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Electric-field gradient in dilute V-based alloys

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Electric-field gradients (EFG's), due to substitutional transition-metal impurities in vanadium have been evaluated using a discrete-lattice static method. The valence and size EFG's are generated simultaneously with the help of perfect and imperfect crystal potentials. The EFG's at the first- and second-nearest neighbors (1NN, 2NN) of the impurity are calculated for the dilute alloys $\underline{\text{V}}\text{Nb}$, $\underline{\text{V}}\text{Mo}$, $\underline{\text{V}}\text{Ta}$, and $\underline{\text{V}}\text{W}$. The d -band effects of both the host and impurity are included through the crystal potential. The calculated results are in agreement with the experimental values. The valence EFG is larger than the size EFG at the 1NN while the size EFG starts dominating at the 2NN sites.

I. INTRODUCTION

Most of the theoretical investigations of electric-field gradients (EFG's) have been carried out in substitutional dilute alloys of fcc structure.¹ The continuum model of lattice is used for the size EFG. Recently, the EFG's in Cu and Al alloys have been studied using the discrete-lattice model.² On the other hand, the transitional alloys are much less studied for many reasons. In the experimental study of dilute alloys of vanadium, it has been found that even a few parts per 10⁶ impurity in these alloys reduce the peak-to-peak intensity in the NMR signal and give distorted line shapes.^{3,4} Second, the electronic structure of transitional alloys is complex. Therefore the theoretical study of these systems becomes a characteristically difficult problem. Only a few theoretical studies of EFG's have been made^{5,6} in vanadium alloys and these too have been limited to the continuum model of the lattice. Recently, we⁷ have performed *ab initio* calculations for the impurity-induced strain field due to transition-metal (TM) impurities in V using the lattice static method (hereafter this paper is referred to as I). We² have also developed a parameter-free formalism for EFG's in dilute cubic alloys which has been successfully applied to dilute alloys of fcc symmetry. It is therefore interesting to apply this EFG formalism to transitional dilute alloys of vanadium.

We present a brief review of the theory in Sec. II. The calculations and results are presented in Sec. III, and the results are discussed in Sec. IV.

II. THEORY

As discussed in I, the total change in the crystal potential $\Delta\Phi(r)$ in the presence of an impurity is the sum of

two contributions, i.e.,

$$\Delta\Phi(\mathbf{r}) = \Delta\phi^v(\mathbf{r}) + \Delta\phi^s(\mathbf{r}), \quad (1)$$

where

$$\Delta\phi^v(\mathbf{r}) = \phi_I(\mathbf{r}) - \phi_H(\mathbf{r}), \quad (2)$$

$$\Delta\phi^s(\mathbf{r}) = \sum'_n [\phi_H(\mathbf{r} - \mathbf{R}_n) - \phi_H(\mathbf{r} - \mathbf{R}_n^0)]. \quad (3)$$

Here $\phi_H(\mathbf{r})$ and $\phi_I(\mathbf{r})$ are the host and impurity ion potentials and \mathbf{R}_n^0 and \mathbf{R}_n are the atomic coordinates in the perfect and imperfect crystals, respectively. $\Delta\phi^v(\mathbf{r})$ and $\Delta\phi^s(\mathbf{r})$ are the contributions to $\Delta\Phi(r)$ from the excess impurity valence ΔZ and the impurity-induced strained field, respectively. The prime in Eq. (3) denotes that $\mathbf{r} \neq \mathbf{R}_n$ and \mathbf{R}_n^0 . The same convention continues.

The EFG tensor \mathbf{V} at $\mathbf{r} = \mathbf{R}_m$, the m th nearest neighbor (m NN) of the impurity, is obtained by taking the second derivative of $\Delta\Phi(\mathbf{r})$, which is given as

$$\mathbf{V}(\mathbf{R}_m) = \mathbf{V}^v(\mathbf{R}_m) + \mathbf{V}^s(\mathbf{R}_m), \quad (4)$$

where the valence EFG

$$\mathbf{V}^v(\mathbf{R}_m) = [1 - \gamma(\mathbf{r})][\nabla \cdot \nabla \Delta\phi^v(\mathbf{r})]_{\mathbf{r}=\mathbf{R}_m}, \quad (5)$$

and the size EFG

$$\mathbf{V}^s(\mathbf{R}_m) = [1 - \gamma(\mathbf{r})][\nabla \cdot \nabla \Delta\phi^s(\mathbf{r})]_{\mathbf{r}=\mathbf{R}_m}. \quad (6)$$

Here $[1 - \gamma(\mathbf{r})]$ is the Sternheimer antishielding factor. As $\gamma(\mathbf{r})$ approaches its saturation value γ_∞ (asymptotic value) at distances less than the 1NN distance, $\gamma(\mathbf{r})$ is therefore replaced by γ_∞ in the present calculations.⁸

The Cartesian components of traceless valence EFG tensor are defined as

$$q_{\alpha\beta}^v(\mathbf{R}_m) = V_{\alpha\beta}^v(\mathbf{R}_m) - \frac{1}{3} \sum_{\alpha} V_{\alpha\alpha}^v(\mathbf{R}_m), \quad (7)$$

where

$$V_{\alpha\beta}^v(\mathbf{R}_m) = (1 - \gamma_{\infty}) \nabla_{\alpha} \nabla_{\beta} [\Delta\phi^v(r)]_{r=\mathbf{R}_m}. \quad (8)$$

Here α and β ($=x, y, z$) are the Cartesian coordinates. Similarly, the Cartesian components of traceless size EFG tensor $q_{\alpha\beta}^s$ are

$$q_{\alpha\beta}^s(\mathbf{R}_m) = V_{\alpha\beta}^s(\mathbf{R}_m) - \frac{1}{3} \sum_{\alpha} V_{\alpha\alpha}^s(\mathbf{R}_m), \quad (9)$$

where

$$V_{\alpha\beta}^s(\mathbf{R}_m) = (1 - \gamma_{\infty}) \nabla_{\alpha} \nabla_{\beta} \times \sum'_{n(\neq m)} [\phi_H(\mathbf{r} - \mathbf{R}_n) - \phi_H(\mathbf{r} - \mathbf{R}_n^0)]_{r=\mathbf{R}_m}. \quad (10)$$

The second term in Eq. (10) involves the sum over the perfect cubic lattice; therefore, its Laplacian vanishes due to symmetry reasons. But in numerical calculations we use Eq. (10) as such for convergence reasons.

The total EFG is obtained by adding the corresponding components of valence and size EFG's, i.e.,

$$V_{\alpha\beta}(\mathbf{R}_m) = V_{\alpha\beta}^v(\mathbf{R}_m) + V_{\alpha\beta}^s(\mathbf{R}_m). \quad (11)$$

The components of traceless EFG tensor q are given as

$$q_{\alpha\beta} = V_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \sum_{\alpha} V_{\alpha\alpha}. \quad (12)$$

The 3×3 matrix of $q_{\alpha\beta}$ is diagonalized to obtain the eigenvectors and the corresponding eigenvalues. The maximum eigenvalue is taken along the line joining the host and impurity atoms, i.e., the [111] direction for the 1NN and the [100] direction for the 2NN in the bcc lattice. The corresponding eigenvector is taken along the Z axis of the EFG coordinate system. It is called the parallel direction, and the EFG is denoted as $q_{ZZ} = q_{\parallel}$. The other two eigenvalues are written as $q_{YY} = q_{\perp}$ and $q_{XX} = q_{xx}$. The asymmetry parameter $\eta = |q_{XX} - q_{YY}| / |q_{ZZ}|$.

III. CALCULATIONS AND RESULTS

A. Scattering potential

We have used the analytical form of the interionic potential due to Wills and Harrison⁹ for the evaluation of impurity-induced strain field in dilute alloys of V in paper I. We use the same interionic potential in Eqs. (5)–(11) to evaluate the valence and size EFG's at the displaced positions of the host ions. The explicit form of the potential for the host metal in atomic units is

$$\phi_H(r) = [\phi_H^{\text{FE}}(r) + \phi_H^c(r) + \phi_H^b(r)], \quad (13)$$

where

$$\phi_H^{\text{FE}}(r) = Z_{sH} \cosh^2(\kappa r_{cH}) \frac{e^{-\kappa r}}{r}, \quad (14)$$

$$\phi_H^c(r) = \frac{225}{\pi^2} \frac{r_{dH}^6}{r^8}, \quad (15)$$

$$\phi_H^b(r) = - \left[1 - \frac{Z_{dH}}{10} \right] \left[\frac{12}{n} \right]^{1/2} \frac{28.1}{\pi} \frac{r_{dH}^3}{r^5}. \quad (16)$$

Here n is the number of 1NN's in a crystalline structure and Z_{sH} and Z_{dH} are the number of s and d electrons per host atom which are related to the host valency z_H as $Z_{sH} + Z_{dH} = z_H$. $\phi_H^{\text{FE}}(r)$ is the free-electron contribution obtained from the Ashcroft empty core model potential in conjunction with Thomas-Fermi screening. ($1/\kappa$) is the Thomas-Fermi screening length, and r_{cH} is the model potential core radius. $\phi_H^c(r)$ is the contribution arising from the shift in the d -band center and depends upon the d -state radius r_{dH} of the host atom. $\phi_H^b(r)$ arises from the finite d -band width.¹⁰ The impurity-ion potential $\phi_I(r)$ is obtained by replacing the subscript H by I in Eqs. (13)–(16) and therefore

$$\phi_I(r) = \phi_I^{\text{FE}}(r) + \phi_I^c(r) + \phi_I^b(r). \quad (17)$$

B. EFG

The double derivatives of the excess impurity potential $\Delta\phi^v(r)$ can be written as

$$V_{\alpha\beta}^v(\mathbf{r}_m) = (1 - \gamma_{\infty}) [\nabla_{\alpha} \nabla_{\beta} \Delta\phi^{\text{FE}}(r) + \nabla_{\alpha} \nabla_{\beta} \Delta\phi^c(r) + \nabla_{\alpha} \nabla_{\beta} \Delta\phi^b(r)], \quad (18)$$

where

$$\Delta\phi^{\text{FE}}(r) = \phi_I^{\text{FE}}(r) - \phi_H^{\text{FE}}(r), \quad (19)$$

$$\Delta\phi^c(r) = \phi_I^c(r) - \phi_H^c(r), \quad (20)$$

$$\Delta\phi^b(r) = \phi_I^b(r) - \phi_H^b(r). \quad (21)$$

From Eqs. (13)–(16) one can readily find $\nabla_{\alpha} \nabla_{\beta} \phi_H^{\text{FE}}(r)$, $\nabla_{\alpha} \nabla_{\beta} \phi_H^c(r)$, and $\nabla_{\alpha} \nabla_{\beta} \phi_H^b(r)$ at the displaced position of the host ions. Similarly, one can evaluate $\nabla_{\alpha} \nabla_{\beta} \phi_I^{\text{FE}}(r)$, $\nabla_{\alpha} \nabla_{\beta} \phi_I^c(r)$, and $\nabla_{\alpha} \nabla_{\beta} \phi_I^b(r)$ from Eq. (17) and hence the derivatives in Eq. (18). Using Eq. (18) in Eq. (7), one can evaluate $q_{\alpha\beta}(\mathbf{R}_m)$, which gives the components of traceless valence EFG tensor. Similarly, Eq. (13) is used in Eqs. (9) and (10) to evaluate $q_{\alpha\beta}^s(\mathbf{R}_n)$. The displaced position \mathbf{R}_n in Eq. (10) is taken from I, and the derivatives are evaluated at the displaced positions of the host ions. The sum over NN's of the impurity in Eq. (10) is carried out until convergence up to three decimal places is achieved.

The experimental values of the EFG are available for the V alloys with $3d$, $4d$, and $5d$ impurities. Therefore we apply the above formalism to calculate the EFG in these alloys. The antishielding factor γ_{∞} for V metal is -11.0 .⁴ The model potential parameters are taken from Wills and Harrison.⁹ The calculated values of valence and size EFG's due to the TM impurities Nb, Mo, Ta, and W at the 1NN and 2NN sites are given in Table I. The results are in reasonable agreement with the experimental values at the 1NN sites. On the whole the calculated results are on the higher side than the experimental

TABLE I. Calculated and experimental values of the EFG (\AA^{-3}) at 1NN and 2NN sites for Nb, Mo, Ta, and W impurities in V. v , s , and t denote valence, size, and total EFG's, respectively.

Impurities	EFG components			$ q ^{\text{calc}}$ [Expt.]	
	q_{xx}	q_{\perp}	q_{\parallel}		
1NN					
Nb	v	-0.766	-0.766	1.532	1.01 [0.84]
	s	0.262	0.262	-0.524	
	t	-0.504	-0.504	<u>1.008</u>	
Mo	v	-0.327	-0.327	0.654	0.40 [0.34]
	s	0.129	0.129	-0.258	
	t	-0.198	-0.198	<u>0.396</u>	
Ta	v	-1.057	-1.057	2.114	1.54 [1.00]
	s	0.286	0.286	-0.572	
	t	-0.771	-0.771	<u>1.542</u>	
W	v	-0.442	-0.442	0.884	0.71 [0.71]
	s	0.086	0.086	-0.172	
	t	-0.356	-0.356	<u>0.712</u>	
2NN					
Nb	v	-0.089	-0.089	0.178	0.56
	s	-0.191	-0.191	0.383	
	t	-0.280	-0.280	<u>0.561</u>	
Mo	v	-0.028	-0.028	0.056	0.31
	s	-0.127	-0.127	0.255	
	t	-0.155	-0.155	<u>0.311</u>	
Ta	v	-0.104	-0.104	0.208	0.62
	s	-0.207	-0.207	0.415	
	t	-0.311	-0.311	<u>0.623</u>	
W	v	-0.016	-0.016	0.032	0.33
	s	-0.147	-0.147	0.293	
	t	-0.163	-0.163	<u>0.325</u>	

values, but there are many deficiencies in the experimental results too.⁴

The calculated results for the EFG show the following noteworthy features.

(i) It is found that q^v dominates over q^s in all the alloys of V considered here, which is consistent with the results of Pal *et al.*⁶ Rattan, Prakash, and Singh⁵ also predicted the same behavior in some of the V alloys.

(ii) The maximum component of the EFG is along the parallel direction [111] for the 1NN, which is consistent with the experimental results.⁴

(iii) The present discrete-lattice calculations yield a cylindrically symmetric size EFG tensor q^s , which is consistent with earlier calculations.⁶ The cylindrical symmetry of q^s is due to the bcc symmetry of the host lattice and the use of the central crystal potential, which gives $\eta=0$. The inclusion of the asymmetric nature of the d states in the valence effect may yield a small but finite value of η .

(iv) q_{\parallel}^v is much larger than q_{\parallel}^s for Nb and Ta impurities, while both are comparable for Mo and W impurities at the 1NN.

(v) Although EFG at the 2NN site is less than that at the 1NN site, it is large. Further, at the 2NN site q_{\parallel}^s dominates over q_{\parallel}^v , contrary to the situation at the 1NN site. Such a trend in the EFG was also found in dilute alloys with fcc structure. The large values of the EFG at the 2NN sites show that the impurities are not screened in the Wigner-Seitz (WS) cell, which is consistent with the results of Podlucky *et al.*¹¹ The situation in the dilute alloys of fcc structure is quite different as the EFG at the 2NN sites is quite small in these alloys.² It shows that the impurity is nearly screened in the WS cell of the impurity atom in the dilute alloys of fcc structure, which is consistent with the results of Dederichs *et al.*¹²

IV. DISCUSSION

In the present investigations, the uncertainties in the EFG due to asymptotic and preasymptotic behavior of charge density, core enhancement factor, and size strength parameter no longer exist.¹ The d -band characteristics of the host and impurity are included explicitly in the ionic potential. The calculations are internally consistent as the impurity-induced strain field, used here, has been calculated with the help of same interionic potential.⁹ The calculated values of the EFG reproduce the trend of experimental results. The present results can be improved by using a more reliable *ab initio* interionic potential. One of the methods is to calculate $\phi_i(r)$ and $\phi_H(r)$ using dielectric screening theory.¹³ In the end we would like to say that, to the best of our knowledge, this is the first calculation of the EFG in dilute alloys of bcc structure which uses the full discrete-lattice model for the evaluation of both the valence and size EFG's.

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