Electric Field Gradient in Aluminium due to Vacancy and Muon *

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The electric field gradients (EFG) in aluminium due to a monovacancy and the interstitial muon are evaluated. The valence effect EFG q^v is calculated using perturbed electron density $\delta n(\boldsymbol{r})$ values obtained from density functional theory in an analytic expression which is valid at all distances from the impurity. The size effect EFG q^s is evaluated using a new oscillatory form for the near neighbour (nn) displacements. The numerical values of q^s are computed using fractional nn displacements available in the literature. For the total EFG good agreement with experiment is obtained without the use of any parameter.

Key words: Nuclear Quadrupole Interaction, Electric Field Gradient

1. Introduction

In a cubic crystal, the electric field gradient (EFG) vanishes at the site of any ion due to cubic symmetry [1]. The presence of an impurity in a cubic host locally destroys the cubic symmetry and thus produces a non-vanishing EFG at the site of the host near neighbours (nn) – thus leading to a non-vanishing nuclear quadrupole interaction of the host nuclei. Conventionally, for computational convenience the EFG is split into a) the valence effect EFG q^v, arising from the perturbation $\delta n(\boldsymbol{r})$ of the ambient electron density, and b) the size effect EFG q^s, arising from the strain on the host nn due to the misfit of the impurity ion in a host ion site.

Asymptotic and pre-asymptotic solutions for q^v have been obtained [2, 3]. Sagalyn and Alexander [4] proposed a new method to evaluate q^v using integration and a special geometry. In addition, they evaluated q^s using the point ion model of Faulkner [5] and the expression

$$\boldsymbol{u}(\boldsymbol{r}) = D\boldsymbol{r}/r^3 \tag{1}$$

for the displacement of the host ions. Here, D is a constant. This formalism has been used by others with some modifications [6].

A solution for q^v, valid at all distances from the impurity, was given by Ponnambalam and Jena (PJ) [7], who showed that their results went over to the earlier asymptotic and pre-asymptotic ones at the appropriate limits. In addition, in the evaluation of q^s, they used the following oscillatory form for the displacement of the host ions:

$$\boldsymbol{u}(\boldsymbol{r}) = A\cos(2k_F r + \phi)\,\boldsymbol{r}/r^3, \tag{2}$$

where $\boldsymbol{k}_F$ is the Fermi wave vector while A and ϕ are constants.

In the case of a muon and a vacancy in Al and Cu, Tripathi et al. [8] and Schmidt et al. [9] have carried out a lattice sum in the evaluation of q^s, using available lattice displacements. Recently, using KKR-Green's function method, Dederichs et al. [10] have evaluated the EFG's in Cu alloys. They find that much of the EFG is caused by the d-electrons of the Cu ion under consideration.

In this paper, we present our results on the EFG in Al due to a mono-vacancy and a muon in the octahedral interstitial. Unlike Cu alloys, wherein the EFG is complicated by the d-electrons of Cu [10], Al is a simple metal with completely filled inner shells. Hence, q^v is evaluated using the analytic expression of PJ [7] and perturbed electron density $\delta n(\boldsymbol{r})$ values obtained from density functional theory. A new, oscillatory form for the nn displacement is used in the algebraic solution of q^s, while its numerical value is obtained using available nn displacements. Good agreement is obtained with experiment without the use of any parameter. The details of the Theory are presented in Section 2. This is followed by Results and Discussion in Section 3 and the Summary in Section 4.

2. Theory

Let $V(\boldsymbol{r})$ be the electrostatic potential at the site of any host ion surrounding the impurity at the origin in

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a cubic host. If V_{ij} is its derivative with respect to x_i and x_j, then

$$e q_{ij}^{v} = V_{ij} - \delta_{ij} \nabla^2 V/3 . \tag{3}$$

Diagonalizing q_{ij}^{v}, the principal components of q^{v} are obtained. When $V(\boldsymbol{r})$ and hence the perturbed electron density $\delta n(\boldsymbol{r})$ is approximated to be spherically symmetric, the principal components of q^{v} are parallel ($\parallel$) and perpendicular ($\perp$) to the direction connecting the impurity to the host and are given by the following analytic expressions [7]:

$$\begin{aligned} q_{\parallel}^{v} &= \frac{8\pi}{3} \alpha(\boldsymbol{k}_F) \left[\delta n(\boldsymbol{r}) + \frac{3}{4\pi r^3} \{ Z_{\text{eff}} - Z(r) \} \right] \\ &= -2 q_{\perp}^{1v} = -2 q_{\perp}^{2v} , \end{aligned} \tag{4}$$

where $\alpha(\boldsymbol{k}_F)$ is the Bloch enhancement factor which takes into account the departure of the electronic wavefunctions from plane wave character as well as anti-shielding effects [2]

$$Z(r) = \int_0^r \delta n(r') \, dv' \quad \text{and} \quad Z_{\text{eff}} = Z(\infty) . \tag{5}$$

The components q_{ij}^{s} of the size effect EFG, linear in the strain components ε_{ij}, are given by [4, 7]

$$e q_{ij}^{s} = \delta_{ij}(F_{11} - F_{12}) \left(\varepsilon_{11} - \frac{1}{3} \sum_k \varepsilon_{kk} \right) + 2(1 - \delta_{ij}) F_{44} \varepsilon_{ij} , \tag{6}$$

where F_{ij}'s are components of a fourth rank tensor. For an FCC host, these are given, in the point ion model as [11]

$$F_{11} - F_{12} = -3 F_{44} = 9 Z e/d_1^3 = 18 \sqrt{2} Z e/a_L^3 , \tag{7}$$

where Z is the host's valency, d_1 is the first nn distance and a_L the lattice constant. Equation (7) with $Z=1$ agrees with the result of Faulkner [5]. Faulkner's result, which was derived for monovalent Cu, has been used incorrectly for polyvalent Al by the earlier groups [6, 7]. In this paper (7), which is valid for polyvalent hosts like Al, is used. The elastic strain tensor ε_{ij} is given in terms of the nn displacements $\boldsymbol{u}(\boldsymbol{r})$ as

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) . \tag{8}$$

Thus, the computation of q_{ij}^{s} requires an analytic expression for $\boldsymbol{u}(\boldsymbol{r})$.

Both lattice statics calculations [12] and EXAFS measurements [13] indicate that the displacements are radial along the symmetry directions [100], [110] and [111]. Due to this and due to simplicity in calculations, the nn displacements are taken to be radial. Since different nn's may move differently (i.e. some inward and some outward), (1) is oversimplified. This problem is overcome by the oscillatory form of $\boldsymbol{u}(\boldsymbol{r})$ in (2), which reduces to (1) if $(2 k_F r + \phi) = 0$.

Now, in a simplified model, the displacement of an nn is influenced by the difference in the sizes and charges of the impurity and host ion. In the case of the latter, one is aware that the impurity-host charge difference tends to be screened out by the re-arrangement of the conduction electrons as given by the perturbed electron density $\delta n(r)$. Hence it is not unreasonable to expect the displacement field to exhibit the Friedel oscillations of $\delta n(r)$. Consequently, the nn displacements are assumed to be of the form

$$\boldsymbol{u}(\boldsymbol{r}) = A \cos(2 k_F r + \phi) \, \boldsymbol{r}/r^4 , \tag{9}$$

where A and ϕ are constants while $\boldsymbol{k}_F$ is the Fermi wave vector. The choices of $2 k_F$ as the scaling factor and of r^4 in the denominator (instead of the r^3 in (2)) have no fundamental justification except that now $|\boldsymbol{u}(\boldsymbol{r})|$ is of the same form as the asymptotic $\delta n(r)$ [2].

Using (7), (8), and (9) in (6), the following result is obtained for the pth nn:

$$q_{ij}^{s} = L_p [\delta_{ij} - \tfrac{2}{3}(1 - \delta_{ij})] (2 \delta_{ij} - 6 x_i x_j / d_p^2) , \tag{10}$$

$$L_p = 9 \sqrt{2} Z \, a_L^{-3} f_p (1 + k_F^2 d_p^2/3) . \tag{11}$$

Here, d_p is the position of the pth nn with fractional displacement f_p, Z is the host valency and a_L the lattice constant. It should be noted that in [7] L_p involves $\cos(2 k_F r + \phi)$ which is evaluated using the equilibrium conditions of elasticity theory. Herein, however, L_p is re-expressed in terms of f_p whose values are available from lattice statics calculations.

Diagonalizing q_{ij}^{s} in (10), the principal components of q^{s} are obtained as

$$\begin{aligned} q_{\parallel}^{s} &= -4L &&= -2 q_{\perp}^{1s} &&= -2 q_{\perp}^{2s} , && \text{along [100]}, \\ q_{\parallel}^{s} &= L &&= q_{\perp}^{1s}/2 &&= -q_{\perp}^{2s}/3 , && \text{along [110]}, \\ q_{\parallel}^{s} &= 8L/3 &&= -2 q_{\perp}^{1s} &&= -2 q_{\perp}^{2s} , && \text{along [111]}, \\ q_{\parallel}^{s} &\approx 2.463 L = 7.389 q_{\perp}^{1s} &&= -0.881 q_{\perp}^{2s} , && && \text{along [211]}. \end{aligned} \tag{12}$$

It should be noted that along [211] none of the components of q^{s} are exactly along the parallel direction, although the first component's direction is fairly close to that. (In this case one may combine q_{ij}^{v} with q_{ij}^{s} and diagonalize the resultant matrix. However, this result differs very little from that using the approximate one in (12).)

Table 1. The largest component of the total EFG q in nm^{-3} and the asymmetry parameter η for Al host.

Impurity	nn	f_p [11, 17]	Theory		Exp. [18]	
			q	η	q	η
Vacancy	1	−0.0174	285	0.30	280	0.65
	2	−0.0093	376	0	–	0
	3	−0.0023	98	0.78	93	–
	4	−0.0007	43	0.26	69	–
Muon	1	0.0273	166	0	180	0

Combining the components of q^s in (12) with those of q^v_{ij} in (4), the total EFG q is obtained with components $|q_3| \geq |q_2| \geq |q_1|$ and the asymmetry parameter

$$\eta = (q_1 - q_2)/q_3 \,. \tag{13}$$

3. Results and Discussion

We have evaluated $\delta n(r)$ values in the spherical solid approximation based on density functional theory [14]. In this, the host ions are replaced by bare-ion pseudopotentials. The potentials of all atoms at a given distance from the impurity are spherically averaged and added to the effective potential acting upon the electrons. For the bare-ion pseudopotential we have used Aschroft's form [15] with a core radius of 1.12 a.u. Using these $\delta n(r)$ values and the $\alpha(\boldsymbol{k}_F)$ values from [16] in (4) and (5), the principal components of q^v are obtained.

Using Singhal's values of the nn fractional displacements f_p for an Al-vacancy [12] and the mean of the f_1 values from [17] for the muon in (11) and (12), the principal components of q^s are obtained. Combining these with q^v, the principal components of the total EFG and the asymmetry parameter η are obtained. The results are presented in Table 1.

The table shows that the agreement between theory and experiment is good. The major discrepancy is in η for the 1st nn of Al-vacancy. This is attributed to the neglect of asphericity in $\delta n(r)$.

In order to investigate the effects of asphericity qualitatively, the principal components of q for the 1st nn of Al-vacancy are written (in nm^{-3}) as

$$\begin{aligned} q_{\parallel} &= (-1700 + \underline{1694}) - \ 94 = -100, \\ q^1_{\perp} &= \quad (850 - \ \underline{847}) - 188 = -185, \\ q^2_{\perp} &= \quad (850 - \ \underline{847}) + 282 = \quad 285; \quad \eta = 0.30. \end{aligned} \tag{14}$$

Here, the first terms are contributions from eZ_{eff}, the underlined terms are from the spherically symmetric $\delta n(r)$ and the last terms are from the size EFG. (The sum of the first two terms inside the brackets gives q^v.) Let $q^v_{\parallel}(\delta n)$ go up by 3%, i.e. by 51 nm^{-3} due to asphericity, with the corresponding decrease of 26 nm^{-3} in each of the $q^v_{\perp}(\delta n)$, since the sum of the three is zero, then the largest component of q is 259 nm^{-3} while η moves up to 0.63, both of which are in good agreement with the experimental values of 280 nm^{-3} and 0.65, respectively.

4. Summary

The electric field gradients (EFG) due to a monovacancy and muon in Al have been evaluated. The valence EFG q^v is evaluated using $\delta n(r)$ values obtained from density functional theory in an analytic expression which is valid at all distances from the impurity. In the evaluation of the size EFG q^s: a) A new oscillatory form, which is identical to the asymptotic Friedel oscillatory form of $\delta n(r)$, is used for the nn displacements. b) A new expression which is corrected for the valency of the host, is used for the F-tensor coefficients. c) The components of q^s are evaluated using the available fractional displacements of nn's, and not using the equilibrium conditions of elasticity as in [7]. Without the use of any free parameter, good agreement is obtained with experiment.

In order to check the theory further, it would be desirable to have the fractional nn displacements f_p for other impurities in Al.

One major drawback of the present work is that it splits the EFG into q^v and q^s and then evaluates them separately. Combining these two into a single, unified calculation is desirable.

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