ELECTRIC FEILD GRADIENT CALCULATIONS IN DILUTE ALLOYS COPPER

BY

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DECLARATION

I hereby declare that this thesis has been prepared by me and that it is a record of my review of some literature and my own research work. It has not been presented in any previous application for a higher degree.

All quotations are indicated and the sources of information are acknowledged by means of references

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10th Dec. 1990
Date

CERTIFICATION

This thesis entitled "[Electric Field gradient calculations in dilute alloys of Copper] by Usman Yahaya-Joe meets the regulation governing the award of the Degree of Master of Science in Physics of Ahmadu Bello University, Zaria, and it is approved for its contribution to knowledge.

Chairman, Supervisory Committee — Date 14-1-91

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DEDICATION

To

"Al-Us"

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[U. YAHAYA-JOE]

TABLE OF CONTENTS

Content		Page
Title		i
Declaration		ii
Certification		iii
Dedication		iv
Acknowledgements		v
Table of Contents		vi
List of Tables		vii
List of Figures		viii
List of Appendices		ix
CHAPTER ONE		
	Abstract	1
	Introduction	2
CHAPTER TWO - THE ELECTRIC FIELD GRADIENT TENSOR		
2.1	Definiton of the Electric Field Gradient Tensor	5
2.2	Electric Field Gradient due to a Single Point Charge	5
2.3	The Electric Field Gradient in Crystal	7
2.4	The Electric Field Gradient in Metals and Alloys	10
CHAPTER THREE - THEORETICAL CALCULATIONS OF THE EFG IN CUBIC METALS AND ALLOYS		12
CHAPTER FOUR - THE PONNAMBALAM-JENA THEORY OF THE EFG		
4.1	The Valence Effect Contribution	20
4.2	The Size Effect Contribution to the EFG	22
4.3	Derivation of the Expression for the 'Direct' Size Effect	26
CHAPTER FIVE - ELECTRIC FIELD GRADIENT CALCULATIONS USING THE PONNAMBALAM-JENA THEORY		
5.1	Valence Effect Calculations	28
5.2	Size Effect Calculations	32
	REFERENCES	45
	APPENDICES	46

LIST OF TABLES

Table		Page
1	Displaced positions of host atoms and valence effect contribution to the EFG for first nearest neighbour (1nn) distance. $\bar{\alpha}$ = 25.6.	33
2	Valence effect contribution to the EFG for (1nn) using the value $\bar{\alpha}(K_\infty)$ = 34	34
3	Results of 1 nn EFG calculations for fifth row impurities in copper. $\bar{\alpha}$ = 25.6, λ = -1.0	39
4	Results of 1 nn EFG calculations for fifth row impurities in copper. $\bar{\alpha}$ = 25.6, λ = -1.4.	40
5	Comparison of Sagalyn and Alexander (1977) results with those obtained in this work	41
6	Results of EFG calculations at second nearest neighbour (2nn) distance displaced. $\bar{\alpha}$=34.0, λ=7.5	42
7	Comparison of calculated EFG values with that of Sagalyn and Alexander (1977) for 2 nn calculations	43

LIST OF FIGURES

Figure		Page
1	Site of impurity and host atoms	17

LIST OF APPENDICES

Appendix		Page
I	The Hurd-Gordon scattering phase shifts for Fermi level for copper solvent	46
II	Derivatives of the Hurd-Gordon scattering phase shifts for Fermi level for copper solvent	47
III	Lattice expansion of copper due to alloying obtained from Blatt (1957)	48

ABSTRACT

A re-view of the Electric Field Gradient (EFG) tensor has been carried out.

The theoretical models proposed by Kohn and vosko (1960) SI and in *and* Friedel (1960), Sagalyn, Pashkin and Harrison (1961), Sagalyn and Alexander (1977) and Ponnambalam *and* Jena (1931) have been reviewed-

The Ponnambaiam and Jena theory (1991) was used to calculate t*he* EPG tensor tor fourth and fifth row impurities in copper.

Results of first nearest neighbour (1nn) and second nearest neighbour (2nn) calculations show good agreement with experimental values.

For fifth row impurities using the value of row=25.6 and gamma=1.0; the mean percentage deviation between calculated values and experimental values was 4,S per cent for Inn For 2nn, using the value of row=34.0, gamma=7.5, a *mean* percentage deviation or 12.5 per cent was obtained. Where row and gamma are the Bloch enhancement factor and strain coupling parameter respectively.

The[3] results show that the Ponnambalam—Jena theory account for the EFG results better *than* the previous theories.

CHAPTER I

INTRODUCTION

The Electric Field Gradient (EFG) at a point in a charge bearing environment may be defined as, the gradient of the electric field at that point.

Theoretical studies of EFG in cubic metals and alloys were pioneered by Bloembergen and Rowland (1953). In their experimental studies, they noticed there was a sharp drop in the Nuclear Magnetic Resonance (NMR) signals for dilute copper alloys compared with signals from the pure copper crystal.

The presence of an impurity in the copper crystal (as, is the case in the copper alloy) leads to a loss of cubic symmetry. With the absence of cubic symmetry there exists non vanishing EFG's at the nuclear sites. The EFG's and Nuclear Quadropole moment interactions perturb the nuclear energy levels, such that resonance does not occur at a single frequency. This is responsible for the sharp drop in NMR signals.

The theory put forward by Bloembergen and Rowland (1953), gave results that were much less than the limiting value of EFG required to explain the disappearance in NMR signals.

The next step in the improvement of the theory was by Kohn and Vosko (1960) and Blandin and Friedel (1960). They were able to account semi-quantitatively for the experimental wipe-out numbers, by calculating the EFG produced by the long-range oscillatory screening charge cloud, which surrounds the impurity atom.

Results obtained from calculations in this work show good agreement with experimental values and an overall improvement over the results of Sagalyn and Alexander (1977).

CHAPTER II

THE ELECTRIC FIELD GRADIENT

2.1 Definition of the Electric Field Gradient

The electric field (EFG) at a point in a charge bearing environment is defined as the gradient of the electric field at that point.

i.e. $EFG = \bar{\nabla}\bar{E}$ 2.1.1

$= -\bar{\bar{\nabla}}\bar{\nabla}V$ 2.1.2

where $\bar{E}$ and V are the electric field and electric potential at that point respectively.

The electric field gradient gives information about the variation of the electric field in the charge bearing environment.

2.2 The electric field gradient due to a single point charge

A point charge, q, situated at a point $r=(x^2 + y^2 + z^2)^{1/2}$ in the cartesian co-ordinate system will give rise to a potential

$V = q/r$ (in Gaussian units) 2.2.1

at the origin

This also gives rise to an electric field

$$E = -\nabla V = -\left[\frac{\delta V}{\delta x}.\hat{x} + \frac{\delta V}{\delta x}.\hat{y} + \frac{\delta V}{\delta x}.\hat{z}\right] \quad 2.2.2$$

The EFG due to this point charge is defined as

$$EFG = -\overline{\nabla\nabla V} = -\begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix} \qquad 2.2.3$$

where $V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$ $(x_i, x_j = x, y, z)$ 2.2.4

$$V_{ij} = q(3x_i x_j - r^2\delta_{ij})/r^5 \qquad 2.2.5$$

In spherical polar co-ordinates defined as

$x = r\sin\theta\cos\phi$ $y = r\sin\theta\sin\phi$ and $z = r\cos\theta$

$$\begin{aligned} V_{xx} &= q(3\sin^2\theta\cos^2\phi - 1)r^{-3} \\ V_{yy} &= q(3\sin^2\theta\cos^2\phi - 1)r^{-3} \\ V_{zz} &= q(3\cos^2\theta - 1)r^{-3} \end{aligned} \qquad 2.2.6$$

$$\begin{aligned} V_{xy} &= V_{yx} = 3qr^{-3}\sin^2\theta\sin\phi\cos\phi \\ V_{xz} &= V_{zx} = 3qr^{-3}\sin\theta\cos\theta\cos\phi \\ V_{yz} &= V_{zy} = 3qr^{-3}\sin\theta\cos\theta\sin\phi \end{aligned} \qquad 2.2.7$$

The EFG tensor is a 3X3 second rank tensor. At first glance there are only six independent elements.

The number of independent elements is reduced to four because Laplace equation must be satisfied.

i.e. $\nabla^2 V = V_{xx} + V_{yy} + V_{zz} = 0$ 2.2.8

To standardize and simplify EFG computations, a unique set of axes known as "The principal axis of the EFG tensor" is defined. This is a unique co-ordinate system for which all the off diagonal elements are zero and the diagonal elements are ordered such that

$$V_{xx} \leq V_{yy} \leq V_{zz} \qquad 2.2.9$$

The EFG defined in this manner is said to be in

standard form. Thus in standard form the EFG is defined by only two independent parameters usually chosen as

$$V_{zz} = eq \qquad 2.2.10$$

and the asymmetry parameter

$$\eta = (V_{xx} - V_{yy})/V_{zz} \qquad 2.2.11$$

where $0 < \eta < 1$ 2.2.12

The asymmetry parameter is a measure of deviation from cylindrical symmetry.

2.3 THE ELECTRIC FIELD GRADIENT IN CRYSTAL

The simplest approach for calculating the EFG at a lattice site in a crystal structure is that of the crystal field theory. In this approach the EFG is calculated relative to a central ion or nucleus chosen as the centre of the co-ordinate axis. Charges surrounding the central ion are then treated as point charges. The EFG at the origin is consequently made up of contributions from two fundamental sources, namely:

i) Charges from distant atoms and ions surrounding the central ion. Their contribution is known as the ligand/lattice contribution to the EFG.

ii) The electron distribution around the central ion itself. This is known as the valence contribution to the EFG.

THE LIGAND/LATTICE CONTRIBUTION TO THE EFG

This contribution consists of a direct and indirect effect. The direct effect is a consequence of the field of the surrounding ions at the origin.

For a collection of n charges the net direct ligand contribution to the EFG at a reference lattice site will be the elementwise sum of the contributions to the EFG by individual charges. That is

$$(V_{ij})_L = \sum_{n}^{k} q_k (3x_{ki}x_{kj} - r^2\delta_{ij})/r^5 \quad 2.3.1$$

where q_k is the charge and (x_{k1}, x_{k2}, x_{k3}) is the position of the k^{th} atom.

Due to the symmetrical nature of the EFG tensor, the direct ligand contribution to the EFG tensor for a charge distribution with cubic symmetry is zero. The indirect ligand contribution consists of the effect of the surrounding ions on the ambient electron distribution in the reference ion.

Studies by Sternheimer (1950) have shown that the electron distribution of the central atom is distorted by the presence of non cubic charge distribution in the surrounding crystal lattice. This phenomenon is known as "Sternheimer anti-shielding" and is compensated for by multiplying the (V_{ij}) by the factor $(1-\gamma_\infty)$ where γ_∞ is known as the Sternheimer anti-shielding factor.

THE VALENCE CONTRIBUTION TO THE EFG TENSOR

The valence contribution is computed by summing up the mean contribution to the EFG due to each of the

central ion electrons. This implies taking the expectation value of the quantity, $-e(3\cos^2\theta-1)r^{-3}$ for each electron in the valence orbital state $|i\rangle$ i.e.

$$(V_{zz})_{val} = -e\sum_i \langle i|3\cos^2\theta-1|i\rangle \qquad 2.3.2$$

For a continous charge distribution;

$$(V_{zz})_{val} = \int_\tau \rho(r,\theta,\phi)(3\cos^2\theta-1)r^{-3}d\tau \qquad 2.3.3$$

Studies by Sternheimer (1950) have shown that this value of the EFG at the origin has to be corrected. This arises from the fact that due to the screening of valence electrons from the nucleus by the inner shell electrons, the full effects of the valence electrons are not felt at the nucleus. Hence $(V_{zz})_{val}$ has to be corrected by multiplying it with a factor (1-R) where R is known as Sternheimer shielding factor. In most chemical applications only the p and d electrons are considered. The f-electrons rarely participate in chemical bonding, while the s electrons have a spherically symmetric distribution.

For a spherically symmetric distribution,

$$\rho(r,\theta,\phi) = \rho(r)$$

$$\text{thus } (V_{zz})_{val} = \int_0^\infty \rho(r)dr \int_0^{2\pi} d\phi \int_0^{\pi} (\cos^2\theta-1)\sin\theta d\theta \qquad 2.3.4$$

$$= 0 \text{ from the } \theta \text{ integration}$$

Thus the s electrons do not contribute directly to the EFG. There is however an indirect contribution due to Sternheimer shielding and anti-shielding phenomena.

The net EFG due to valence and ligand effect is the given by

$V_{zz}=(1-\gamma_\infty)(V_{zz})_L+(1-R)(V_{zz})_{val}$ 2.3.5

where γ_∞ and R are as defined earlier. $(V_{zz})_{val}$ and $(V_{zz})_L$ are the valence and ligand contribution to the EFG respectively.

The asymmetry parameter η is defined by

$\eta(V_{zz})=V_{xx}-V_{yy}=(1-\gamma_0)(V_{zz})_L+(1-R)(V_{zz})_{val}\eta_{val}$ 2.3.6

where

$(V_{xx})_{val}=-e\sum_i\langle limi|3\sin^2\theta\cos^2\phi-1|limi\rangle\langle r^{-3}_i\rangle$ 2.3.7

$(V_{yy})_{val}=-e\sum_i\langle limi|3\sin^2\theta\sin^2\phi-1|limi\rangle\langle r^{-3}_i\rangle$ 2.3.8

The EFG calculations above are only applicable to systems that can satisfactorily be represented with the crystal field theory, such as ionically bonded systems.

2.4 THE ELECTRIC FIELD GRADIENT IN METALS AND ALLOYS

The method of crystal field theory calculations are not applicable to the study of electric field gradients in metals and Alloys.

This is because the assumption that the surrounding ions are treated as point charges is not applicable in this case. The valence electrons in metals and alloys are non-localised, as such, it is impracticable to assign position co-ordinates to them. The unique distribution and interaction of electrons in metalic and alloy systems have to be taken into account in EFG calculations.

In alloy systems formed by the introduction of an impurity atom into a substitutional host lattice site, the impurity atom perturbs the host lattice configuration in two main ways:

i) There is lattice relaxation/dilation as a result of difference in size between the host and impurity atoms. This leads to loss of cubic symmetry in an initially cubic system. Thus a non-vanishing EFG exists at the nuclear sites. This effect is known as the "size effect" in EFG calculations.

ii) The ambient electron distribution in the atoms is perturbed due to the difference in valencyybetween the host and impurity atoms. The resulting non-symmetric distribution of charge leads to a non-vanishing EFG at nuclear sites. This effect is known as the "valence effect" in EFG calculations.

The success of any EFG theory on alloys depends on the accuracy to which the two effects above and other effects caused by the introduction of an impurity in a metallic host are reduced. In the following chapter, a review is made of the development of EFG theory in metallic alloys.

CHAPTER III

THEORETICAL CALCULATIONS ON THE EFG IN CUBIC METALS AND ALLOYS

Pioneering work by Bloembergen and Rowland (1953) on the studies of EFG distribution in cubic metals had been mainly experimental. They carried out Nuclear Magnetic Resonance studies in non-magnetic dilute alloys of copper. These experiments showed that the intensity of NMR signals in metallic Cu^{63} decreases rapidly when small quantities of other elements were alloyed with it.

These unexpected experimental results were explained in terms of the nuclear quadropole interactions. In a pure metal with perfect cubic symmetry, the nuclear quadropole interaction is zero. The introduction of an impurity destroys this cubic symmetry and electric field gradients will appear at nuclear sites. The nuclear magnetic resonance absorption will be perturbed by the resulting second order electric quadropole interactions. The magnitude of these electric field gradients is such that they act on nuclear quadropole moments as far as the sixth and seventh nearest neighbours.

In accounting for these electric field gradients, Bloembergen and Rowland (1953) assumed a screened Coulomb potential based on the Thomas-Fermi model of the form,

$$V = e/r . e^{-kr} \qquad 3.1.1$$

where $K = 10^8 cm^{-1}$

Differentiating this expression twice,

$eq = \partial F_r / \partial r = (2e/r^3) e^{-Kr}(1+Kr+1/2K^2r^2)$ 3.1.2

Using this expression they calculated the EFG of α - Brass (80%Cu; 20%Zn). The calculations showed that Zn atom will produce a gradient at the 1st nearest Cu nuclear site ($r = 2.55 \times 10^{-8}$ cm) of

$$q = 6.4 \times 10^{22} \ cm^{-3} \qquad 3.1.3$$

This is much smaller than the experimental limiting value of

$$q > 4.8 \times 10^{23} \ cm^{-3} \qquad 3.1.4$$

for the NMR line to escape detection.

Kohn and Vosko (1960) discarded the Coulomb type screened potential which gives an exponentially decreasing charge density.

They adopted the long range screening proposed by Friebel (1952). That is a screening charge that falls off much more slowly with distance, namely as r^{-3} multiplied by a sinusoidal function of r.

They derived a simple expression for the induced electric field gradients q valid at large distances from the impurity, namely:

$$q = 8\pi/3 \ \alpha(K_F) \rho_{na}(r) \qquad 3.1.5$$

where $\alpha(K_F)$ is the Bloch enchancement factor which takes into account the orthogonality of the perturbed free-electron-like states to the occupied core orbitals of the host ion. The asymptotic expression for induced charge density is given by

$$\rho_{na}(r) = A\cos(2K_F r + \theta)/r^3 \qquad 3.1.6$$

where A and θ are, respectively the amplitude and

phase factors. These parameters depend on the strength of the impurity potential through scattering phase shifts at Fermi level.

With this formulation Kohn and Vosko were able to explain the qualitative features concerning wipe out numbers and dependence of EFG on impurity valence.

Kohn and Vosko (1960), Blandin and Friedel (1960) and Rowland (1960) in their theories on EFG found only minor correlations between the strains expected around different solutes, and their effectiveness in reducing the resonance signals. They therefore considered the size effect contribution to the EFG neglible. These theories that considered the size effect contribution insignificant were then known as valence-effect theories.

With the advent of more sophisticated experimental techniques, results obtained showed that the EFG's were much greater than that predicted by the best valence effect theories. Furthermore, the valence effect theories failed to account for lack of cylindrical symmetry of EFG at first nearest neighbour (1nn) sites, contradicting experimental data which had shown that η varied virtually over the entire range $0 < \eta < 1$. Ragalyn, Fashkin and Harrison (1961) were able to develop a quantitative theory to show that the size effect contribution to the EFG tensor was not negligible.

They derived their expression for the size effect by assuming an isotropic field-gradient-strain relationship. That is, a linear point relationship is assumed between the elastic strain tensor and the

electric field gradient tensor. Thus the principal axes of the field gradient quadric and the strain quadric always coincide. This point relationship is expressible in terms of a fourth order field-gradient-strain tensor Fmn, where m,n take values 1 through 6 in the voigt notation, of elasticity theory.

Using a displacement vector

$$\vec{u} = (\vec{r}/r^3)(\Delta V/4\pi\gamma_E) \qquad 3.1.7$$

where $\vec{u}$ is the displacement of a point defect in a homogenous elasic continuum, at a position defined by the vector, r.

ΔV is the change in volume per impurity

γ_E is expressed as $\gamma_E = 3(1-\bar{\sigma})/(1+\bar{\sigma})$

$\bar{\sigma}$ is the poisson ratio.

They derived an expression for the size effect EFG for an fcc crystal as

$$q_\lambda = 1/e(V_{zz}-1/3\nabla^2 V) = -(27/2^{3/2}\pi\gamma_E)a^{-1}(da/dc)r^{-3}\lambda \qquad 3.1.8$$

1/a. da/dc is the fractional change in lattice parameter per unit concentration of impurity λ is a dimensionless adjustable parameter. Combining the size effect calculations based on their theory and the valence effect contribution based on Kohn and Vosko (1960) theory, Sagalyn et al got better agreement with experimental results than previous theories. The next major step in the development of EFG theory was by Sagalyn and Alexander (1977). They used a unique geometrical model to account for the valence effect contribution to the EFG. They were able to show that at near neighbours to the impurity, contributions from

outside the host atomic sphere have the same order of magnitude as contributions for the screening charge inside the host atomic sphere. Previous valence effect theories had predicted a contribution of the order of 10 per cent. The Sagalyn and Alexander set up is as in Figure 1.

The FFG contributions due to each of these regions is as outlined below.

REGION C

$$q^{c}_{11} = \alpha 4\pi K_F^3 \left(\frac{2/3 A\cos(2k_F R+\phi)}{(k_F R)^3} + \frac{2/3 k_F B\cos(2k_F R+\xi) - A\sin(2k_F R+\phi)}{(k_F R)^4} \right) \qquad 3.1.9$$

where K_F is the Fermi wave vector

α is the Bloch enchancement factor defined earlier.

The coefficients A, B and phase constants ϕ and ξ may be determined in terms of the Hurd-Gordon phase shifts. The term with R^{-3} was derived by Kohn and Vosko (1960) and by Blandin and Friedel (1960). The terms with R^{-4} were derived by adding the Alfred Van-Ostenberg preasymptotic screening charge term to the asymptotic screening

REGION A

$$q^{a}_{11} = -(1/e)2_1 \cdot 2_1(1-\gamma_\infty)/R^3 \qquad 3.1.10$$

where

2_1 is the nei charge in region a

γ_∞ is the Sternheimer anti-shielding factor.

$$2_1 = -e\int_{R-d/2}^{\infty} \delta n(r) dr \qquad 3.1.11$$

where $\delta n(r)$ is in the form given by Alfred and Van Ostenberg (1969)

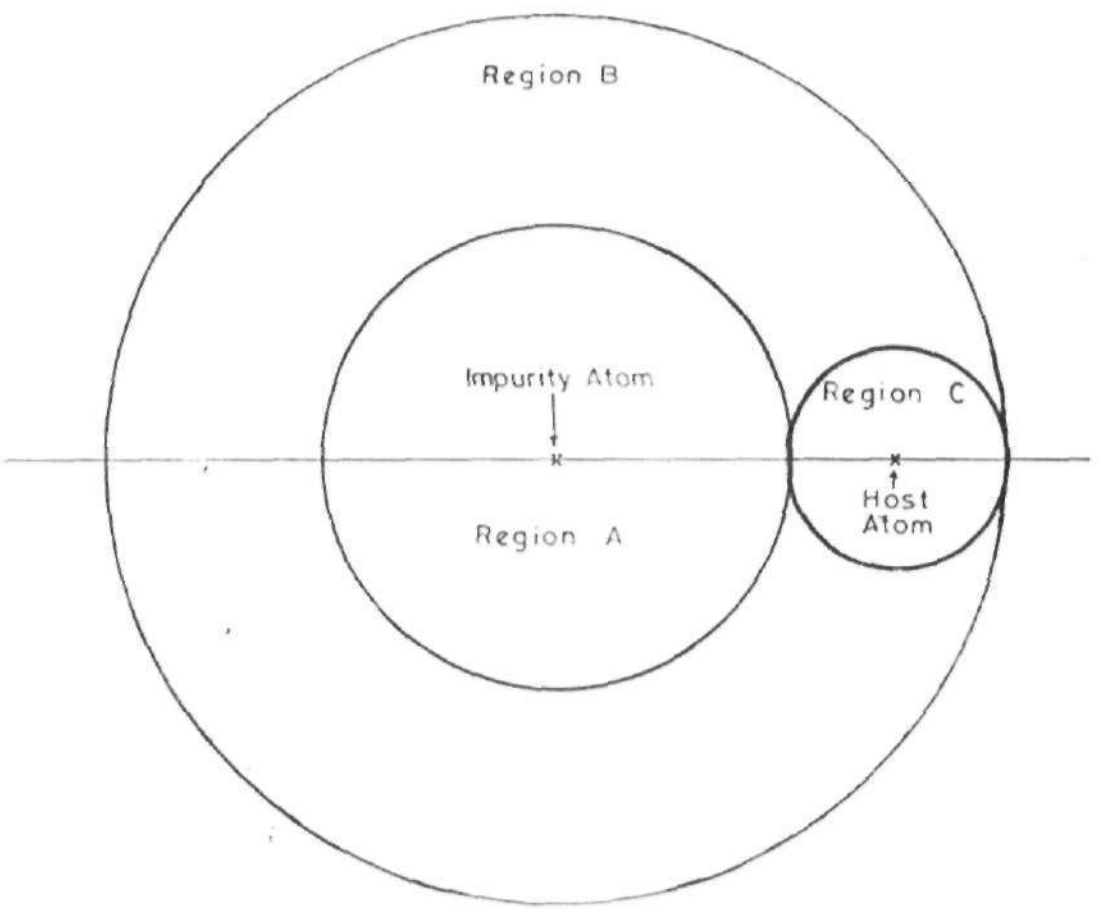


FIG.1: Geometry used in calculation of valence effect EFG by Sagalyn and Alexandex (1977). The host–impority seperation is denoted by R.

$$\delta n(r) = A\cos(2K_F r+\psi)/r^3 + B\cos(2K_F r+\xi)/r^4 \qquad 3.1.12$$

where the coefficients and phase constants are the same as in equation 3.1.9 above.

For region B they derived

$$q^B_{11} = \delta 4\pi\hbar K_F^3 (1-\gamma_\infty)\left[\frac{\sin K_F d}{(K_F d)^3} - \frac{\cos(K_F d)}{(K_F d)^2}\right]\frac{\cos(2K_F R+\phi)}{(K_F R)^3} \qquad 3.1.13$$

all terms in equation 3.1.10 are as defined earlier.

Thus the net valence effect EFG due to the three regions is

$$q^V_{11} = q^A_{11} + q^B_{11} + q^C_{11} \qquad 3.1.14$$

For their size effect calculations, Sagalyn and Alexander (1977) were able to distinguish three effects which give rise to the size effect contribution.

Two of these effects affect the valence effect calculations, and, are thus, indirect.

The first indirect effect is that the host atoms in the alloy will occupy positions different from those that they will occupy in the real lattice. Thus the nearest neighbour distances from the impurity would have to be determined and valence effect calculations carried out at such distances. The second indirect effect is the effect of the Blatt correction on the scattering phase shifts and consequently the induced electron densities. Sagalyn and Alexander (1977) however used the Hurd-Gordon (1968) scattering phase shifts, where account of the Blatt correction is taken.

The third effect is direct. This is based on the postulate that the EFG of a lattice site contains a term proportional to the local strain. Sagalyn and Alexander (1977) continued with the formulation of

Sagalyn et al (1961) but with an important modification. They dropped the isotropy condition adopted by Sagalyn et al (1961). Instead they adopted a point charge model which leads to a non-zero asymmetry parameter at first nearest neighbour sites. This assumption is in better agreement with experimental values than the isotropy condition which leads to zero asymmetry parameter at first nearest neighbour sites. The results of size effect calculations by Sagalyn and Alexander (1977) are as follows:

$$q^{S}_{xx} = \frac{54(2)^{1/2}}{16\lambda\gamma_\infty}\,\frac{1}{a}\,\frac{da}{dc}\,\frac{\lambda}{d^3_1} \qquad 3.1.15$$

$$q^{S}_{zz} = -\frac{81(2)^{1/2}}{16\lambda\gamma_\infty}\,\frac{1}{a}\,\frac{da}{dc}\,\frac{\lambda}{d^3_1} \qquad 3.1.16$$

$$q^{S}_{zz} = \frac{27(2)^{1/2}}{16\lambda\gamma_\infty}\,\frac{1}{a}\,\frac{da}{dc}\,\frac{\lambda}{d^3_1} \qquad 3.1.17$$

and at 2NN site

$$q^{S}_{zz} = q^{S}_{xx} = -2q^{S}_{yy} = -2q^{S}_{xx} \qquad 3.1.18$$

$$= -\frac{108(2)^{1/2}}{16\lambda\gamma_\infty}\,\frac{1}{a}\,\frac{da}{dc}\,\frac{\lambda}{d^3_2} \qquad 3.1.19$$

where $1/a.da/dc$, λ and γ_∞ are as defined in eqns. 3.1.7 and 3.1.8, d_1 and d_2 are the first and second nearest neighbour distances respectively. The principal values of the total EFG tensor at Mn site is then

$$q_{xx} = q^{V}_{xx} + q^{S}_{xx} = -1/2q^{V}_{zz} + 2q^{S}_{zz} \qquad 3.1.19$$

$$q_{yy} = q^{V}_{yy} + q^{S}_{yy} = -1/2q^{V}_{zz} - 3q^{S}_{zz} \qquad 3.1.20$$

$$q_{zz} = q^{V}_{zz} + q^{S}_{zz} \qquad 3.1.21$$

Sagalyn and Alexander using the formulation briefly described

CHAPTER IV

THE PONNAMBALAM-JENA THEORY OF THE EFG

Ponnambalam and Jena (1981) published a new formulation for electric field gradient calculations. The detailed derivations of the valence and size effect contributions are presented in the following sections.

4.1 The valence effect contribution

For the valence effect derivation the jellium model is assumed, where, the metal is described by a uniform positive background charge together with an interacting electron gas.

If the impurity atom is placed in a substitutional lattice site and taken as the origin, then the spatial distribution of positive charges in the host metal is given by

$$\rho_+(r) = Z_i e\delta(r) + n_e e\theta(r-R_{ws}) \qquad 4.1.1$$

where

R_{ws} is the radius of the Wigner Seitz cell

Z_i is the atomic no. of the impurity

n_e is the average number density of the host medium

e is the magnitude of the electron charge

$\theta(r)$ is the heaviside function which ensures that impurity occupies a substitutional site. It is defined as

$$\theta(\tau) = \begin{cases} 0 & \tau<0 \\ 1 & \tau>0 \end{cases} \qquad 4.1.2$$

The corresponding electron charge density distribution is given by

$$\rho_-(r) = -e\delta n(r) - n_e e \qquad 4.1.3$$

$\delta n(r)$ is the perturbation on the ambient electron

distributions induced by the impurity.

The total charge density is

$$\rho(r) = \rho_+(r) + \rho_-(r) \qquad 4.1.4$$

Satisfies the charge neutrality condition:

$$\int_0^\infty \rho(r)d\tau = 0 \qquad 4.1.5$$

assuming a spherically symmetric distrbution of charge around the impurity atom, the potential for r>Rws is given by

$$V(r) = e/r\int_0^r \rho(r')d^3r' + e/r\int_r^\infty \rho(r')d\tau' \qquad 4.1.6$$

$$V(r) = e/r\left[Z_x\int_0^r \delta(r')d\tau' - n_\infty\int_0^r \beta(Rws-r')d\tau'\right] - e/r\int_0^r \delta n(r')d^3r' - -e\int_r^\infty \delta n(r')d\tau' \qquad 4.1.7$$

The first term of equation 4.1.7 arises from the impurity atom placed at the origin.

The second term is the electron contribution from the Wigner Seitz cell of the impurity atom.

The third term is the contribution from the perturbed electron density in the region $0 < r' < r$

The fourth term arises from the contribution of the perturbed electron density from $r' > r$

The equation above may be rewritten as:

$$V(r) = e/rZ_x - e/rn_\infty\int_0^r \beta(Rws-r')d\tau' - e/r\int_0^r \delta n(r')d\tau' - \int_r^\infty \frac{\delta n(r')}{r'}d\tau' \qquad 4.1.8$$

$$e/rZ_x - e/rn_\infty\int_0^r \beta(Rws-r')d\tau' = eZeff \qquad 4.1.9 \qquad 4.1.$$

where

$$Zeff = Z_x - Z_M(1 + 3/\gamma_m\, 1/a.da/dc) = \delta n(r')d\tau' \qquad 4.1.10$$

Note that this form of Zeff already takes into account the Riali correcion.

where Z_x and Z_M are valence of impurity and host respectively

$\gamma_m = 3(1-\sigma)/(1+\sigma)$

where σ is Poisson's ratio

1/a.da/dc is the frartional change in lattice constant per

unit atomic concentration of impurity. Thus,

$$V(r) = eZeff - \frac{e}{r}\int_0^r \delta n(r')d^3r' - e\int_r^\infty \delta n(r')d^3r'$$

differentiating eqn. (11) twice gives 4.1.11

$$\frac{d^2V(r)}{dr^2} = \frac{2e}{r^3}\left[Zeff - Z(r)\right] + 4\pi e\delta(r) \qquad 4.1.12$$

where

$$Z(r) = \int_0^r \delta n(r')d^3r'$$

Since the potential is assumed to have spherical symmetry

$$\delta^2V/\delta z^2 = q(3\cos^2\beta - 1)r^{-3} = q(2\cos^2\beta - \sin^2\beta)r^{-3}$$

$$\cos^2\theta\, d^2V/dr^2 + \sin^2\theta\, 1/r\, dV/dr \qquad 4.1.14$$

by choosing $\beta=0$ to be along direction connecting the host and impurity atoms,

$$V_{zz} = \delta^2V/\delta z^2 = d^2V/dr^2 \qquad 4.1.15$$

Poisson's equation for r>Rws

$$\nabla^2V = 4\pi e\delta n(r) \qquad 4.1.16$$

where $\delta n(r)$ is as defined in eqns 4.1.1–4.1.4

The traceless EFG tensor due to electron screening is given by

$$eq_{zz} = V_{zz} - 1/3\nabla^2V \qquad 4.1.17$$

Substituting equations 4.1.12 – 4.1.16 in 4.1.17 gives

$$q_{zz}(r) = 8\pi/3\delta n(r)\ 2/r^3(Zeff - Z(r)) \qquad 4.1.18$$

and taking the Bloch enhancement factor into account

$$q^{\vee}{}_{zz} = 8\pi/3\Omega(K_e)\left[\delta n(r)) + 3/4\pi r^3(Zeff - Z(r)\right] \qquad 4.1.19$$

4.2 THE SIZE EFFECT CONTRIBUTION TO THE EFG

The size effect contribution is made up of the 'direct' and 'indirect' size effects. The 'indirect' effect consists of recalculating the valence effect contribution at the new displaced nearest neighbour sites. The difference in size and electrostatic potential between host

comparing equations 4.2.5 and 4.2.2

The condition for isotropy in a cubic system is

$$C_{11} - C_{12} = 2C_{44} \qquad 4.2.6$$

Assuming that the elastic field at nn sites is isotropic, putting equation 4.2.1 in 4.2.2

The equilibrium condition is given by

$$\tan(2K_F r+\Phi) = (4K_F^2 r^2 - n(n-3))/4(n-2)K_F r \qquad 4.2.7$$

Thus, the phase angle 0 of equation 4.2.1 may be calculated for various nn sites using equation 4.2.7. It is worth noting that Φ is not an adjustable parameter but is fixed by the equilibrium condition.

DETERMINATION OF THE EXPONENT n

Since the displacement $\vec{u}$ in equation 4.2.1 has to decrease with disiance; $n > 2$

when $n = 2$ this implies $u = 0$ or $4K_F^2 r^2 = -2$

Both these conditions are physically unacceptable.

Thus n has values $n > 3$

Using equation 4.2.1 to find the relative strength of displacement between the ith and jth nn

$$\frac{u(d^o_i)}{u(d^o_i)} = \frac{\cos(2K_F d^o_i + \Phi_i)}{\cos(2K_F d^o_j + \Phi_j)} \left(\frac{d^o_j}{d^o_i}\right)^{n-1} \qquad 4.2.8$$

where d^o_i and d^o_j, are respectively, the distances of the i^{th} and j^{th} neighbour from the impurity in the absence of relaxation. From the equilibrium condition equation 4.2.7, it can be shown that:

$$\frac{\cos(2K_F d^o_i + \Phi_i)}{\cos(2K_F d^o_j + \Phi_j)} \simeq \frac{d^o_j}{d^o_i} \qquad 4.2.9$$

combining eqs. 4.2.8 and 4.2.9 gives

$$\frac{u(d^0_i)}{u(d^0_j)} = \left(\frac{d^0_i}{d^0_j}\right)^n \qquad 4.2.10$$

taking i = 1 and j = 2, that is, first and second nearest neighbours respectively

equation 4.2.10 gives

$$\frac{u(d^0_i)}{u(d^0_j)} \quad \begin{matrix} 2^{n/2} \text{ for simple cubic and fcc lattice} \\ (4/3)^{n/2} \text{ for bcc lattice} \end{matrix} \qquad 4.2.11$$

On comparison of the results of 2 eq. 4.2.11 and computer simulation studies, of Girifalco and Weizer (1960). The best choice for n is found to be

n = 3 for fcc 4.2.12

n = 6 for bcc

DETERMINATION OF THE AMPLITUDE, A, OF THE DISPLACEMENT VECTOR

The Amplitude A in equation 4.2.1 may be determined by using the relation (Blatt, 1950)

$$\Delta Z = Z^*_i - Z^*_H(1-\delta V/\Omega) = Z^*_i - Z^*_H(1+3/\gamma_G \cdot 1/a.da/dc$$

$$\delta V/\Omega = 3/\gamma(1/a.da/dc) \qquad 4.2.13$$

$Z^*_i(Z^*_H)$ is the valence of impurity (host) atom. $\delta V/\Omega$ is the fractional change in volume of cell occupied by the impurity. All other terms are as defined earlier in equation 4.1.10 values of $1/a.da/dc$ and γ_G are obtained from tabulated experimental values (Pearson, 1958).

Thus all the parameters required to calculate the distance between the impurity and the relaxed inn host atom are now defined.

4.3 DERIVATION OF THE EXPRESSION FOR THE 'DIRECT' SIZE EFFECT

The components of the symmetry elastic strain tensor are given by

$$\epsilon_{ij} = \tfrac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right); \qquad i,j=1,2,3 \qquad 4.2.14$$

where x_1, x_2, x_3 are cartesian co-ordinates and

$$u = u_{x1} + u_{x2} + u_{x3} \qquad 4.2.15$$

using equation 4.2.1 and the equilibrium condition 4.2.8

$$\epsilon_{xx} = \frac{A\cos(2K_2 r+\phi)}{2r^3}\left[\frac{2(n-2)-4K_2^2x^2-n(n-1)x^2/r^2)}{(n-2)r^{n-3}}\right]$$

$$\epsilon_{xy} = -\frac{A\cos(2K_2 r+\phi)}{2r^3}\left[\frac{n(n-1)-4K_2^2r^2)}{6(n-2)r^{n-5}}\right]\frac{6xy}{r^2} \qquad 4.2.16$$

The other components of ϵ_{ij} may be obtained from equation 4.2.16 by cyclic permutation of x, y, and z.

The strain contribution to the EFG tensor is relaxed to ϵ_{ij} by a fourth ranked tensor F.

assuming cubic symmetry around the host atom, the stress-strain relation in a cubic crystal is

$$\tau_{ij}=\delta_{ij}((C_{11}-C_{12})\epsilon_{ij}+C_{12}\Sigma\epsilon_{xx}))+(1-\delta_{ij})2C_{44}\epsilon_{ij} \quad 4.2.17$$

Thus

$$V_{ij}=\delta_{ij}((F_{11}-F_{12})\epsilon_{ij}+F_{12}\Sigma\epsilon_{xx})+(1-\delta_{ij})2F_{44}\epsilon_{ij} \quad 4.2.18$$

The traceless EFG tensor is given by

$$q_{ij} = V_{ij} - 1/3\delta_{ij}\nabla^2 V \qquad 4.2.19$$

substituting eqn. 4.2.18 in 4.2.19 gives

$$eq_{xx} = (F_{11}-F_{12})(\epsilon_{xx}-1/3\Sigma\epsilon_{xx}) \qquad 4.2.20$$

$$eq_{xy} = F_{44}(2\epsilon_{xy})$$

combining 4.2.16 and 4.2.20 then gives

$$q^s_{ij} = L_V\left[\delta_{ij} + (1-\delta_{ij})\frac{2F_{44}}{(F_{11}-F_{12})}\right](2\delta_{ij} - 6\frac{x_i x_j}{d_V^2}) \qquad 4.2.21$$

with

$$L_v = \frac{(F_{11}-F_{12})}{e}\cdot\frac{A\cos(2K_F d_v + \phi_v)}{2d_v^3}\left[\frac{n(n-1)+4K_F^2 d_v^2}{6(n-2)d^{n-3}}\right] \qquad 4.2.22$$

d_v is the relaxed equilibrium distance of V^{th} nn

δ_{ij} is the Kronecker delta.

The components of the F tensor are obtained from Faulkner's (1969) point charge model, namely,

$$F_{11}-F_{12} = -3F_{44} = 9\lambda e/d_1^3 \qquad 4.2.23$$

where d_1 is the first nearest neighbour distance λ is an adjustable dimensionless strain coupling parameter which is designed to correct for the fact that the solid is idealized by point charges.

putting equation 4.2.23 in 4.2.21 and 4.2.22 and putting n=3 gives

$$q^s_{ij} = L_v(\delta_{ij}-2/3(1-\delta_{ij}))(2\delta_{ij}-6x_ix_j)/d_v^2 \qquad 4.2.24$$

where

$$L_v = \frac{4.5\lambda}{d_1^3}\frac{A\cos(2K_F d_v + \phi_v)}{d_v^3}(1+2/3K_F^2 d_v^2) \qquad 4.2.25$$

Equations 4.2.24 and 4.2.25 represent the strain induced contribution to the EFG as derived by Ponnambalam and Jena.

The equations derived in this chapter will be used for the calculations in this work. It is worthy to note that the valence effect contribution derived by Ponnambalam and Jena was not based on any of the previous valence effect theories. The size effect derivation however closely follows the method of Sagalyn and Alexander (1977) except for the difference in the displacement vector. The Ponnambalam and Jena (1981) method has been tested for various systems with favourable results (Ponnambalam and Jena, 1984, 1985, 1986), in this work it is applied to dilute alloys of copper. The detailed calculations including numerical values used and results obtained are presented in the next chapter.

CHAPTER V

ELECTRIC FIELD GRADIENT CALCULATIONS USING THE PONNAMBALAM-JENA THEORY

5.1 VALENCE EFFECT CALCULATIONS

Calculations of the induced electron charge around impurities:

The continuum model is assumed for the valence effect calculation. In this model, the effect of the lattice ions on the electron distribution is neglected and the positive background is approximated by a homogenous density distribution number. The respective electron distributions around the host and impurity atoms occupying the substituiional site are calculated by representing the external perturbation as

$$n^{H}_{ext}(r) = Z_H\delta(r) + n_0\Phi(r-R_{WS})$$
$$n^{I}_{ext}(r) = Z_I\delta(r) + n_0\Phi(r-R_{WS}) \qquad 5.1.1$$

where Z_H and Z_I are, respectively, the host and impurity atomic numbers.

The electrostatic potential caused by this external perturbation is given by

$$\nabla^2\phi^H(r) = 4\pi e(n^H_{ext}(r)-n'_H(r))$$
$$\nabla^2\phi^I(r) = 4\pi e(n^I_{ext}(r)-n'_I(r)) \qquad 5.1.2$$

where $n^H(r)$ and $n^I(r)$ are respectively the corresponding electron number density distribution around the host and impurity atom.

The induced charge is obtained in the density functional theory by solving the variational equations.

$$\left\{-\frac{\hbar^2\nabla^2}{2m} + V_{eff}[n(r), r]\right\}\psi_i(r) = \epsilon_i\psi_i(r) \qquad 5.1.3$$

$$n(r) = \sum_i^{occ} |\psi_i(r)|^2 \qquad 5.1.4$$

for both the host and impurity atoms seperately.

The effective potential Veff in eqn. (3) is obtained by adding the electrostatic potential & to the exchange correlation potential Vxc in the local density approximation. Equations 5.1.2 and 5.1.3 are then solved self consistently.

The quantity relevant in the valence effect EFG calculation is, however, the difference between the induced charge around the impurity and host atom, namely,

$$\Delta n(r) = n^I(r) - n^H(r) \qquad 5.1.5$$

where $n_I(r)$ and $n_H(r)$ are the impurity and host electron densities respectively.

An exact method for calculating this density is the density functional theory.

In this work, an attempt was made to calculate the electron densities using the energy density formalism. Unfortunately, self consistency was not attained.

Ponnambalam and Jena (1986) reported that they could not attain convergence for $n^I(r)$ for the copper host, due to the effect of the d-electrons which tend to oscillate between the bound and scattering states.

Thus for such cases the Alfred and Van Ostenberg (1969) expression is used. In this formulation $\Delta n(r)$

is expressed as an infinte series in terms of scattering phase shifts and their derivations.

The preasymptotic form

$$\delta n(r) = A\cos(2K_F r + \varphi) r^{-3} + B\cos(2K_F r + \xi) r^{-4} \qquad 5.1.7$$

is used in this work.

where A and B are amplitude coefficients φ and ξ are phase constants.

A, B, φ and ξ may be determined using the Hurd-Gordon phase shifts and their derivatives in Alfred-Van-Osterberg equations namely;

$$A\cos\varphi = \frac{-\sum_{\ell=0}^{\infty}(2\ell+1)(-1)^{\ell}\sin[2\eta_\ell(\epsilon_F)]}{4\pi^2} \qquad 5.1.8$$

$$A\sin\varphi = \frac{-\sum_{\ell=0}^{\infty}(2\ell+1)(-1)^{\ell}\sin^2[\eta_\ell(\epsilon_F)]}{2\pi^2} \qquad 5.1.9$$

$$B\cos\xi = \frac{\sum_{\ell=0}^{\infty}(2\ell+1)(-1)^{\ell}\left[\frac{2\ell(\ell+1)}{k_F}\sin^2(\eta_\ell(\epsilon_F)) + \left(\frac{\partial\eta_\ell(\epsilon_k)}{\partial k}\right)_{k_F}\sin[2\eta_\ell(\epsilon_F)]\right]}{4\pi^2}$$

$$B\sin\xi = \frac{\sum_{\ell=0}^{\infty}(2\ell+1)(-1)^{\ell}\left[\frac{\ell(\ell+1)}{k_F}\sin(2\eta_\ell(\epsilon_F)) + \left(\frac{\partial\eta_\ell(\epsilon_k)}{\partial k}\right)_{k_F}\sin[2\eta_\ell(\epsilon_F)]\right]}{4\pi^2}$$

where $\eta_\ell(\epsilon_F)$ and $\frac{\partial\eta_\ell(\epsilon_k)}{\partial k}$ are the scattering phase shifts and their derivaiives at the Fermi level.

The Hurd-Gordon (1968) phase shifts used are reproduced in Appendix I.

The Z-terms in equation (5.1.6) had been expressed by Ponnambalam and Jena (1986) as

$$Z_{eff} - Z(r) = 4\pi\left[-A\cos\varphi\, Ci(x) - A\sin\varphi\left\{\pi/2 - Si(x)\right\}\right.$$
$$\left. + 2k_F B\cos\xi\left\{\frac{\cos x}{x} + Si(x) - \pi/2\right\} - 2k_F B\sin\xi\left\{\frac{\sin x}{x} - Ci(x)\right\}\right]$$

5.1.12

where A, B, ϕ and I are as earlier defined.

$X = 2K_F r$, while Si(x) and Ci(x) are the sine and cosine integrals given by

$$Si(x) = \int_0^x \frac{\sin u}{u}\,du \qquad 5.1.13$$

$$Ci(x) = \int_0^x \frac{\cos u}{u}\,du \qquad 5.1.14$$

The values of the sine and cosine integrals for relevant x values corresponding to 1nn distances were obtained from Abramowitz and Stegun (1972). For the 2nn distances, the asymptotic expression

$$Ci(x) = \sin x/x - \cos x/x^2 \qquad 5.1.15$$

and

$$Si(x) = \cos x/x - \sin x/x^2 + \pi/2 \qquad 5.1.16$$

due to Gagalyn and Alexander (1977) were used.

The terms above, (induced charge density and Z-terms) were calculated at the displaced sites. The displaced 1nn positions were evaluated with the use of the experimentally derived values of $\delta V/\Omega$ that is the fractional change in size of the cell occupied by impurity. The values used in this work were obtained from Blatt (1957). The new displaced host sites for the 1nn were evaluated using the following simple relationship,

$$d_{new} = (r^3(1+\delta v/\Omega))^{1/3})/2 + 4.830 \text{ (a.u)} \qquad 5.1.17$$

where d_{new} is the new displaced host site.

r is the radius of the cell occupied by copper atom (= 2.55×10^{-8} cm, Blatt (1957)).

4.830 a.u is the relaxed 1nn distance for the pure copper crystal.

For the 2nn valence effect contribution, the same procedure outlined above is followed. The calculation of the displaced host sites is however different.

Calculations were done for the two values of $\xi(K_F)$ given by Ponnambalam and Jena (1986); that is $\xi = 34.0$ and $\xi=25.6$. The results of these calculations showing the Z term and total valence contributions are given in Tables 1 and 2.

5.2 SIZE EFFECT CALCULATIONS

As discussed earlier, the size effect introduces three contributions to the EFG tensor. Two indirect effects and one direct effect.

The first indirect effect, which is the displacement of host atoms due to the presence of impurity, has already been taken into account and evaluated under the valence effect calculations. The second indirect contribution, is the effect of the Blatt correction on the induced electron density distribution. This effect is taken care of by the use of the Hurd-Gordon scattering phase shifts. These Hord-Gordon coefficients take into account the Blatt correction in their derivation.

Thus, this leaves only the direct effect contribution to be evaluated. The expression for the direct effect is given by equations 4.7.21 and 4.7.22 namely:

$$q^{\infty}_{ij}=L_v(\delta_{ij}-2/3(1-\delta_{ij}))(2\delta_{ij}-\delta x_i x_j)$$

where

$$L_v=\frac{4.5\lambda}{d_1^5}\frac{A\cos(2K_F d_v+\phi_v)}{d_v^3}(1+2/3K_F d_v)$$

where d_v is the v^{th} nn distance

λ is a dimensionless adjustable parameter (strain

Table 1 Displaced positions of host atoms and valence effect contribution to the FFG for 1 nn distance. $\bar{\alpha}$ = 25.6; δn, Z-term in units of $(10^{3}nm^{-3}$

Impurity Element	Displacement	δu-term	Z-term	Total
Zn	4.864	-0.059	-0.026	-0.086
Ga	4.876	-0.112	-0.067	-0.179
Ge	4.886	-0.437	-0.073	-0.510
As	4.908	-1.034	-0.010	-1.044
Cd	4.955	-0.097	-0.038	-0.135
In	4.975	-0.203	-0.073	-0.276
Sn	4.983	-0.330	-0.044	-0.374
Sb	4.999	-0.630	0.062	-0.568
Ag	4.921	0.085	0.025	0.110

Table 2 Valence effect contribution to the EFG for using the value $\tilde{E}(K_F) = 34.0$; δn, Z-term, and total in units of $(10^3 nm^{-3}$

Impurity Element	Displacement	δn-term	Z-term	Total
Zn	4.864	-0.078	-0.034	-0.114
Ga	4.876	-0.148	-0.088	-0.237
Ge	4.886	-0.580	-0.097	-0.678
As	4.908	-1.373	-0.013	-1.387
Cd	4.955	-0.129	-0.050	-0.179
In	4.975	-0.269	-0.097	-0.366
Sn	4.983	-0.438	-0.058	-0.496
Sb	4.999	-0.836	+0.082	-0.755
Ag	4.921	0.113	0.033	0.146

coupling parameter which compensates for the fact that the solid is idealized by point charges) equation 5.2.2 may be rewritten as

$$\frac{\Delta V}{V} = \frac{4.5\lambda}{d_1^2}\left(\frac{u}{d}\right)(1 + 2/3K^2_{ij}r^2) \qquad 5.2.3$$

where u is the displacement of the ion at the distance d.

For an fcc crystal along the (110) direction (e.g. 1st or 4th nn's).

$$x_i = x_j = d/(2)^{1/2} \quad x_k = 0 \qquad 5.2.4$$

Thus eqns above become

$$\varepsilon^{ij} = \frac{\Delta V}{V}\begin{pmatrix} -1 & 2 & 0 \\ 2 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \qquad 5.2.5$$

Diagonalizing, the principal components of strain are then

$$\varepsilon^{11} = \frac{\Delta V}{V} \qquad 5.2.6$$

$$\varepsilon^{12} = 2\frac{\Delta V}{V} \qquad 5.2.7$$

$$\varepsilon^{22} = -3\frac{\Delta V}{V} \qquad 5.2.8$$

In an fcc crystal along the (100) direction (second and eigth nn's)

$$x_i = d \qquad x_j = x_k \qquad 5.2.9$$

so that

$$\varepsilon^{ij} = \frac{\Delta V}{V}\begin{pmatrix} -4 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \qquad 5.2.10$$

Defining the parallel direction to be along the line connecting the impurity and resonating host atom, the principal components of the strain tensor are:

$$\varepsilon^{11} = -4\frac{\Delta V}{V} \qquad 5.2.11$$

$$\varepsilon^{12} = \varepsilon^{22} = 2\frac{\Delta V}{V} \qquad 5.2.12$$

In a cubic crystal, (100),(110), and (111) are symmetry directions. The principal axes of the size and valence effect contributions coincide, thus, the components of q^V and q^S may be added up algebraically to get total EFG q.

$$q_{zz} = q^V_{zz} + q^S_{zz} \qquad 5.2.13$$

$$q^1 = q^{1V} + q^{1S} = -1/2q^V_{zz} + q^{1S} \qquad 5.2.14$$

$$q^2 = q^{2V} + q^{2S} = -1/2q^V_{zz} + q^{2S}, \qquad 5.2.15$$

Note that along (100) and (111) directions $q^{1S}_z = q^{2S}=-1/2q^S_{zz}$ leading to $q^1=q^2 = -1/2q_{zz}$ consequently $\lambda=0$ along these directions. Thus for the 2NN calculated in this work the principal component of the EFG is $q_{zz}=q^V_{zz}+q^S_{zz}$. Along the direction where the 1nn lies (110) $q^{1S}_{zz}=q^{2S}_{zz}$. Thus, it is not possible to say a priori which would be the largest component of the EFG and it has a non-zero asymmetry parameter η.

For the 1nn the principal values of the EFG are given by

$$q_{zz}=L+M \qquad q^{(1)}_z=2L-M/2 \qquad q^{(2)}_z=-3L-M/2$$

where

$$L=\frac{4.5}{d_1^3}\lambda\,\frac{y}{d_V}(1+2/3K\gamma_\infty F^2) \qquad 5.2.17$$

and

$$M(r)=(8\pi)/3.R(K_F)\left[\delta n(r)+3/4\pi r^3(Zeff-Z(r)\right] \qquad 5.2.18$$

Results for the size effect calculations have been combined with the valence effect results. The adjustable parameters in the calculations are $R(K_F)$ for the valence effect calculations and λ for the size effect calculations. Results presented are for $R(K_F)$ = 25.6; λ = -1.0 and -1.4 for 1nn and $R(K_F)$=34.0; λ = 7.5 for 2nn.

Valence and size effect calculations were carried out with the aid of a computer program, reproduced in Appendix IV.

Tables 3 and 4 show the final results of the EFG computations for group V impurities in copper at 1 nn column one of these tables show the impurity element while columns two and three show the valence and size effect contributions respectively. The principal values of the EFG obtained by use of equation 5.1.12-15 are given in columns four, five and six. The component having the largest magnitude is underlined and, it is by definition the theoretical EFG q. The seventh and eight columns give the experimentally obtained EFG's and percentage deviation with theoretical values respectively.

Table 5 shows a comparison of the results obtained from this work and that by Sagalyn and Alexander (1977). Column one of this table shows the impurity element. Column two shows the calculated EFG values while column three shows the experimentally obtained EFG values. Column four show the EFG values calculated by Sagalyn and Alexander (1977). Columns five and six show the percentage deviations for the calculated EFG values for this work and that by Sagalyn and Alexander respectively.

Table 6 shows the results of EFG calculations at 2 nn displaced host sites. Column one shows the impurity element of the alloy system. Column two shows the new displaced 2 nn sites. Columns three, four and five show the valence, size and total EFG's respectively.

Column one of Table 7 shows the impurity valence. Column two, three and four show the computed, experimental and Sagalyn and Alexander EFG's respectively. Columns five and six show the mean percentage deviations of the computed EFG in this work and that by Sagalyn and Alexander (1977) respectively.

Table 3 Impurities in Copper α=25.6; λ=-1.0. Results of inn EFG calculations for fifth row impurities in copper. All results are in units ($10^{3}nm^{-3}$)

Impurity Element	$q^{v}_{\parallel}$	$q^{\sim}_{\parallel}$	$q_{\parallel}$	$q^{1}_{\perp}$	$q^{2}_{\perp}$	$\lvert q \rvert_{expt}$	% deviation
Cd	-0.135	-0.119	-0.254	-0.171	<u>0.425</u>	0.414	2.6
In	-0.276	-0.138	-0.414	-0.139	<u>0.553</u>	0.607	8.8
Sn	-0.374	-0.146	-0.520	-0.105	<u>0.625</u>	0.632	1.1
Sb	-0.568	-0.161	-0.729	-0.039	<u>0.768</u>	0.719	6.8

Average percentage deviation = 4.8 per cent.

The principal value of EFG for each impurity is underlined.

Table 4 Results of inn EFG calculations for fifth row impurities in copper E=25.6; λ=-1.4. All results are in units ($10^{3}nm^{-3}$

Impurity Element	q^{v}_{11}	q^{s}_{11}	q_{11}	q^{1}_{1}	q^{2}_{1}	$\|q\|_{expt}$	% deviation
Cd	-0.135	-0.167	0.032	0.402	-0.434	0.414	4.8
In	-0.276	-0.194	-0.082	<u>0.525</u>	-0.553	0.607	13.5
Sn	-0.374	-0.204	-0.169	<u>0.596</u>	-0.625	0.632	5.6
Sb	-0.568	-0.226	-0.342	<u>0.736</u>	-0.768	0.719	2.3

Average percentage deviation = 6.55 per cent.

The principal value of EFG for each impurity is underlined.

Table 5 Comparison of Sagalyn and Alexander (1977) results with those obtained in this work. EFG values in units ($10^{3}nm^{-3}$). Results are for Inn sites

Impurity Element	q^{thet}	q^{expt}	q_{SA}	% deviation (thet.)	% deviation (SA)
Cd	0.425	0.414	0.367	2.6	11.0
In	0.553	0.607	0.501	-8.8	17.0
Sn	0.625	0.632	0.672	-1.1	6.0
Sb	0.768	0.719	1.042	6.8	45.0

Mean percentage deviation for this work = 4.8 per cent.

Mean percentage deviation for Sagalyn and Alexander = 19.7 per cent.

Table 6 Results of EFG calculations at 2nn displaced host sites. All EFG values are in units of (10^3 nm^{-3}). ξ = 34.0; λ = 7.5

Impurity element	Displaced nn site (av)	q^{V}_{zz}	q^{R}_{zz}	$q=q^{V}_{zz}+q^{R}_{zz}$
Zn	6.843	0.011	0.022	0.033
Ga	6.847	0.040	0.029	0.069
Ge	6.850	0.204	0.035	0.239
As	6.858	0.504	0.049	0.553
Cd	6.875	0.029	0.080	0.109
In	6.883	0.061	0.093	0.154
Sn	6.885	0.149	0.097	0.246
Sb	6.891	0.349	0.107	0.456

Table 7 Comparison of calculated EFG values with that of Sagalyn and Alexander (1977). All EFG values in units ($10^{3}nm^{-3}$). Results are for Znn sites

Impurity Element	q^{thet}	q^{expt}	q_{sa}	% deviation (thet)	% deviation (SA)
Zn	0.033	0.024	0.035	32.0	41.4
Ge	0.239	0.240	0.234	0.4	2.5
Cd	0.109	0.112	0.149	2.6	33.1
Sn	0.246	0.316	0.302	22.1	4.4
Sb	0.456	0.482	0.483	5.6	0.3

Mean percentage deviation for this work = 12.5 per cent.

Mean percentage deviation for Sagalyn and Alexander = 16.4 per cent.

From the results tabulated above, it is clear that the EFG's computed using the Ponnambalam-Jena theory gives better agreement with experimental results than that computed using the Sagalyn and Alexander (1977) theory.

The mean percentage deviation between computed and experimental values for fifth row impurities in copper at 1 nn is 4.8 per cent, whilst for 2 nn is 12.5 per cent. It is expected that if the energy density functional formalism is used to compute the induced electron densities, still better agreement will be achieved between theoretical and experimental values.

This work has shown that the Ponnambalam Jena theory accounts for EFG's for dilute alloys of copper at 1 nn and 2 nn with remarkable success. The deficiencies of this theory as a complete quantitative theory of the EFG are as follows: The separation of the valence of the valence and size effect calculations. The absence of an apriori scheme to evaluate the strain coupling parameter μ, and the failure of the theory to take into account the periodic array of lattice ions. It suffices here to say than the Ponnambalam-Jena theory is a successful semi-quantitative theory for EFG calculations in metals as illustrated by results of several computations.

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APPENDIX I The Hurd-Gordon scattering phase shifts for Fermi level for copper solvent

S/No	Solute	$*_0$	$*_1$	$*_2$	$*_3$	$*_4$
1	Zn	0.33078	0.24815	0.05438	0.00579	0.00039
2	Ga	0.57929	0.54004	0.12135	0.01187	0.00077
3	Ge	0.90509	0.89796	0.14742	0.01022	0.00051
4	As	1.29487	1.32427	0.11130	0.00477	0.00016
5	Cd	0.29977	0.14458	0.02139	0.00167	0.00008
6	In	0.59275	0.43368	0.07123	0.00579	0.00031
7	Sn	0.82056	0.76278	0.12641	0.00932	0.00048
8	Sb	1.08776	1.12579	0.14889	0.00838	0.00035
9	Ag	-0.24211	-0.71110	-0.00916	-0.00062	-0.00003

APPENDIX II Derivatives of the Hurd-Gordon scattering phase shifts at Fermi level for copper solvent

S/No	Solute	η_0	η_1	η_2	η_3	η_4
1	Zn	-0.99439	0.33802	0.37699	0.06586	0.00605
2	Ga	-1.65053	0.20945	0.85266	0.18662	0.01194
3	Ge	-2.13389	0.04108	1.16337	0.17291	0.00809
4	As	-2.33763	-0.17259	0.99402	0.05991	0.00261
5	Cd	0.67149	0.40114	0.16460	0.01990	0.00132
6	In	-1.56943	0.65429	0.54052	0.06845	0.00492
7	Sn	-2.03053	0.31384	0.98142	0.11140	0.00762
8	Sb	-2.27323	-0.22668	1.24890	0.10291	0.00573
9	Ag	0.09322	-0.26489	-0.07205	-0.00748	-0.00041

Appendix III Lattice expansion of copper due to alloying obtained from Platt (1957): α = 0.35, γ = 1.444

Solute	$(1/a)(da/dc)$	$\delta V/\Delta$	Zeff
Zn	0.055	0.1142	0.8858
Ga	0.075	0.1560	1.8440
Ge	0.092	0.1910	2.8090
As	0.130	0.2700	3.7300
Ag	0.155	0.3220	-0.3220
Cd	0.220	0.4570	0.5430
In	0.260	0.5400	1.4600
Sn	0.277	0.5750	2.4250
Sb	0.310	0.6440	3.3560

Table 3 Results of 1nn EFG calculations for fifth row impurities in copper ($\tilde{R}$ = 25.6; λ =-1.0. All results are in units ($10^{3}nm^{-3}$)

Impurity Element	q^{V}_{zz}	q^{S}_{zz}	q_{zz}	q^{1}_{z}	q^{2}_{z}	q_{exp}	
Cd	-0.135	-0.119	-0.254	-0.171	<u>0.425</u>	0.414	2.6
In	-0.276	-0.138	-0.414	-0.139	<u>0.553</u>	0.607	8.8
Sn	-0.374	-0.146	-0.520	-0.105	<u>0.625</u>	0.632	1.1
Sb	-0.568	-0.161	-0.729	-0.039	<u>0.768</u>	0.719	6.8

Average percentage deviation = 4.8 per cent.

The principal value of EFG for each impurity is underlined.

```
C     *** THIS PROGRAM COMPUTES THE ELECTRIC FIELD GRADIENT ****
C                 *** FOR DILUTE ALLOYS OF COPPER. ****
C
C#####################################################################
C                                                                     #
C              I N P U T        P A R A M E T E R S                   #
C                                                                     #
C     ALLOY-------IMPURITY                                            #
C     FRCH -------FRACTIONAL CHANGE IN VOL. OCCUPIED BY IMPURITY      #
C     A1   -------HURD-GORDON PHASE SHIFTS                            #
C     A2   -------DERIVATIVES OF THE HURD-GORDON PHASE SHIFTS         #
C     CIX  -------COSINE INTEGRAL                                     #
C     SIX  -------SINE INTEGRAL                                       #
C                                                                     #
C#####################################################################


      program final(us1,f10,tape5=us1,tape6=us0)
      dimension a1(10),a2(10),gamma(10),q1(10),q2(10),q3(10)
      dimension szr1(10),szr2(10),szr3(10),qnr1(10),qnr2(10)
      dimension qnr(10),znr(10),szr(10),fnnd(10),f(10),g(10)
      dimension dnr(10),theta(10)
      character*20 alloy(10)
      write(6,100)
      write(6,100)
      write(6,100)
      write(6,100)
      write(6,115)
      write(6,120)
      do 10 k=1,9
      frc=.719
      read(5,3)alloy(k)
      read(5,*)frac
      read(5,*)(a1(i),i=1,5)
      read(5,*)(a2(i),i=1,5)
      read(5,*)cix,six
      write(6,110)alloy(k)
      write(6,125)(a1(i),a2(i),i=1,5)
      call fnn(frac,fnnd,k)
      call vanos(a1,a2,f,g,theta,gamma,k)
      call valence(f,fnnd,theta,g,gamma,dnr,cix,six,znr,qnr,szr,k)
10    continue
      write(6,135)
      write(6,136)
      write(6,137)
      do 12 kk=1,9
      write(6,138)alloy(kk),f(kk),g(kk),theta(kk),gamma(kk),fnnd(kk)
12    continue
```

```
      write(6,140)
      write(6,141)
      write(6,142)
      call efg(szr,qnr,q1,q2,q3)
      do 31 k=1,9
      write(6,143)alloy(k),dnr(k),znr(k),qnr(k),q1(k),q2(k),q3(k)
   31 continue
      do 32 j=1,9
      szr(j)=-szr(j)*1.4
   32 continue
      do 33 i=1,9
      qnr(i)=qnr(i)*34./25.6
   33 continue
      write(6,144)
      write(6,142)
      call efg(szr,qnr,q1,q2,q3)
      do 34 k=1,9
      write(6,143)alloy(k),dnr(k),znr(k),qnr(k),q1(k),q2(k),q3(k)
   34 continue
    3 format(b20)
  100 format(//,10x," RESULTS OF EFG CALCULATIONS",
     *" IN DILUTE ALLOYS OF COPPER",//)
  101 format(17x,"THE FERMI WAVE VECTOR IS .719 a.u.",///)
  102 format(17x,"REPEATED NN DISTANCE IS 4.830 a.u ",///)
  103 format(20x,"  I N P U T   P A R A M E T E R S ",//)
  110 format(20x,820)
  115 format(45x,"THE HURD GORDON COEFFICIENTS",//)
  120 format(20x,"IMPURITY",12X,"PHASE SHIFTS",13X,"DERIVATIVES",//)
  125 format(40x,f8.5,17x,f8.5)
  130 format(10x,"FRACTIONAL CHANGE IN VOLUME OF CELL",
     *" OCCUPIED BY IMPURITY",F6.4,//)
  135 format(30x,////," C O M P U T E D  V A L U E S ",//)
  136 format(2x,"IMPURITY",32x,"ALFRED VAN OSTENBERG CONSTANTS",11x,
     *"DISPLACED NN",//)
  137 format(30x,"A",14X,"B",14x,"PHI",12x,"JAI",9x," (a.u)")
  138 format(a20,4(f15.6),5x,f8.3/)
  139 format(10x,"DISPLACED NN DISTANCE IS ",f8.3)
  140 format(20x,////,"F I N A L    R E S U L T S ",//)
  141 format(10x,"FOR ALPHA=25.6  & LAMBDA= -1.0",//)
  142 format(26x,"del nr",5x,"z-term",6x,"total",8x,"  q1  ",
     *5x,"  q2  ",6x,"  q3  ")
  143 format(a20,4(f10.3,2x))
  144 format(10x,///,"FOR ALPHA=25.6  & LAMBDA=-1.4",//)
  145 format(10x,"FOR ALPHA=34.0  & LAMBDA= 1.3",//)
  146 format(10x,"FOR ALPHA=34.0  & LAMBDA= -0.9",//)
      stop
      end
```

```
C  THIS SUBROUTINE CALCULATES THE DISPLACED
C       FIRST NEAREST NEIGHBOUR DISTANCE
C
      subroutine fnn(f1,f2,k)
      dimension f2(10)
       r1=(2.66**3)*(1+f1)
       c=1./3.
       r2=(r1**c)-2.66
       f2(k)=(6.8303+r2/2.)/sqrt(2.)
       return
       end


C  THIS SUBROUTINE CALCULATES THE ALFRED-
C            VAN OSTENBERG CONSTANTS
C

      subroutine vanos(a1,a2,v3,v4,v5,v6,k)
      dimension a1(10),a2(10),v3(10),v4(10),v5(10),v6(10)
      fk=.719
      acosp=0.0
      asinp=0.0
      bcosj=0.0
      bsinj=0.0
      do 20 ll=1,5
      l=ll-1
      acosp=acosp+((2*l+1)*(-1)**l)*(sin(2*a1(ll)))
      asinp=asinp+((2*l+1)*(-1)**l)*((sin(a1(ll)))**2)
      bcosj=bcosj+((2*l+1)*(-1)**l)*(((2*l*(l+1)/fk)*(sin(a1(ll)))**
     1+a2(ll)*sin(2*a1(ll))))
      bsinj=bsinj+((2*l+1)*(-1)**l)*(((l*(l+1)/fk)*sin(2*a1(ll)))
     1+a2(ll)*cos(2*a1(ll)))
   20 continue
      dcosp=-acosp/(4*(22./7.)**2)
      esinp=-asinp/(2*(22./7.)**2)
      fcosj=bcosj/(4*(22./7.)**2)
      gsinj=-bsinj/(4*(22./7.)**2)
      tanp=esinp/dcosp
      v5(k)=atan(tanp)
      v3(k)=esinp/sin(v5(k))
      tanj=gsinj/fcosj
      v6(k)=atan(tanj)
      v4(k)=gsinj/sin(v6(k))
      return
      end
```

```
C  THIS SUBROUTINE CALCULATES THE VALENCE AND
C     SIZE EFFECT CONTRIBUTIONS TO THE EFG
C

      subroutine valence(va1,va2,va3,va4,va5,va6,va7,va8,va9
     1,va10,va11,k)
      dimension va1(10),va2(10),va3(10),va4(10),va5(10),va6(10)
     .,va9(10),va10(10),va11(10)
      fk=.719
      dr=(va1(k)*cos(2.*fk*va2(k)+va3(k)))/(va2(k)**3)
      dr1=(va4(k)*cos(2.*fk*va2(k)+va5(k)))/(va2(k)**4)
      dr2=dr1+dr
      va6(k)=(1./(.529**3))*dr2*8.*(22./7.)*25.6/3.
      x=2.*fk*va2(k)
      z1=-va1(k)*cos(va3(k))*va7
      z2=-(va1(k)*sin(va3(k)))*(11./7.-va8)
      z3=2.*fk*va4(k)*cos(va5(k))*(cos(x)/x+va8-11./7.)
      z4=-2.*fk*va4(k)*sin(va5(k))*(sin(x)/x-va7)
      zz=z1+z2+z3+z4
      va9(k)=zz*4.*(22./7.)*(31.2/((va2(k)*.529)**3))
      va10(k)=va9(k)+va6(k)
      w=(4.33*.529)**4
      va11(k)=-4.5*(va2(k)-4.33)*9.04/w
      return
      end

C  THIS SUROUTINE CALCULATES THE COMPONENTS OF THE EFG
C

      subroutine efg(e1,e2,e3,e4,e5)
      dimension e1(10),e2(10),e3(10),e4(10),e5(10)
      do 51 l=1,9
      e3(l)=e1(l)+e2(l)
      e4(l)=2.*e1(l)-e2(l)/2.
      e5(l)=-2.*e1(l)-e2(l)/2.
   51 continue
      return
      end
```