') \) is vanishingly small (Cohen and Reif 1957). An additional contribution of 10\( \% \) is added for the outer region. Following KV, we evaluate Eqs. (3.23) and (3.24) in the effective core region which gives

\[ V_{f}^{s}(r_{n}) = -2\pi A \int_{0}^{R_{n}} \int_{0}^{\infty} \frac{R_{m} \cos(2k_{F} |r'| + r_{n})}{r'^{3} |r'| + r_{n}^{3}} (3 \cos^2 \theta' - 1) \, dr' \, \sin \theta' \, d\theta' \quad (3.25) \]

and

\[ V_{\text{dep}}^{s}(r_{n}) = -\frac{2}{n} \sum_{m} \int_{0}^{\infty} \int_{0}^{R_{m}} \frac{D_{1} + D_{2} \sin(2k_{F} |r'| + r_{n}) + D_{3} \sin(2k_{F} |r'| + r_{n})}{r'^{3} |r'| + r_{n}^{3}} (3 \cos^2 \theta' - 1) \, r'^{2} \sin \theta' \, d\theta' \, dr' \quad (3.26) \]

where \( A \) and \( F \) are determined from Eq. (2.55).
\[ D_1 = \frac{2}{1} (21+1) P_1(\cos \theta) S_1(k_F) \left[ 2\sqrt{3} \frac{\Delta A}{\Delta E_1} - \sqrt{5} A_2(E_F)(E_F - E_d) \right] \]
\[ \left\{ 2B + A' \left( \ln 2 + \frac{\pi}{2} \right) \right\} \]
(3.27)

\[ D_2 = \frac{2}{1} (21+1) P_1(\cos \theta) C_1(k_F) \left[ - \frac{\Delta A}{\Delta E_0} - \sqrt{3} \frac{\Delta A}{\Delta E_1} + \sqrt{5} A_2(E_F) \right] \]
\[ (E_F - E_d) A' \]
(3.28)

and

\[ D_3 = \frac{2}{1} (21+1) P_1(\cos \theta) C_1(k_F) \left[ \frac{\Delta A}{\Delta E_0} + \sqrt{3} \frac{\Delta A}{\Delta E_1} + \sqrt{5} A_2(E_F) \right] \]
\[ (E_F - E_d) A' \]
(3.29)

The quantities \( S_1(k_F), C_1(k_F), \sin(x), \sin(x), \frac{\Delta A}{\Delta E_0}, \frac{\Delta A}{\Delta E_1} \) and \( \frac{\Delta A}{\Delta E} \) are the same as defined in section 3.1. It is to be noted that KV tactfully introduced the Bloch character in the expression of \( \delta n(r) \) before evaluating the explicit expression for \( \frac{\delta n(r)}{r} \). In the first approximation KV took the Fermi wave vector \( k_F \) parallel to \( r' = r + r_n \) to evaluate \( \delta n(r) \). In the next step, assuming \( r' \) to be small, \( k_F \) is taken parallel to \( r_n \), this enabled them to build in the Bloch character in the expression for \( \delta n(r) \) and which lead to the finite value of the integrals involved in evaluating the core enhancement factor \( \alpha \). However, this approximation will be valid only for \( r_n = 0 \) or \( r_n \) parallel to \( r_n \), In the evaluation of \( \alpha \), the integration over \( r_n \) is involved and if \( k_F \) is taken parallel to \( r_n \), the angular integration of denominator in the expression for \( \alpha \) will vanish, which would lead to a diverging value of \( \alpha \).

If we follow the same approximation as used by KV to
evaluate the EFG from $\delta n^{F}(\vec{r})$, the angular integration in Eq. (3.23) will vanish. Therefore we assume that for large distances, 
\[ \cos(2k_F|\vec{r} + \vec{r}_n| + \phi) \approx \cos(2k_F r_n + \phi) \]
and evaluate integral in Eq. (3.23). The analytical expression obtained is as follows:

\[ V_{q_{\parallel F}}(r_n) = 4\pi\Lambda \frac{\cos(2k_F r_n + \phi)}{r_n} \ln \left[ 1 - \left( \frac{R}{r_n} \right)^2 \right]. \]  
(3.30)

Similar simplifications are carried out in Eq. (3.24) and the final result obtained is as follows:

\[ V_{q_{\text{dep}}}(r_n) = \frac{4}{\sqrt{\Lambda}} \left( D_1 + D_2 \sin(2k_F r_n) + D_3 \sin(2k_F r_n) \right) \ln \left[ 1 - \left( \frac{R}{r_n} \right)^2 \right]. \]  
(3.31)

The Eqs. (3.30) and (3.31) are the contributions to the EFG along $\vec{r}_n$.

3.2.2 The Sagalyn-Alexander model

SA divided the impurity perturbed region into three sub-regions: the impurity sphere (region A), the host sphere (region C) and the volume between the outer and inner sphere excluding region C (region B) as shown in Fig. 3.3. The $V_q$ is evaluated in these regions separately and the respective contributions are added up.

As mentioned in section 3.1, in TMMP theory, the potential is non-local for the distances $r'<R_m$ and local beyond $R_m$. Therefore we define a sphere of radius $R_m$ equivalent to region C. Lodge and Sholl (1974) also used the similar limits of region C in evaluating the EFG in hexagonal metals. This leads
\[
V(c) = V_f(c) + V_{\text{dep}},
\]
\[
V_f(c) = q_{f||} + q_{f\parallel}^{\text{dep}},
\]
where \( q_{f||} \) and \( q_{f\parallel}^{\text{dep}} \) are given by Eqs. (3.30) and (3.31).

The contributions of regions A and B are evaluated in the same manner as discussed by SA, i.e.,

\[
q_{f||}^{(A)} = \frac{3\pi}{r_n^3} (1 - \gamma_c) \int_{r_n-R_m}^{R_m} r^2 \delta n(r) \, dr
\]

and

\[
q_{f\parallel}^{(B)} = -\frac{3\pi}{r_n^3} (1 - \gamma_c) \int_{r_n}^{R_m} r^2 \delta n(r) \, dr - \frac{3\pi}{r_n^3} (1 - \gamma_c) \delta n'(r_n)
\]

\[+ 2\pi (1 - \gamma_c) \int_{0}^{R_m} \int_{0}^{\pi} \delta n(r) \left( \frac{3\cos^2 \theta - 1}{r'} \right) \sin \theta \, d\theta \, dr'. \]

To evaluate explicit expression for (3.33) and (3.34) the contribution of preasymptotic region is incorporated by substituting \( \delta n(r) \) due to Alfred and Van Ostenburg given by Eq. (2.54). The angular and radial integrations in Eq. (3.34) are carried out numerically. The other components of valence effect contribution to EPC are obtained as given in Eq. (2.58).

The direct and indirect size effect contributions are evaluated in the same manner as discussed in article 2.2. Here it is to be emphasized that the valence effect contribution is evaluated exactly in the RMFT theory. It does not involve any uncertain parameter like \( \alpha \). Size effect contribution still involves the size strength parameter \( \lambda \). Therefore present
theory is effectively reduced to one parameter theory.

3.3 Application to Dilute Cu-Alloys

We use formalism developed in section 3.2 to evaluate EFG and \( \eta \) for dilute alloys of copper. The results in both the KV and SA models are presented separately.

3.3.1 KV model

First we carry out the systematic comparison of our results with the calculations of KV. We use the same phase shifts as used by KV. The contributions to EFG due to on (r) and on dep (r) at the 1NN and at the 2NN for the fourth and fifth row impurities are shown in Table 3.2. Evidently the depletion hole contribution is larger than the free electron contribution almost by an order of magnitude. The depletion hole and the free electron contributions are additive for CuGe and CuSn alloys while these are substractive for all other alloys at the 1NN site. At the 2NN site both the contributions are additive except for the case concerning Sb. An algebraic sum of these two contributions and a 10% enhancement for outer region gives the total EFG in KV model. These results along with KV results are also tabulated in Table 3.2. Our calculated values are found much smaller as compared to KV results or the experimental values (given in Tables 3.5 and 3.6). In KV theory the enhancement factor simply multiplies the calculated EFG. However an explicit calculation shows that the contributions due to Bloch character and free electron character are
additive and substractive for different impurities. If we divide the $q_{KV}$ by $\alpha \approx 23.3$, the quotient values are of the same order of magnitude as found in our explicit calculations. Therefore $\alpha$ of KV theory may not be sufficient to account for the unexplained character of the electron wave function in the core region. It may simply be regarded as a parameter to obtain an agreement between calculated and experimental values. This $\alpha$ will account for both the remaining valence electron contribution and the size effect contribution.

In our calculations the antishielding factor is completely ignored. KV indicated that this may enhance EFG by 20%. Again the depletion hole contribution approximately accounts the Bloch character of charge density in the core region. Even if we assume that our calculations underestimate the valence effect contribution by 50%, the calculated values do not show any agreement with the experiment. Our calculations do not include any adjustable parameter. Therefore we conclude that the valence effect contribution to EFG in dilute alloys of copper is very small. This was also pointed out by Prakash and Lucasson (1979) and by Dwozechek et al. (1978) in explaining the capture radii and wipe out numbers for dilute copper alloys.

We use Eqs. (2.82) and (2.83) to calculate the size effect contribution to the EFG and we give different components of the EFG and $\lambda$ at 1NN in Table 3.3. Size effect parameter $\lambda = 80$ and 20 are found to be quite appropriate for the fourth and fifth row impurities. The results at the 2NN are shown in
Table 3.4 where the value of $\lambda$ is found to be $-25$. These $\lambda$-values are of the same order as obtained by SA. At the 1NN the size effect increases for Zn, Ga and Ge respectively while the valence effect is maximum for Ga. Among the fifth row impurities, both the valence and size effects are maximum for Sb. The calculated values of EFG are in reasonably good agreement with the experimental values. Our results show a closer agreement with experiment than those of KV. The results for 2NN are in moderate agreement with the experimental values (given in Table 3.6). For the fourth row impurities, the calculated values are lower than those of KV (Table 3.2) while for the fifth row impurities they are higher. Compared with the experimental values the maximum deviation is for CuIn alloy.

The calculated values of $\gamma$ deviate from the experimental values by $20^\circ - 60^\circ$. This may be because the asphericity of charge distribution of the outer region is not taken into account. Also the sign of the EFG components is not known with certainty.

3.3.2 SA model

We adopt the calculated values of SA for regions A and B and evaluate the contribution of region C using Eqs. (3.30) and (3.31). The Hurd-Gordon (1968) phase shifts are used. The parameter $\alpha$ is not introduced as it was by SA but is instead calculated explicitly as discussed earlier. The size effect contribution is evaluated using $\lambda$ as a variable parameter and
the respective asymmetry parameters are also calculated. These results along with the experimental values and the results due to SA are presented in Tables 3.5 and 3.6 for 1NN and 2NN respectively. Following SA, first we choose only two values of $\lambda$, one for the fourth row and one for the fifth row impurities. The calculated values of $q$ and $\eta$ at the 1NN are overall in good agreement with the experimental values for $\lambda=87$ and 25 for the fourth and fifth row impurities, respectively. The maximum deviation is about 50% for the CuAg alloy which is well within experimental uncertainties.

The values of $\eta$ for the fourth row elemental alloys are quite close to the experimental values, unlike those for the fifth row elemental alloys which are in poor agreement with the experimental values. The results at 2NN are again in good agreement with the experimental values as well as with the results of SA. It is important to note that our one parameter theory (size effect parameter $\lambda$) gives comparable results to those obtained by SA using two parameters ($\alpha$ and $\lambda$). The anomalous direction of the main principal axis in CuGe alloy is also correctly obtained.

The various impurities have different atomic sizes and chemical valencies, therefore the parameter $\lambda$ which partly accounts for the size strength and partly for the shielding of the impurity may be at variance for different impurities. Therefore we made an attempt to vary $\lambda$ separately for every impurity to get a close agreement between the calculated and experimental values of $\beta$. This yielded a systematic trend
in the values of $\lambda$ which is evident from the tabulated values in Table 3.5 for the 1NN. $\lambda$ is found to be 104, 92 and 71 for CuZn, CuGa and CuGe alloys respectively. Thus it is in decreasing order from Zn to Ge impurities. Similar calculations are done for fifth-row impurities and $\lambda$ is found to increase from CuAg to CuSb alloy with the exception of CuSn alloy. $\lambda$ is much larger for the fourth row impurities than for the fifth row impurities, which indicates that the fourth row impurities are effectively harder than the fifth row impurities. The overall agreement with the experimental values of $\eta$ for the fourth and fifth row impurities, is also improved. Similar calculations are also carried out for $q$ at 2NN but because the exact experimental values of $q$ for CuGa and CuIn were not available, a definite trend in $\lambda$ could not be observed.

As discussed in chapter 2, we estimated the effective charge on the impurity $|\Delta Z_e|$ in the FL model and $q_{1NN}$ vs $|\Delta Z_e|$ are plotted in Fig. 3.4(a) for the fifth row elemental alloys. Within the experimental errors as suggested by N von (1975) the experimental results for CuAg, CuCd, CuIn, CuSn and CuSb alloys show linear correlation with $|\Delta Z_e|$. Except for CuSn alloy the calculated values too show the similar trend. Fig. 3.4(b) shows $q_{1NN}$ vs $|\Delta Z_e|$ for the fourth row impurities. The calculated values show a systematic correlation with $|\Delta Z_e|$. The experimental values for Zn and Ga impurities are in expected trend while for CuGe it is on lower side. However within the error bars, the experimental EFGs are proportional to $|\Delta Z_e|$. 

Fig. 3.5(a) and 3.5(b) show the results $|\gamma_{1NN}|$ vs $|\Delta Ze|$ for the fifth and fourth row impurities respectively. For the fourth-row alloys the linear correlation in calculated and experimental $|\gamma_{1NN}|$ and $|\Delta Ze|$ is quite evident. Leaving aside CuAg alloy the experimental values for the fifth row alloys, CuCd, CuIn, CuSn and CuSb again show the same correlation with $|\Delta Ze|$. However the calculated values for these alloys are a little scattered. The results for $|q_{2NN}|$ vs $|\Delta Ze|$ are shown in Fig. 3.6(a) and 3.6(b) for the fifth and fourth row impurities respectively. For the fifth row alloys, the experimental results for In and Cd alloys are lower. However the other results along with calculated values show the linear correlation with $|\Delta Ze|$.

The correlation between the calculated $|q_{NN}|$ and $|\Delta Ze|$ is improved in this chapter as compared to the results obtained in the last chapter. A careful analysis to determine the net charges on host and impurity ions is still needed (Visnov et al. 1979).

3.4 Discussion

We adopted the TIP theory to evaluate the LFG and $\gamma$ in the present calculations. The Bloch character of the electron wave function and the distortions in core-polarization are included through the change in depletion hole charge density which arises due to non-local character of the model potential. Therefore the band structure effects are incorporated in our calculations although in a simplified manner. The calculational
efforts are greatly reduced and the theory is reduced to a
one parameter theory. The exchange and correlation inter-
actions between the conduction electrons have only a negligible
effect on the screening charge density as pointed out by Lodge
and Sholl (1974) and by Fukai and Watanabe (1970), there­
fore these corrections are neglected in the present calculations.

We evaluated the depletion hole contribution and the
free electron contribution to \( \eta \) and we found the depletion
hole contribution to be larger than the free electron con­
tribution, because the d-band is broad and below the Fermi surface.
This contribution is expected to be more pronounced in transi­
tion metal alloys. Overall the size affect contribution is
found to be very large as compared to valence effect contribu­
tion. Therefore we conclude that size affect is dominating in
dilute alloys of copper with non-transition metal impurities.

The results for \( \eta \) and \( q \) in the present formalism are
in better agreement with the experimental values as compared
to those obtained by KV and SI while we use only a single
parameter and include the valence and size effect contributions
explicitly. This gives the present theory a distinct advantage.

In the present calculations, the change in screening
charge distribution is assumed to be spherical symmetric and
only the first order perturbation theory is used. Higher order
perturbation theory may include the anisotropic screening
charge distribution (Watson et al. 1965 and Beissner 1979) which
may further improve the results. These calculations will
certainly be intricate. However, a more careful abinitio
calculations are required to evaluate the size effect contribution.
Very recently an interesting calculation of BEGs due to monovacancy in Al (Ponnambalam and Jena (1981)) has appeared. These authors assumed that the induced charge density and the potential are spherically symmetric around the vacancy. Poisson equation is solved self-consistently in the density functional formalism to obtain the perturbations caused in the positive and negative charge distribution of the metal due to the defect and an expression for the electric field gradient is obtained, which consists of KV term and an additional term accounting for the charge perturbation in the vicinity of the defect. Additional term is equivalent to preasymptotic term accounted for by SA if the potential and induced charge perturbation given by Eq. (3.21). In SA model the change in charge density in the vicinity of nearest neighbour is also underestimated. Certainly these are the weaknesses in the theory. However a comparison with KV results is relevant and an estimation of BEG due to change in depletion hole charge density is new one.

Sagalyn and Alexander used the isotropic continuum limit for the displacement vector while Ponnambalam and Jena (1981) used the displacement vector $A \cos (2k_r r + \Phi) \nabla / r^2$. This choice is motivated by the well known oscillatory dependence of scattering charge density and potential at large distance from the point defect and is equivalent to assume that the defect induced electronic and elastic potentials have the same oscillatory nature which may not be true. Even if one accepts this assumption the oscillatory character of elastic potential
may not be valid at nearest neighbour distances as discussed by Poonambalam and Jana. However the uncertainties in the size effect contribution are accounted for in parameter $\lambda$ in our calculations.
TABLE 3.1: The model potential parameters and other physical constants in a.u. for copper. $R_m$ is model radius, $a$ is lattice parameter, $k_d$ is Fermi wavevector for d bands, $V_d$ is d-resonance width, $\Delta_0$, $\Delta_1$ and $\Delta_2$ are potential well depths for $l = 0, 1$ and 2 and $\Sigma_0$ and $\Sigma_1$ are the corresponding eigenvalues, $\gamma_\infty$ is the Sternheimer antiscreening factor.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>$q_{V,\text{dep}}$</th>
<th>$q_{V,f}$</th>
<th>$q_{V,KV}$</th>
<th>$q_{\Sigma_0}$</th>
<th>$q_{\Sigma_1}$</th>
<th>$q_{\Sigma_2}$</th>
<th>$q_{\Delta_0}$</th>
<th>$q_{\Delta_1}$</th>
<th>$q_{\Delta_2}$</th>
<th>$\gamma_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.0083 -0.0029</td>
<td>0.006</td>
<td>0.236</td>
<td>0.0043</td>
<td>0.0006</td>
<td>0.0054</td>
<td>-0.48</td>
<td>-0.84</td>
<td>-17.36</td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>0.0316 -0.0061</td>
<td>0.029</td>
<td>0.492</td>
<td>0.0104</td>
<td>0.0012</td>
<td>0.013</td>
<td>-0.194</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>-0.0122 -0.0044</td>
<td>-0.013</td>
<td>0.436</td>
<td>0.0050</td>
<td>0.0014</td>
<td>0.007</td>
<td>-0.247</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>-0.0064 0.0014</td>
<td>-0.006</td>
<td>0.136</td>
<td>-0.0026</td>
<td>-0.0003</td>
<td>-0.003</td>
<td>-0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.0077 -0.0021</td>
<td>0.006</td>
<td>0.236</td>
<td>0.0042</td>
<td>0.0006</td>
<td>0.005</td>
<td>-0.106</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>0.0241 -0.0041</td>
<td>0.022</td>
<td>0.422</td>
<td>0.0036</td>
<td>0.0010</td>
<td>0.011</td>
<td>-0.167</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>-0.0100 -0.0017</td>
<td>-0.013</td>
<td>0.377</td>
<td>0.0043</td>
<td>0.0011</td>
<td>0.006</td>
<td>-0.215</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>-0.0666 0.0049</td>
<td>-0.068</td>
<td>-0.111</td>
<td>0.0068</td>
<td>0.0001</td>
<td>-0.010</td>
<td>-0.084</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 3.3: $q$ (including both the valence and size effect contributions in units of $10^{-24} \text{cm}^2$) and $\eta$ at 1NN shell for copper alloys. $\lambda = 80$ for the fourth-row impurities and $\lambda = 20$ for the fifth row impurities. The KV model is used to evaluate the valence effect contribution. The underlined values are the largest components of $\mathbf{EFG}$s which define $q_{ij} = q$. 

<table>
<thead>
<tr>
<th>Impurity</th>
<th>EFG contribution</th>
<th>$q_{xx}$</th>
<th>$q_{yy}$</th>
<th>$q_{zz}$</th>
<th>$q$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>Total</td>
<td>0.271</td>
<td>-0.413</td>
<td>0.143</td>
<td>-0.413</td>
<td>0.310</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>0.274</td>
<td>-0.410</td>
<td>0.137</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Valence</td>
<td>-0.003</td>
<td>-0.003</td>
<td>0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>Total</td>
<td>0.354</td>
<td>-0.566</td>
<td>0.212</td>
<td>-0.566</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>0.368</td>
<td>-0.552</td>
<td>0.184</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Valence</td>
<td>-0.014</td>
<td>-0.014</td>
<td>0.028</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Total</td>
<td>0.457</td>
<td>-0.663</td>
<td>0.206</td>
<td>-0.663</td>
<td>0.378</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>0.448</td>
<td>-0.672</td>
<td>0.224</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Valence</td>
<td>0.009</td>
<td>0.009</td>
<td>-0.018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>Total</td>
<td>0.190</td>
<td>-0.277</td>
<td>0.087</td>
<td>-0.277</td>
<td>0.372</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>0.187</td>
<td>-0.280</td>
<td>0.093</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Valence</td>
<td>0.003</td>
<td>0.003</td>
<td>-0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>Total</td>
<td>0.255</td>
<td>-0.390</td>
<td>0.135</td>
<td>-0.390</td>
<td>0.310</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>0.253</td>
<td>-0.387</td>
<td>0.128</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Valence</td>
<td>-0.003</td>
<td>-0.003</td>
<td>0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>Total</td>
<td>0.289</td>
<td>-0.461</td>
<td>0.172</td>
<td>-0.461</td>
<td>0.254</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>0.300</td>
<td>-0.450</td>
<td>0.150</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Valence</td>
<td>-0.011</td>
<td>-0.011</td>
<td>0.022</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>Total</td>
<td>0.329</td>
<td>-0.476</td>
<td>0.148</td>
<td>-0.476</td>
<td>0.380</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>0.322</td>
<td>-0.483</td>
<td>0.161</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Valence</td>
<td>0.007</td>
<td>0.007</td>
<td>-0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>Total</td>
<td>0.376</td>
<td>-0.479</td>
<td>0.103</td>
<td>-0.479</td>
<td>0.570</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>0.342</td>
<td>-0.513</td>
<td>0.171</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Valence</td>
<td>0.034</td>
<td>0.034</td>
<td>-0.068</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 3.4: \( q \) (including both the valence and size effect contributions in units of \( 10^{-24} \) cm\(^3\)) at 2NN shells in dilute alloys of copper. \( \lambda = -25 \) for all the alloys. \( q^S \) and \( q^V \) are the size and valence effect contributions respectively and \( q \) is the sum of them. KV model is used to calculate the valence effect contribution.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>( q^S )</th>
<th>( q^V )</th>
<th>( q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.062</td>
<td>0.005</td>
<td>0.067</td>
</tr>
<tr>
<td>Ga</td>
<td>0.083</td>
<td>0.013</td>
<td>0.096</td>
</tr>
<tr>
<td>Ge</td>
<td>0.102</td>
<td>0.007</td>
<td>0.109</td>
</tr>
<tr>
<td>Ag</td>
<td>0.170</td>
<td>-0.003</td>
<td>0.167</td>
</tr>
<tr>
<td>Cd</td>
<td>0.233</td>
<td>0.005</td>
<td>0.243</td>
</tr>
<tr>
<td>In</td>
<td>0.250</td>
<td>0.011</td>
<td>0.261</td>
</tr>
<tr>
<td>Sn</td>
<td>0.302</td>
<td>0.006</td>
<td>0.308</td>
</tr>
<tr>
<td>Sb</td>
<td>0.322</td>
<td>-0.010</td>
<td>0.312</td>
</tr>
</tbody>
</table>
### Table 3.5: Calculated $q$ (in units of $10^{24}$ cm$^{-3}$) and $\eta$ at 1NN shells in dilute copper alloys.

The 3A model is used to evaluate the valence effect contribution. $q_{\text{exp}}$ and $\eta_{\text{exp}}$ are the experimental values and $q_{\text{3A}}$ and $\eta_{\text{3A}}$ are the results due to 3A. $q_{\text{cal}}$ and $\eta_{\text{cal}}$ are the results of the present calculations.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>$\Lambda$</th>
<th>$q_{\text{cal}}$</th>
<th>$\eta_{\text{cal}}$</th>
<th>$\Lambda$</th>
<th>$q_{\text{cal}}$</th>
<th>$\eta_{\text{cal}}$</th>
<th>$q_{\text{exp}}$</th>
<th>$\eta_{\text{exp}}$</th>
<th>$q_{\text{3A}}$</th>
<th>$\eta_{\text{3A}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>87</td>
<td>-0.449</td>
<td>0.296</td>
<td>105</td>
<td>-0.536</td>
<td>0.302</td>
<td>0.534</td>
<td>0.265</td>
<td>-0.445</td>
<td>0.324</td>
</tr>
<tr>
<td>Ce</td>
<td>87</td>
<td>-0.565</td>
<td>0.545</td>
<td>92</td>
<td>-0.597</td>
<td>0.533</td>
<td>0.599</td>
<td>0.930</td>
<td>-0.563</td>
<td>0.555</td>
</tr>
<tr>
<td>Se</td>
<td>87</td>
<td>0.620</td>
<td>0.939</td>
<td>71</td>
<td>0.530</td>
<td>0.757</td>
<td>0.528</td>
<td>0.905</td>
<td>0.622</td>
<td>0.928</td>
</tr>
<tr>
<td>Ag</td>
<td>25</td>
<td>-0.344</td>
<td>0.343</td>
<td>16</td>
<td>-0.221</td>
<td>0.348</td>
<td>0.216</td>
<td>0.725</td>
<td>0.231</td>
<td>0.611</td>
</tr>
<tr>
<td>Cd</td>
<td>25</td>
<td>-0.488</td>
<td>0.301</td>
<td>21</td>
<td>-0.410</td>
<td>0.285</td>
<td>0.414</td>
<td>0.036</td>
<td>0.367</td>
<td>0.148</td>
</tr>
<tr>
<td>In</td>
<td>25</td>
<td>-0.516</td>
<td>0.431</td>
<td>28</td>
<td>-0.614</td>
<td>0.420</td>
<td>0.607</td>
<td>0.320</td>
<td>0.501</td>
<td>0.313</td>
</tr>
<tr>
<td>Sn</td>
<td>25</td>
<td>-0.512</td>
<td>0.904</td>
<td>30</td>
<td>-0.632</td>
<td>0.796</td>
<td>0.632</td>
<td>0.630</td>
<td>0.672</td>
<td>0.851</td>
</tr>
<tr>
<td>Zn</td>
<td>25</td>
<td>0.626</td>
<td>0.403</td>
<td>30</td>
<td>0.710</td>
<td>0.592</td>
<td>0.719</td>
<td>0.740</td>
<td>-1.042</td>
<td>0.736</td>
</tr>
</tbody>
</table>
TABLE 3.6: $q$ (including both the valence and size effect contributions in units of $10^4\text{cm}^{-3}$) at 2NN shells for copper alloys with $\chi = -25$. SA model is used to calculate valence effect contribution. The description is the same as that of Table 3.5.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>$q_{cal}$</th>
<th>$q_{exp}$</th>
<th>$q_{SA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.058</td>
<td>0.025</td>
<td>0.035</td>
</tr>
<tr>
<td>Ga</td>
<td>0.082</td>
<td>$&lt;0.220$</td>
<td>0.088</td>
</tr>
<tr>
<td>Ge</td>
<td>0.115</td>
<td>0.240</td>
<td>0.234</td>
</tr>
<tr>
<td>Ag</td>
<td>0.171</td>
<td>0.174</td>
<td>0.086</td>
</tr>
<tr>
<td>Cd</td>
<td>0.237</td>
<td>0.112</td>
<td>0.149</td>
</tr>
<tr>
<td>In</td>
<td>0.290</td>
<td>$&lt;0.120$</td>
<td>0.195</td>
</tr>
<tr>
<td>Sn</td>
<td>0.311</td>
<td>0.316</td>
<td>0.302</td>
</tr>
<tr>
<td>Sb</td>
<td>0.354</td>
<td>0.482</td>
<td>0.483</td>
</tr>
</tbody>
</table>
**Fig. 3.1** $r\,\delta n(r)$ versus $r$ for CuZn alloy. The change in free electron charge distribution $r\,\delta n(r)$ is represented by the chain curve. The changes in $s$, $p$, and $d$ components of depletion hole charge density are represented by crossed-chain curve ($r\,\delta n_{s}(r)$), the broken curve ($r\,\delta n_{p}(r)$) and the dotted curve ($r\,\delta n_{d}(r)$) respectively. The full curve represents the total change in depletion hole charge density ($r\,\delta n_{d}(r)$). $R_m$ is model core radius around $1\,\mu m$.

**Fig. 3.2** $r\,\delta n(r)$ versus $r$ for CuSn alloy. The notation is the same as that of Fig. 3.1.

**Fig. 3.3** $A$ model for the impurity perturbed region. $A$ is impurity region, $C$ is host region and $B$ is rest of the region.

**Fig. 3.4** $|q_{1NS}| \text{ versus } |\Delta Z_{f}|$ for the (a) fifth and (b) fourth row impurities. Squares represent the calculated values and circles represent the experimental values.

**Fig. 3.5** $|\eta_{1NS}| \text{ versus } |\Delta Z_{f}|$ for the (a) fifth and (b) fourth row impurities. The description is the same as that of Fig. 3.4.

**Fig. 3.6** $|q_{2NS}| \text{ versus } |\Delta Z_{f}|$ for the (a) fifth and (b) fourth row impurities. The description is the same as that of Fig. 3.4.
Fig. 3.1
Fig. 3.2
Fig. 3.3