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Strain field due to substitutional transition-metal impurities in bcc metals: Application to dilute vanadium alloys

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The formalism for the generalized Kanzaki lattice static method is developed for a metallic crystal with bcc symmetry. The interactions up to second-nearest neighbors are included in the derivation of the dynamical matrix, impurity-induced force, and the atomic displacements. The formalism is applied to calculate the strain field due to 3*d*, 4*d*, and 5*d* substitutional transition-metal impurities (Ti, Cr, Mn, Fe, Nb, Mo, Ta, and W) in the vanadium metal, the only bcc systems in which the study of electric field gradients has been performed. The effective ion-ion interaction potential for the transition metals, proposed by Wills and Harrison, which includes properly the *d*-band effects, is used in the numerical calculations. In all the systems the atomic displacements are calculated up to 21 nearest neighbors and these show oscillatory behavior. The maximum displacement (or strain field) is caused by a Ta impurity and is about 3.5% of the first-nearest-neighbor distance. The strain field is found to depend, both in strength and range, on the excess ion-ion interaction potential due to the impurity. The atomic displacements exhibit the same trend, as shown by x-ray studies of the fractional change in the lattice parameter.

I. INTRODUCTION

The introduction of a substitutional impurity in an otherwise perfect crystal changes the electrostatic interactions in the vicinity of the impurity.[1,2] The change in the electrostatic interactions is brought about by two distinct physical effects: the different electronic structure and different size of the impurity. Both cause a change in the atomic force constants between the impurity and host atoms. The two effects are in fact interrelated. The altered electrostatic interactions force the host atoms to move to new equilibrium positions, thus producing a strain field in the host lattice around the impurity.[3–5] Precise knowledge of the impurity-induced strain field is of immense importance in studying several electronic properties such as the redistribution of conduction-electron density, residual resistivity, electric field gradient, self-energy of the impurity, diffusion, etc.[6–10]

The theoretical study of the impurity-induced strain field can be classified into three categories: elastic continuum models,[9] computer simulations,[11,12] and lattice static methods.[4,5,13] The merits and demerits of these methods are discussed in our recent paper.[14] Out of these, the lattice static method is the most suitable as it takes care of the discrete nature of the whole lattice. The two lattice static methods, Kanzaki and Green-function methods,[5,13] are based on the Born–von Karman theory of crystalline solids. The Kanzaki and Green-function methods are different in approach, but are equivalent. Recently, we[14] have generalized the Kanzaki method to evaluate the strain field so that it is applicable to different types of impurities. It is applied to evaluate the strain field due to substitutional impurities in Al and Cu, having fcc structure, where the excess impurity potential is evaluated using the dielectric screening theory. It has been found that the calculation of the strain field due to a substitutional transition-metal (TM) impurity in a TM host does not exist, which may be due to the complexity of the systems. A TM impurity causes resonant scattering of the conduction electrons in a metallic system,[15] which is difficult to deal with theoretically. Therefore precise knowledge of the interionic potential in such complicated systems was not available. Wills and Harrison[16] have given an effective interionic potential for the TM's which includes the *d*-band effects approximately. We therefore think it worthwhile to apply the lattice static method[14] for evaluating the strain field due to the substitutional TM impurities in a TM host with bcc structure.

The plan of the paper is as follows. In Sec. II we give necessary expressions of the lattice static method with reference to the bcc crystal structure. In Sec. III we apply the formalism to calculate the strain field due to 3*d*, 4*d*, and 5*d* TM impurities in vanadium (V) metal. The results are discussed in Sec. IV.

II. THEORY

Consider a perfect monatomic crystal where $\mathbf{R}_n^0$ and $\phi(\mathbf{r})$ denote the lattice points and ion-ion pair potential, respectively. Let a substitutional impurity, assumed to be situated at the origin, be introduced in the crystal which displaces the surrounding host ions to new equilibrium positions defined as

$$\mathbf{R}_n = \mathbf{R}_n^0 + \mathbf{u}(\mathbf{R}_n^0) , \tag{1}$$

where $\mathbf{u}(\mathbf{R}_n^0)$ is the displacement of the *n*th nearest neighbor (nNN) of the impurity. Kanzaki[13] assumed that

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$\mathbf{u}(\mathbf{R}_n^0)$ are produced by an appropriate distribution of external forces (Kanzaki forces) in the lattice which depend upon the nature of the impurity. The total energy of the strained lattice can be expanded in powers of $\mathbf{u}(\mathbf{R}_n^0)$, which in the harmonic approximation is given as

$$\Phi=\sum_n \phi(\mathbf{R}_n)=\Phi_0-\sum_{n,\alpha} u_\alpha(\mathbf{R}_n^0)F_\alpha(\mathbf{R}_n^0) + \frac{1}{2}\sum_{n,\alpha}\sum_{n',\beta} u_\alpha(\mathbf{R}_n^0)u_\beta(\mathbf{R}_{n'}^0)\phi_{\alpha\beta}(n,n') , \tag{2}$$

where

$$F_\alpha(\mathbf{R}_n^0)=-\left.\frac{\partial\phi}{\partial u_\alpha(\mathbf{R}_n^0)}\right|_{u_\alpha(\mathbf{R}_n^0)=0} , \tag{3}$$

$$\phi_{\alpha\beta}(n,n')=\left.\frac{\partial^2\phi}{\partial u_\alpha(\mathbf{R}_n^0)\partial u_\beta(\mathbf{R}_{n'}^0)}\right|_{u_\alpha(\mathbf{R}_n^0)=u_\beta(\mathbf{R}_{n'}^0)=0} . \tag{4}$$

Here α and β ($=1$, 2, 3) denote the Cartesian components. $\Phi_0=\sum_n\phi(\mathbf{R}_n^0)$ is the total potential energy of the perfect lattice and $F_\alpha(\mathbf{R}_n^0)$ is the α component of the external force acting on the atom $\mathbf{R}_n^0$. $\phi_{\alpha\beta}(n,n')$ are the force constants which satisfy the crystal symmetries.[17] The equilibrium values of $\mathbf{u}(\mathbf{R}_n^0)$ are obtained by minimizing Φ with respect to $\mathbf{u}(\mathbf{R}_n^0)$, which gives

$$F_\alpha(\mathbf{R}_n^0)=\sum_{n',\beta}\phi_{\alpha\beta}(n,n')u_\beta(\mathbf{R}_{n'}^0) . \tag{5}$$

Equation (5) shows that $\mathbf{u}(\mathbf{R}_n^0)$ can be evaluated if one knows $F_\alpha(\mathbf{R}_n^0)$ and $\phi_{\alpha\beta}(n,n')$. It is convenient to express $\mathbf{u}(\mathbf{R}_n^0)$ in terms of normal coordinates $\mathbf{Q}(\mathbf{q})$ as

$$\mathbf{u}(\mathbf{R}_n^0)=\sum_q \mathbf{Q}(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{R}_n^0) , \tag{6}$$

where $\mathbf{q}$ is the wave vector in Fourier space. The normal coordinates satisfy the property $\mathbf{Q}^*(\mathbf{q})=\mathbf{Q}(-\mathbf{q})$. With the help of Eq. (6), one can Fourier transform the total energy Φ of the strained lattice. The equilibrium state is then obtained by minimizing Φ with respect to $\mathbf{Q}(\mathbf{q})$ to get

$$\sum_\beta [N\phi_{\alpha\beta}(-\mathbf{q})Q_\beta(\mathbf{q})-F_\beta(\mathbf{q})\delta_{\alpha\beta}\delta_{-\mathbf{q},\mathbf{q}}]=0 , \tag{7}$$

where

$$F_\alpha(\mathbf{q})=\sum_n F_\alpha(\mathbf{R}_n^0)\exp(i\mathbf{q}\cdot\mathbf{R}_n^0) , \tag{8}$$

$$\phi_{\alpha\beta}(\mathbf{q})=\sum_{n-n'}\phi_{\alpha\beta}(n-n')\exp[-iq\cdot(\mathbf{R}_{n'}^0-\mathbf{R}_n^0)] . \tag{9}$$

N is the total number of atoms in the lattice. $\mathbf{F}(\mathbf{q})$ and $\phi_{\alpha\beta}(\mathbf{q})$ are the Fourier transforms of $\mathbf{F}(\mathbf{R}_n^0)$ and $\phi_{\alpha\beta}(n-n')$, and $\phi_{\alpha\beta}(\mathbf{q})$ is usually called the dynamical matrix.

The dynamical matrix for a crystal structure can be obtained from Eq. (9). $\phi_{\alpha\beta}(n)$ for a central ion-ion potential can be written as

$$\phi_{\alpha\beta}(n)=\left.\frac{\partial^2\phi}{\partial r_\alpha\partial r_\beta}\right|_{\mathbf{r}=\mathbf{R}_n^0}=\frac{R_{n\alpha}^0R_{n\beta}^0}{|\mathbf{R}_n^0|^2}(A_n-B_n)+\delta_{\alpha\beta}B_n , \tag{10}$$

where

$$A_n=\left.\frac{\partial^2\phi}{\partial r^2}\right|_{\mathbf{r}=\mathbf{R}_n^0} , \quad B_n=\left.\frac{1}{|\mathbf{R}_n^0|}\frac{\partial\phi}{\partial r}\right|_{\mathbf{r}=\mathbf{R}_n^0} . \tag{11}$$

$R_{n\alpha}^0$ is the α Cartesian component of $\mathbf{R}_n^0$. In a metallic crystal, the ions are screened by the conduction electrons thereby decreasing the ionic potentials faster, which exhibit oscillatory behavior at large distances. It has been found that in the d-band metals the screening is very heavy.[18-20] Therefore the major contribution to $\phi_{\alpha\beta}(\mathbf{q})$ and $F_\alpha(\mathbf{q})$ in these systems is expected to arise from a few NN's. Including the interactions up to 2NN's (the simplest approximation), $\phi_{\alpha\beta}(\mathbf{q})$ for a bcc structure, from Eqs. (9) and (10), becomes

$$\begin{aligned}\phi_{\alpha\alpha}(\mathbf{q})&=\tfrac{8}{3}(A_1+2B_1)[1-\cos(q_\alpha a/2)\cos(q_\beta a/2)\cos(q_\gamma a/2)]+4A_2[\sin^2(q_\alpha a/2)+\sin^2(q_\beta a/2)+\sin^2(q_\gamma a/2)] ,\\ \phi_{\alpha\beta}(\mathbf{q})&=\tfrac{8}{3}(A_1-B_1)\sin(q_\alpha a/2)\sin(q_\beta a/2)\sin(q_\gamma a/2) ,\end{aligned} \tag{12}$$

with $\alpha\neq\beta\neq\gamma$. Here a denotes the lattice parameter.

One can also obtain the Fourier transform of the Kanzaki force $F_\alpha(\mathbf{q})$ from Eqs. (3) and (8). Considering only the 1NN interactions one gets, for the bcc structure,

$$F_\alpha(\mathbf{q})=\frac{8}{\sqrt{3}}iF_{\mathrm{I}}\sin(q_\alpha a/2)\sin(q_\beta a/2)\sin(q_\gamma a/2) , \tag{13}$$

with

$$F_{\mathrm{I}}=-\left[\frac{\partial}{\partial r}\Delta\phi(r)\right]_{r=\mathbf{R}_{\mathrm{I}}^0} , \tag{14}$$

where $\alpha\neq\beta\neq\gamma$. Here F_{I} is the force acting on the 1NN site, the position of which is given by $\mathbf{R}_{\mathrm{I}}^0$. $\Delta\phi(\mathbf{r})$ is the excess interionic potential due to a substitutional impurity and is defined as[14]

$$\Delta\phi(\mathbf{r})=\phi_{\mathrm{IH}}(\mathbf{r})-\phi_{\mathrm{HH}}(\mathbf{r}) , \tag{15}$$

where $\phi_{\mathrm{HH}}(\mathbf{r})$ and $\phi_{\mathrm{IH}}(\mathbf{r})$ are the host-host and impurity-host interionic potentials. Similarly, considering only the 2NN interactions, $F_\alpha(\mathbf{q})$ becomes

$$F_\alpha(\mathbf{q})=i2F_{\mathrm{II}}\sin(q_\alpha a) , \tag{16}$$

where

$$F_{\mathrm{II}} = -\left[\frac{\partial}{\partial r}\Delta\phi(\mathbf{r})\right]_{r=\mathbf{R}_2^0} \tag{17}$$

and $\mathbf{R}_2^0$ defines the position of the 2NN site.

With the knowledge of $\phi_{\alpha\beta}(\mathbf{q})$ and $F_\alpha(\mathbf{q})$, one can solve Eq. (7) for $Q_\alpha(\mathbf{q})$ using the properties of determinants. For the radial forces on the 1NN only (usually called the F_{I} system) of the impurity,

$$iQ_1(\mathbf{q}) = \frac{\sqrt{3}F_{\mathrm{I}}}{NA_1}\begin{vmatrix} \sin x\cos y\cos z & G_2 & G_3 \\ \sin y\cos z\cos x & G_1 & G_4 \\ \sin z\cos x\cos y & G_4 & G_1 \end{vmatrix}\Big/\Delta\,, \tag{18}$$

where

$$\Delta = \begin{vmatrix} G_1 & G_2 & G_3 \\ G_2 & G_1 & G_4 \\ G_3 & G_4 & G_1 \end{vmatrix}\,, \tag{19}$$

$$G_1 = \left[1+\frac{2B_1}{A_1}\right][1-\cos x\cos y\cos z] + \frac{3}{2}\frac{A_2}{A_1}(\sin^2 x+\sin^2 y+\sin^2 z)\,, \tag{20}$$

$$G_2 = \left[1-\frac{B_1}{A_1}\right]\sin x\sin y\cos z\,, \tag{21}$$

$$G_3 = \left[1-\frac{B_1}{A_1}\right]\sin x\sin z\cos y\,, \tag{22}$$

$$G_4 = \left[1-\frac{B_1}{A_1}\right]\sin y\sin z\cos x\,, \tag{23}$$

$$x = \frac{q_x a}{2}\,,\quad y = \frac{q_y a}{2}\,,\quad z = \frac{q_z a}{2}\,. \tag{24}$$

$Q_2(\mathbf{q})$ and $Q_3(\mathbf{q})$ can be obtained from $Q_1(\mathbf{q})$ using cubic symmetry.

For the radial forces acting only on the 2NN sites (called the F_{II} system) of the impurity, Eq. (7) gives

$$iQ_1 = \frac{3}{4}\frac{F_{\mathrm{II}}}{NA_1}\begin{vmatrix} \sin 2x & G_2 & G_3 \\ \sin 2y & G_1 & G_4 \\ \sin 2z & G_4 & G_1 \end{vmatrix}\Big/\Delta\,. \tag{25}$$

For the substitutional impurities, Rattan *et al.*[14] have proposed a model to calculate the impurity-induced force given as

$$F_\alpha(\mathbf{R}_n^0) = -\frac{\partial}{\partial u_\alpha(\mathbf{R}_n^0)}\sum_{n'}\Delta\phi(|\mathbf{R}_{n'}|)\,. \tag{26}$$

In the central field approximation, both $\mathbf{u}(\mathbf{R}_n^0)$ and $\mathbf{F}(\mathbf{R}_n^0)$ are parallel to $\mathbf{R}_n^0$; therefore, one can expand $\Delta\phi(|\mathbf{R}_{n'}|)$ in powers of displacements to write

$$F_\alpha(\mathbf{R}_n^0) = -\frac{\partial}{\partial r}\Delta\phi\Big|_{|\mathbf{r}|=|\mathbf{R}_n^0|} - \mathbf{u}(\mathbf{R}_n^0)\frac{\partial^2}{\partial r^2}\Delta\phi\Big|_{|\mathbf{r}|=|\mathbf{R}_n^0|}\,. \tag{27}$$

Equation (27) can be solved in two approximations. If $\mathbf{u}(\mathbf{R}_n^0)$ is very small, the second term in Eq. (27) can be neglected. It is called the first approximation in which the force constants of the host metal remain unchanged in the presence of the impurity. If $\mathbf{u}(\mathbf{R}_n^0)$ is significant, both terms in Eq. (27) should be retained. It is called the second approximation and takes care of the impurity-induced change in the force constants of the lattice. To include the interactions up to 2NN's, the atomic displacements in the F_{I} and F_{II} systems can be combined to evaluate $u_\alpha(\mathbf{R}_n^0)$ in the second approximation just as done by Kanzaki.[13]

III. CALCULATIONS AND RESULTS

In the estimation of impurity-induced strain field in dilute metallic alloys, the central quantity of interest is the excess interionic potential $\Delta\phi(\mathbf{r})$. In a TM the *s* electrons in the outermost shell of the atom get detached and are free to move in the crystal. Therefore the TM ion possesses quasilocalized *d* electrons in the outermost shell, the effect of which should be included in evaluating the ion-ion interaction potential. In the formation of a TM, the *d* shells are broadened into quasilocalized bands, with finite bandwidth, as a result of the Pauli exclusion principle. Further, the *d* band experiences the crystal potential of the TM, as a result of which it suffers distortion. The *d*-band distortion is responsible for the *s*-*d* hybridization and has the effect of shifting the *d*-band center.

In free-electron metal alloys, the calculation of $\Delta\phi(\mathbf{r})$ in the dielectric screening approach is simple because of their on band structure. But in the TM alloys the band structure is anisotropic and complicated, which makes the evaluation of $\Delta\phi(\mathbf{r})$, in the dielectric screening approach, difficult. However, we outline, in the Appendix, the evaluation of $\Delta\phi(\mathbf{r})$ in the dielectric screening approach (not used in the present calculations) and discuss it in light of the present calculations. Wills and Harrison[16] have given the analytical form for the effective interionic potential for TM's which includes the effect of the shift in the *d*-band center and the finite *d*-bandwidth. They have calculated a number of properties such as the bulk modulus, Grüneisen constant, and the elastic constants of a larger number of TM's and obtained reasonable agreement for most of the TM's. Here we use the effective ion-ion interaction potential due to Wills and Harrison for the host metal, which is defined as

$$\phi_{\mathrm{HH}}(r) = \phi_{\mathrm{HH}}^{\mathrm{FE}}(r)+\phi_{\mathrm{HH}}^{c}(r)+\phi_{\mathrm{HH}}^{b}(r)\,, \tag{28}$$

where

$$\phi_{\mathrm{HH}}^{\mathrm{FE}}(r) = Z_{s\mathrm{H}}^2 e^2\cosh^2(\kappa r_{c\mathrm{H}})\frac{e^{-\kappa r}}{r}\,, \tag{29}$$

$$\phi_{\mathrm{HH}}^{c}(r) = Z_{d\mathrm{H}}\frac{225}{\pi^2}\frac{\hbar^2 r_{d\mathrm{H}}^6}{mr^8}\,, \tag{30}$$

$$\phi^{b}_{\mathrm{HH}}(r)=-Z_{d\mathrm{H}}\left[1-\frac{Z_{d\mathrm{H}}}{10}\right]\left[\frac{12}{n}\right]^{1/2}\frac{28.1}{\pi}\frac{\hbar^2 r_{d\mathrm{H}}^3}{mr^5} . \tag{31}$$

Here n is the number of 1NN's in a crystal, $Z_{s\mathrm{H}}$ and $Z_{d\mathrm{H}}$ are the number of s and d electrons in the host atom which are related to the valency Z_{H} as $Z_{s\mathrm{H}}+Z_{d\mathrm{H}}=Z_{\mathrm{H}}$. $\phi^{\mathrm{FE}}_{\mathrm{HH}}(r)$ is the free-electron contribution obtained from the Ashcroft empty-core model potential in conjunction with the Thomas-Fermi approximation. κ is the Thomas-Fermi constant, and $r_{c\mathrm{H}}$ is the model-potential core radius of the host atom. $\phi^{c}_{\mathrm{HH}}(r)$ is the contribution arising from the shift in the d-band center (or s-d hybridization) and depends upon the d-state radius $r_{d\mathrm{H}}$ of the host atom. $\phi^{b}_{\mathrm{HH}}(r)$ is the contribution arising from the finite d-bandwidth and is of the form of a resonant bond.[21] The term $Z_{d\mathrm{H}}(1-Z_{d\mathrm{H}}/10)$ represents the continuous filling of the bonding through antibonding levels. In a TM the s-d hybridization arises from the scattering of mobile s electrons from the d-shell electrons at the ion sites, which causes distortion of the d shells. Therefore the screening of polarized d charge by the s electrons is described by the matrix elements $\langle \mathbf{k}|\Delta_{sd}|d\rangle$, where $|\mathbf{k}\rangle$ and $|d\rangle$ are plane waves and atomic d state and Δ_{sd} is the s-d hybridization potential.[16] The parameter $r_{d\mathrm{H}}$ is determined by the matrix elements $\langle \mathbf{k}|\Delta_{sd}|d\rangle$ and therefore includes the s-d hybridization effects partially. Further, the s-d hybridization changes the s and d charge in a TM atom. The change in d charge, ΔZ_d, is accompanied by an equal and opposite change in s charge, ΔZ_s, to make the atom neutral. Wills and Harrison[16] (and also this paper) used $Z_s=1.5$, which is obtained from self-consistent calculations. In the dielectric screening approach (see the Appendix), the screening, by s electrons, of the polarized d charge at the ionic sites is included through the screened form factors of monopoles and dipoles represented by $A_s(\mathbf{K})/\varepsilon_0(\mathbf{K})$.

Equations (28)–(31) can be generalized to write the interatomic potential for the impurity-host ion interaction in an alloy. Wills and Harrison[16] suggested that the free-electron contribution due to the impurity-host interaction, $\phi^{\mathrm{FE}}_{\mathrm{IH}}(r)$, is obtained by replacing $Z_{s\mathrm{H}}e$ by $(Z_{s\mathrm{H}}Z_{s\mathrm{I}}e^2)^{1/2}$ and $\cosh(\kappa r_{c\mathrm{H}})$ by

$$[\cosh(\kappa' r_{c\mathrm{H}})\cosh(\kappa' r_{c\mathrm{I}})]^{1/2} ,$$

where $Z_{s\mathrm{I}}$ and $r_{c\mathrm{I}}$ are the number of s electrons and the model-potential core radius, respectively, of the impurity. κ changes to the new value κ' as the conduction-electron density changes with the addition of the impurity. The d-electron contribution to the interionic potential depends upon $Z_{d\mathrm{H}}$ and $r_{d\mathrm{H}}$. For the impurity-host interaction in the alloy, $r_{d\mathrm{H}}$ is replaced by $(r_{d\mathrm{H}}r_{d\mathrm{I}})^{1/2}$, where $r_{d\mathrm{I}}$ is the d-state radius of the impurity ion. But very little is known about the variation of the number of d electrons in the d band by the introduction of the impurity. As the simplest approximation, one can take the effective number of d electrons, Z_d^{eff}, in an alloy to be the weighted average (by concentration) of the number of d electrons in the host and impurity ions, i.e.,

$$Z_d^{\mathrm{eff}}=C_{\mathrm{H}}Z_{d\mathrm{H}}+C_{\mathrm{I}}Z_{d\mathrm{I}} , \tag{32}$$

where $Z_{d\mathrm{I}}$ is the number of d electrons in the impurity ion. C_{H} and C_{I} are the concentrations of the host and impurity ions, respectively. Taking into account the above facts, $\phi_{\mathrm{IH}}(r)$ can be written as

$$\phi_{\mathrm{IH}}(r)=\phi^{\mathrm{FE}}_{\mathrm{IH}}(r)+\phi^{c}_{\mathrm{IH}}(r)+\phi^{b}_{\mathrm{IH}}(r) , \tag{33}$$

where

$$\phi^{\mathrm{FE}}_{\mathrm{IH}}(r)=Z_{s\mathrm{H}}Z_{s\mathrm{I}}e^2\cosh(\kappa' r_{c\mathrm{H}})\cosh(\kappa' r_{c\mathrm{I}})\frac{e^{-\kappa' r}}{r} , \tag{34}$$

$$\phi^{c}_{\mathrm{IH}}(r)=Z_d^{\mathrm{eff}}\frac{225}{\pi^2}\frac{\hbar^2 r_{d\mathrm{H}}^3 r_{d\mathrm{I}}^3}{mr^8} , \tag{35}$$

$$\phi^{b}_{\mathrm{IH}}(r)=-Z_d^{\mathrm{eff}}\left[1-\frac{Z_d^{\mathrm{eff}}}{10}\right]\left[\frac{12}{n}\right]^{1/2}\frac{28.1}{\pi}\frac{\hbar^2 r_{d\mathrm{H}}^{3/2} r_{d\mathrm{I}}^{3/2}}{mr^5} . \tag{36}$$

The potential $\phi_{\mathrm{IH}}(r)$ includes the impurity-induced s-d hybridization through $r_{d\mathrm{I}}$ and effective charge $Z_s=1.5$ and the corresponding d charge Z_d. But as the TM impurity is introduced in a different TM host, there may be a further transfer of electrons to or from the s and d bands, as a result of which the conduction-electron charge would rearrange around the impurity site to screen or unscreen it. To include these effects, the d charge on the impurity may be varied (keeping the atom neutral) and its value should be calculated self-consistently. The charge transfer will be appreciable only when the TM's, mixed together to form an alloy, have d-band centers differing by large amount of energy. But most of the TM's considered in this text have their d-band centers close to each other (within a few eV), and therefore the charge transfer may be quite small and neglected here. Hence the application of the potential $\phi_{\mathrm{IH}}(r)$ given by Eqs. (33)–(36) is quite reasonable. Thus, in a metallic alloy the excess interionic potential due to the impurity can be written from Eqs. (15) and (28)–(36) as

$$\Delta\phi(r)=\Delta\phi^{\mathrm{FE}}(r)+\Delta\phi^{c}(r)+\Delta\phi^{b}(r) , \tag{37}$$

where

$$\Delta\phi^{\mathrm{FE}}(r)=\frac{Z_{s\mathrm{H}}e^2}{r}[Z_{s\mathrm{I}}\cosh(\kappa' r_{c\mathrm{H}})\cosh(\kappa'_{c\mathrm{I}})e^{-\kappa' r}-Z_{s\mathrm{H}}\cosh^2(\kappa r_{c\mathrm{H}})e^{-\kappa r}] , \tag{38}$$

$$\Delta\phi^{c}(r)=[Z_d^{\mathrm{eff}}r_{d\mathrm{I}}^3-Z_{d\mathrm{H}}r_{d\mathrm{H}}^3]\frac{225}{\pi^2}\frac{\hbar^2 r_{d\mathrm{H}}^3}{mr^8} , \tag{39}$$

TABLE I. Some physical parameters and atomic force constants at 1NN and 2NN (in a.u.) of V metal.

a	Ω_0	Z	A_1 (10^{-2})	B_1 (10^{-2})	A_2 (10^{-2})	B_2 (10^{-2})
5.7205	93.6	5	−0.446 02	0.229 05	−0.435 44	0.134 17

$$\Delta\phi^b(r)=\left[-Z_d^{\text{eff}}\left\{1-\frac{Z_d^{\text{eff}}}{10}\right\}r_{d\text{I}}^{3/2}+Z_{d\text{H}}\left\{1-\frac{Z_{d\text{H}}}{10}\right\}r_{d\text{H}}^{3/2}\right]\left[\frac{12}{n}\right]^{1/2}\frac{28.1}{\pi}\frac{\hbar^2 r_{d\text{H}}^{3/2}}{mr^5}\ . \tag{40}$$

Equations (33)–(40) are valid at all concentrations. Here $\Delta\phi^{\text{FE}}(r)$ represents the change in the free-electron contribution to the ion-ion interaction potential. $\Delta\phi^c(r)$ gives the contribution arising from the impurity-induced s-d hybridization and therefore describes the effect of the crystal field of the host metal on the impurity atom. The third contribution $\Delta\phi^b(r)$ gives the change in ion-ion interaction potential due to the impurity-induced change in d-band width.

In the present study, we are interested in dilute metallic alloys. In dilute metallic alloys, the conduction-electron density remains nearly the same as that in the pure host metal. Therefore the Thomas-Fermi constant does not change with the addition of the impurity in a dilute alloy. Further, for $c_\text{I} \ll c_\text{H}$, the effective number of d electrons is nearly the same as $Z_{d\text{H}}$ [see Eq. (32)]. Hence for a dilute alloy $\Delta\phi(r)$ can be obtained from Eqs. (37)–(40) by substituting

$$\kappa'=\kappa\ ,\quad Z_d^{\text{eff}}=Z_{d\text{H}}\ . \tag{41}$$

We apply the formalism to calculate the strain field in V-based dilute alloys with 3d, 4d, and 5d substitutional impurities, namely, Ti, Cr, Mn, Fe, Nb, Mo, Ta, and W. The parameters needed to evaluate $\phi_{\text{HH}}(r)$, $\phi_{\text{IH}}(r)$, and $\Delta\phi(r)$, given by Eqs. (28), (33), and (37), respectively, are taken from Wills and Harrison.[16] Some physical parameters and the calculated force constants of V metal are given in Table I. The forces F_I and F_{II}, evaluated in the second approximation, for all the TM impurities, are given in Table II.

Figure 1 shows $\phi_{\text{HH}}(r)$ as a function of r for V metal. The contributions $\phi_{\text{HH}}^{\text{FE}}(r)$ and $\phi_{\text{HH}}^{c}(r)$ are positive and are found to decay fast. On the other hand, $\phi_{\text{HH}}^{b}(r)$ is negative and decreases slowly. The addition of the three contributions gives a minimum in $\phi_{\text{HH}}(r)$ occurring at $r=4.0$ a.u., a distance less than the 1NN distance.

Figure 2 shows $\Delta\phi(r)$ as a function of r for the TM impurities Cr, Mn, Nb, and Ta in the V metal. It has been found that $\Delta\phi(r)$ due to Nb, Mo, Ta, W, and Ti is positive at small values of r and shows a minimum at $r\simeq4.8$ a.u., a distance close to that of 1NN. On the other hand, $\Delta\phi(r)$ due to Cr, Mn, and Fe is negative at small r values and exhibits a maximum at $r\simeq4.8$ a.u. Such a variation of $\Delta\phi(r)$ is due to the fact that $\phi_{\text{HH}}(r)$ is larger than $\phi_{\text{IH}}(r)$ for these impurities. The intercomparison shows

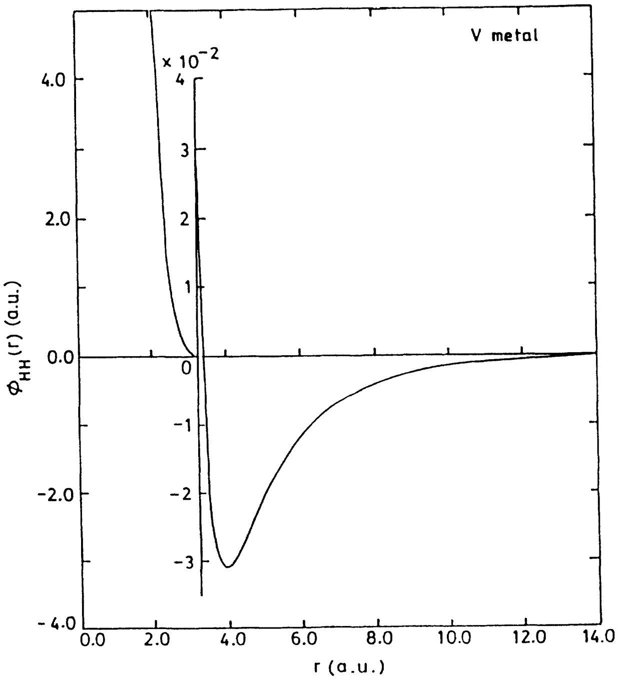

FIG. 1. $\phi_{\text{HH}}(r)$ as a function of r for the V metal.

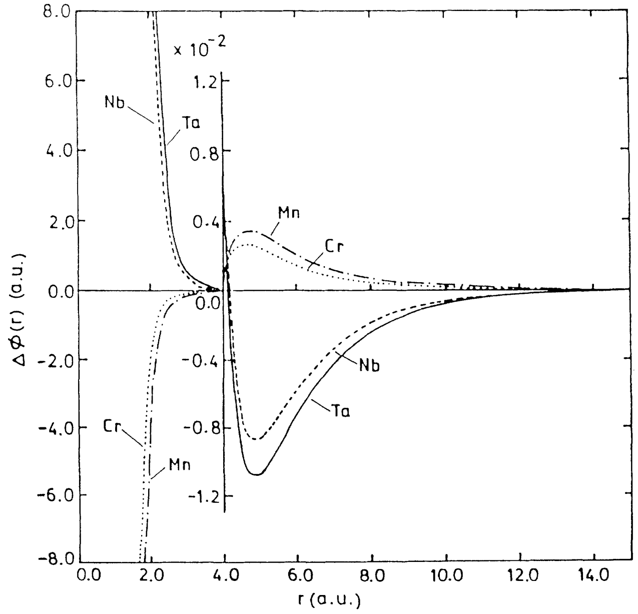

FIG. 2. $\Delta\phi(r)$ as a function of r for Nb, Ta, Cr, and Mn impurities in V metal.

TABLE II. Impurity-induced forces $F_{\rm I}$ and $F_{\rm II}$ (in 10^{-3} a.u.), evaluated in the second approximation, for Ti, Cr, Mn, Fe, Nb, Ta, and W impurities in V metal.

	Ti	Cr	Mn	Fe	Nb	Mo	Ta	W
$F_{\rm I}$	−1.579 08	0.842 25	0.800 98	0.720 68	−1.943 10	−3.195 91	−2.864 42	−5.540 25
$F_{\rm II}$	−1.315 34	0.945 74	1.205 47	1.557 86	−3.095 78	−2.685 34	−3.801 22	−3.631 19

that $\Delta\phi(r)$ is stronger and long ranged for the 4*d* and 5*d* impurities as compared to that for the 3*d* impurities. Among all the TM impurities, $\Delta\phi(r)$ is the strongest for Ta with the maximum range.

The atomic displacements are calculated in the $F_{\rm I}$ and $F_{\rm II}$ systems using Eqs. (6), (18), and (25). The numerical calculations are simplified by replacing the summation over $\mathbf{q}$ by the integration over the cube inscribing the first Brillouin zone (BZ) and using the fact that, for any function $F(\mathbf{q})$,

$$\int_{\rm BZ} F(\mathbf{q})d\mathbf{q}=\frac{1}{4}\int_{\rm cube} F(\mathbf{q})d\mathbf{q}\ , \tag{42}$$

for the bcc structure. The cube edge is $4\pi/a$. The integration is carried out by the Gaussian quadrature method, and a convergence up to five decimal places is achieved. The atomic displacements calculated in the $F_{\rm I}$ and $F_{\rm II}$ systems are then combined to include the interactions up to 2NN's using the method of Kanzaki.[13] The values of $F_{\rm I}$ and $F_{\rm II}$ given in Table II are used to evaluate the atomic displacements $\mathbf{u}(\mathbf{r})$ for the various NN's. Tables III–X give $\mathbf{u}(\mathbf{R}_n^0)$ up to 21 NN's due to Ti, Cr, Mn, Fe, Nb, Mo, Ta, and W, respectively, as these are of interest in the theoretical study of other physical properties.[6–10] Some of the interesting features which emerge out of the present calculated values of $\mathbf{u}(\mathbf{R}_n^0)$ for the different impurities are given below.

(i) The strain field $\mathbf{u}(\mathbf{r})$ is oscillatory in nature, but its strength decreases with the increase of $\mathbf{r}$. It is in agreement with the existing calculations of $\mathbf{u}(\mathbf{r})$ for vacancies and interstitials.[13,14,22–25] One should note that $\mathbf{u}(\mathbf{r})$ is maximum at the 2NN site in all the substitutional TM impurities except for W.

(ii) $\mathbf{u}(\mathbf{r})$ at the 1NN site has the same sign as that of $F_{\rm I}$ and $F_{\rm II}$, but at the 2NN site its sign is opposite to that of $F_{\rm I}$ and $F_{\rm II}$.

(iii) It is found that $\mathbf{u}(\mathbf{r})$ is maximum in magnitude and longest in range for the Ta impurity. Similar behavior is also exhibited by $\Delta\phi(r)$ for Ta. One should note that the maximum value of $|\mathbf{u}(\mathbf{r})|$ in Ta, at the 2NN site, is about 3.5% of the 1NN distance $\mathbf{R}_1^0$. In general, it is found that stronger $\Delta\phi(r)$ will produce a stronger strain field around

TABLE III. Atomic displacements (a.u.) of the NN's of Ti impurity in V metal.

NN's (n_1,n_2,n_3)	Displacement components u_x	 u_y	 u_z	 $\|\mathbf{u}\|$
111	−0.019 03	−0.019 03	−0.019 03	0.032 97
200	0.036 75	0.0	0.0	0.036 75
220	0.009 87	0.009 87	0.0	0.013 95
311	−0.015 75	0.000 87	0.000 87	0.015 80
222	0.012 59	0.012 59	0.012 59	0.021 80
400	0.002 39	0.0	0.0	0.002 39
331	−0.004 35	−0.004 35	0.000 29	0.006 16
420	0.004 41	0.003 30	0.0	0.005 51
422	0.007 27	0.005 77	0.005 77	0.010 93
511	−0.009 86	0.000 40	0.000 40	0.009 88
333	−0.003 85	−0.003 85	−0.003 85	0.006 67
440	0.004 02	0.004 02	0.0	0.005 69
531	−0.006 44	−0.002 01	−0.000 29	0.006 75
600	−0.000 25	0.0	0.0	0.000 25
442	0.005 27	0.005 27	0.003 83	0.008 38
620	0.002 30	0.001 27	0.0	0.002 63
533	−0.004 84	−0.001 31	−0.001 31	0.005 18
622	0.003 88	0.001 93	0.001 93	0.004 74
444	0.004 28	0.004 28	0.004 28	0.007 41
551	−0.003 61	−0.003 61	0.000 10	0.005 11
711	−0.007 70	−0.000 24	−0.000 24	0.007 71
640	0.003 48	0.002 31	0.0	0.004 17
642	0.003 89	0.002 55	0.001 57	0.004 91
731	−0.005 98	−0.000 70	−0.000 13	0.006 02

TABLE IV. Atomic displacements (a.u.) of the NN's of Cr impurity in V metal.

NN's $(n_1,n_2,_3)$	Displacements components u_x	 u_y	 u_z	 $\|\mathbf{u}\|$
111	0.014 57	0.014 57	0.014 57	0.025 23
200	−0.037 07	0.0	0.0	0.037 07
220	−0.011 12	−0.011 12	0.0	0.015 73
311	0.013 80	0.000 18	0.000 18	0.013 80
222	−0.009 88	−0.009 88	−0.009 88	0.017 12
400	−0.009 29	0.0	0.0	0.009 29
331	0.005 04	0.005 04	0.000 09	0.007 12
420	−0.007 86	−0.003 76	0.0	0.008 72
422	−0.008 29	−0.004 63	−0.004 63	0.010 56
511	0.010 43	−0.000 02	−0.000 02	0.010 43
333	0.003 87	0.003 87	0.003 87	0.006 71
440	−0.005 10	−0.005 10	0.0	0.007 22
531	0.007 02	0.002 20	0.000 01	0.007 36
600	−0.005 65	0.0	0.0	0.005 65
442	−0.005 44	−0.005 44	−0.003 02	0.008 27
620	−0.006 18	−0.001 25	0.0	0.006 30
533	0.005 26	0.001 58	0.001 58	0.005 72
622	−0.006 45	−0.001 55	−0.001 55	0.006 81
444	−0.004 02	−0.004 02	−0.004 02	0.006 96
551	0.003 72	0.003 72	0.000 07	0.005 27
711	0.008 91	0.000 14	0.000 14	0.008 91
640	−0.005 05	−0.002 28	0.0	0.005 54
642	−0.004 99	−0.002 34	−0.001 21	0.005 64
731	0.006 78	0.000 45	0.000 09	0.006 79

TABLE V. Atomic displacements (a.u.) of the NN's of Mn impurity in V metal.

NN's	Displacements components			
(n_1,n_2,n_3)	u_x	u_y	u_z	$\lvert\mathbf{u}\rvert$
111	0.019 38	0.019 38	0.019 38	0.033 58
200	−0.057 15	0.0	0.0	0.057 15
220	−0.017 93	−0.017 93	0.0	0.025 35
311	0.019 89	0.000 97	0.000 97	0.019 93
222	−0.013 38	−0.013 38	−0.013 38	0.023 17
400	−0.018 89	0.0	0.0	0.018 89
331	0.008 19	0.008 19	0.000 40	0.011 59
420	−0.014 38	−0.006 09	0.0	0.015 62
422	−0.013 41	−0.006 35	−0.006 35	0.016 14
511	0.016 41	0.000 21	0.000 21	0.016 41
333	0.005 97	0.005 97	0.005 97	0.010 33
440	−0.008 56	−0.008 56	0.0	0.012 11
531	0.011 17	0.003 51	0.000 22	0.011 71
600	−0.012 63	0.0	0.0	0.012 63
442	−0.008 48	−0.008 48	−0.004 09	0.012 67
620	−0.012 07	−0.001 90	0.0	0.012 22
533	0.008 37	0.002 61	0.002 61	0.009 15
622	−0.011 62	−0.002 13	−0.002 13	0.012 01
444	−0.006 00	−0.006 00	−0.006 00	0.010 40
551	0.005 80	0.005 80	0.000 21	0.008 20
711	0.014 49	0.000 16	0.000 16	0.014 49
640	−0.008 81	−0.003 48	0.0	0.009 47
642	−0.008 39	−0.003 44	−0.001 62	0.009 21
731	0.010 95	0.000 53	0.000 12	0.010 96

TABLE VI. Atomic displacements (a.u.) of the NN's of Fe impurity in V metal.

NN's	Displacements components			
(n_1,n_2,n_3)	u_x	u_y	u_z	$\lvert\mathbf{u}\rvert$
111	0.026 00	0.026 00	0.026 00	0.045 03
200	−0.085 27	0.0	0.0	0.085 27
220	−0.027 49	−0.027 49	0.0	0.038 88
311	0.028 35	0.002 11	0.002 11	0.028 51
222	−0.018 18	−0.018 18	−0.018 18	0.031 49
400	−0.032 54	0.0	0.0	0.032 54
331	0.012 63	0.012 63	0.000 84	0.017 88
420	−0.023 61	−0.009 36	0.0	0.025 40
422	−0.020 61	−0.008 72	−0.008 72	0.024 02
511	0.024 79	0.000 56	0.000 56	0.024 80
333	0.008 90	0.008 90	0.008 90	0.015 41
440	−0.013 44	−0.013 44	0.0	0.019 01
531	0.017 00	0.005 36	0.000 52	0.017 83
600	−0.022 58	0.0	0.0	0.022 58
442	−0.012 73	−0.012 73	−0.005 58	0.018 85
620	−0.020 45	−0.002 81	0.0	0.020 64
533	0.012 73	0.004 07	0.004 07	0.013 97
622	−0.018 95	−0.002 92	−0.002 92	0.019 39
444	−0.008 77	−0.008 77	−0.008 77	0.015 19
551	0.008 70	0.008 70	0.000 42	0.012 31
711	0.022 34	0.000 17	0.000 17	0.022 34
640	−0.014 12	−0.005 17	0.0	0.015 04
642	−0.013 18	−0.004 99	−0.002 18	0.014 26
731	0.016 81	0.000 63	0.000 15	0.016 82

TABLE VII. Atomic displacements (a.u.) of the NN's of Nb impurity in V metal.

NN's	Displacements components			
(n_1,n_2,n_3)	u_x	u_y	u_z	$\lvert\mathbf{u}\rvert$
111	−0.050 12	−0.050 12	−0.050 12	0.086 82
200	0.150 90	0.0	0.0	0.150 90
220	0.047 60	0.047 60	0.0	0.067 32
311	−0.052 03	−0.002 79	−0.002 79	0.052 18
222	0.034 67	0.034 67	0.034 67	0.060 06
400	0.051 46	0.0	0.0	0.051 46
331	−0.021 77	−0.021 77	−0.001 14	0.030 81
420	0.038 75	0.016 18	0.0	0.041 99
422	0.035 62	0.016 49	0.016 49	0.042 58
511	−0.043 44	−0.000 65	−0.000 65	0.043 44
333	−0.015 75	−0.015 75	−0.015 75	0.027 28
440	0.022 85	0.022 85	0.0	0.032 31
531	−0.029 61	−0.009 32	−0.000 65	0.031 05
600	0.034 70	0.0	0.0	0.034 70
442	0.022 41	0.022 41	0.010 62	0.033 43
620	0.032 76	0.005 00	0.0	0.033 14
533	−0.022 19	−0.006 96	−0.006 96	0.024 28
622	0.031 27	0.005 52	0.005 52	0.032 24
444	0.015 78	0.015 78	0.015 78	0.027 34
551	−0.015 32	−0.015 32	−0.000 60	0.021 68
711	−0.038 51	−0.000 39	−0.000 39	0.038 52
640	0.023 61	0.009 19	0.0	0.025 34
642	0.022 39	0.009 04	0.004 19	0.024 50
731	−0.029 07	−0.001 34	−0.000 30	0.029 10

TABLE VIII. Atomic displacements (a.u.) of the NN's of Mo impurity in V metal.

NN's	Displacements components			
(n_1,n_2,n_3)	u_x	u_y	u_z	$\lvert\mathbf{u}\rvert$
111	−0.038 94	−0.038 94	−0.038 94	0.067 45
200	0.076 04	0.0	0.0	0.076 04
220	0.020 53	0.020 53	0.0	0.029 03
311	−0.032 39	0.001 70	0.001 70	0.032 48
222	0.025 77	0.025 77	0.025 77	0.044 64
400	0.005 60	0.0	0.0	0.005 60
331	−0.009 07	−0.009 07	0.000 57	0.012 84
420	0.009 45	0.006 88	0.0	0.011 69
422	0.015 12	0.011 83	0.011 83	0.022 55
511	−0.020 45	0.000 79	0.000 79	0.020 48
333	−0.007 96	−0.007 96	−0.007 96	0.013 79
440	0.008 42	0.008 42	0.0	0.011 90
531	−0.013 38	−0.004 17	0.000 57	0.014 03
600	0.000 04	0.0	0.0	0.000 04
442	0.010 92	0.010 92	0.007 84	0.017 31
620	0.005 13	0.002 63	0.0	0.005 77
533	−0.010 05	−0.002 73	−0.002 73	0.010 77
622	0.008 26	0.003 96	0.003 96	0.009 98
444	0.008 82	0.008 82	0.008 82	0.015 28
551	−0.007 48	−0.007 48	0.000 19	0.010 58
711	−0.016 04	−0.000 48	−0.000 48	0.016 05
640	0.007 34	0.004 77	0.0	0.008 75
642	0.008 16	0.005 26	0.003 21	0.010 22
731	−0.012 43	−0.001 42	−0.000 27	0.012 52

TABLE IX. Atomic displacements (a.u.) of the NN's of Ta impurity in V metal.

NN's (n_1,n_2,n_3)	Displacements components u_x	u_y	u_z	$\lvert\mathbf{u}\rvert$
111	−0.060 11	−0.060 11	−0.060 11	0.104 11
200	0.167 90	0.0	0.0	0.167 90
220	0.051 87	0.051 87	0.0	0.073 36
311	−0.053 85	−0.002 12	−0.002 12	0.059 92
222	0.041 21	0.041 21	0.041 21	0.071 38
400	0.050 82	0.0	0.0	0.050 82
331	−0.023 63	−0.023 63	−0.000 91	0.033 42
420	0.039 92	0.017 60	0.0	0.043 63
422	0.038 74	0.019 46	0.019 46	0.047 52
511	−0.047 88	−0.000 37	−0.000 37	0.047 88
333	−0.017 54	−0.017 54	−0.017 54	0.030 37
440	0.024 44	0.024 44	0.0	0.034 57
531	−0.032 46	−0.010 20	−0.000 44	0.034 03
600	0.033 08	0.0	0.0	0.033 08
442	0.024 82	0.024 82	0.012 60	0.037 30
620	0.032 85	0.005 60	0.0	0.033 32
533	−0.024 33	−0.007 50	−0.007 50	0.026 55
622	0.032 42	0.006 52	0.006 52	0.033 71
444	0.017 84	0.017 84	0.017 84	0.030 90
551	−0.016 97	−0.016 97	−0.000 51	0.024 01
711	−0.041 79	−0.000 53	−0.000 53	0.041 79
640	0.024 83	0.010 27	0.0	0.026 87
642	0.023 92	0.010 28	0.005 01	0.026 51
731	−0.031 65	−0.001 73	−0.000 37	0.031 70

TABLE X. Atomic displacements (a.u.) of the NN's of W impurity in V metal.

NN's (n_1,n_2,n_3)	Displacements components u_x	u_y	u_z	$\lvert\mathbf{u}\rvert$
111	−0.049 00	−0.049 00	−0.049 00	0.084 87
200	0.058 58	0.0	0.0	0.058 58
220	0.011 01	0.011 01	0.0	0.015 56
311	−0.033 52	0.005 61	0.005 61	0.034 44
222	0.031 38	0.031 38	0.031 38	0.054 35
400	−0.023 92	0.0	0.0	0.023 92
331	−0.004 34	−0.004 34	0.002 02	0.006 46
420	−0.006 71	0.003 52	0.0	0.007 57
422	0.007 72	0.014 00	0.014 00	0.021 25
511	−0.013 76	0.002 16	0.002 16	0.014 09
333	−0.006 16	−0.006 16	−0.006 16	0.010 68
440	0.002 18	0.002 18	0.0	0.003 09
531	−0.008 16	−0.002 48	0.001 68	0.008 69
600	−0.024 21	0.0	0.0	0.024 21
442	0.007 88	0.007 88	0.009 49	0.014 64
620	−0.011 85	0.002 18	0.0	0.012 05
533	−0.006 16	−0.001 03	−0.001 03	0.006 33
622	−0.004 05	0.004 68	0.004 68	0.007 76
444	0.008 00	0.008 00	0.008 00	0.013 86
551	−0.005 42	−0.005 42	0.000 82	0.007 71
711	−0.007 68	−0.000 76	−0.000 76	0.007 75
640	−0.000 68	0.003 86	0.0	0.003 92
642	0.001 94	0.005 02	0.004 00	0.006 71
731	−0.006 50	−0.002 12	−0.000 37	0.006 85

the impurity as is also expected based on physical arguments.

(iv) Figure 3 shows the variation of $|\mathbf{u}(\mathbf{r})|$, at the 1NN and 2NN sites, as a function of the atomic number of the TM impurity. For comparison, the magnitude of the fractional change in lattice parameter, i.e., $|a^{-1}(da/dc)|$, is also plotted as a function of the atomic number of the impurity. Here c denotes the concentration of the impurity. It is evident from Fig. 3 that the variation of $|\mathbf{u}(\mathbf{r})|$ exhibits the same trend as that of $|a^{-1}(da/dc)|$. We have also investigated the variation of $|\mathbf{u}(\mathbf{r})|$ at the higher NN's (i.e., 3NN's, 4NN's, 5NN's, 6NN's, etc.), and the same trend is observed. It is well known that x-ray-diffraction studies[26] yield an average value of $a^{-1}(da/dc)$ caused by 1 at. % of impurity. Therefore the direct comparison of $\mathbf{u}(\mathbf{r})$ at different NN's, with $a^{-1}(da/dc)$, is not justifiable.

In Fig. 4 is plotted $\mathbf{u}(\mathbf{r})$, for a particular NN, as a function of $a^{-1}(da/dc)$ for the impurities. It shows that, for a particular NN, $\mathbf{u}(\mathbf{r})$ is linearly proportional to $a^{-1}(da/dc)$ except for the Ti impurity. But the slope of the straight line so obtained is different (both in magnitude and sign) for the different NN's; e.g., the slope is negative for the straight line corresponding to the 1NN's and 4NN's, while it is positive for those corresponding to 2NN's and 3NN's. Further, it is found that the average value of the atomic displacements, $\langle \mathbf{u}(\mathbf{r}) \rangle$, evaluated by using the values of $\mathbf{u}(\mathbf{r})$ at the first 7NN's is directly proportional to $a^{-1}(da/dc)$, except for the impurity W, and yields the correct sign of $a^{-1}(da/dc)$.

It is interesting to examine the variation of $\mathbf{u}(\mathbf{r})$ for the elements belonging to a particular series. $\mathbf{u}(\mathbf{r})$ at the 1NN and 4NN sites (Fig. 4) increases approximately linearly as one goes through the $3d$ series from Ti to Fe,

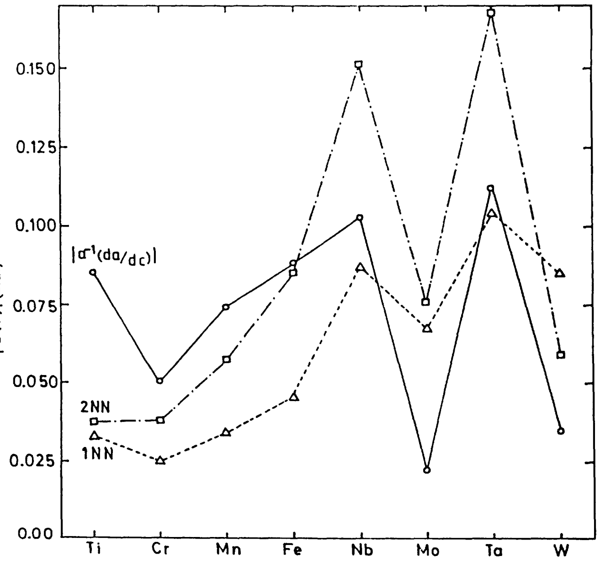

FIG. 3. Magnitude of the atomic displacements $|\mathbf{u}(\mathbf{r})|$ as a function of the atomic number of the impurity. The dashed line joining the triangles and the dot-dashed line joining the squares show $|\mathbf{u}(\mathbf{r})|$ of the 1NN's and 2NN's, respectively, of the impurity. For comparison, the solid line joining the circles shows $|a^{-1}(da/dc)|$ for the different impurities.

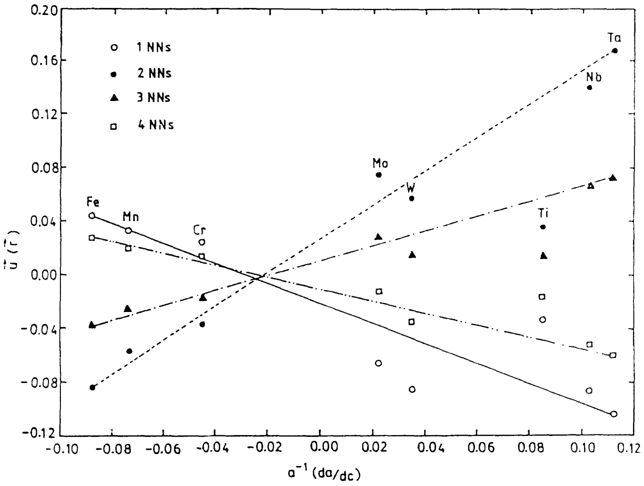

FIG. 4. $\mathbf{u}(\mathbf{r})$ as a function of $a^{-1}(da/dc)$ for the different NN's of the impurities. Open circles, solid circles, triangles, and squares represent $\mathbf{u}(\mathbf{r})$ for the 1NN's, 2NN's, 3NN's, and 4NN's of the impurities, and the corresponding lines passing through them are represented by solid, dashed, dot-dashed, double-dot–dashed lines, respectively.

i.e., with the increase in the number of d electrons. A similar variation of $\mathbf{u}(\mathbf{r})$ is also found in going through the 4d and 5d series. On the other hand, at the 2NN and 3NN sites $\mathbf{u}(\mathbf{r})$ is found to decrease in going through each of the 3d, 4d, and 5d series. The same trend is also found for the higher-order NN's of the impurity. The above-mentioned variation of $\mathbf{u}(\mathbf{r})$ at different NN's is due to its oscillatory behavior.

(v) The strain field $\mathbf{u}(\mathbf{r})$ does not show any dependence on the excess impurity charge $\Delta Z = Z_I - Z_H$. The values of the electric field gradient in the V-based alloys with 3d, 4d, and 5d impurities[27] also does not show any dependence on ΔZ. On the other hand, both the strain field and the electric field gradient show linear dependence on $a^{-1}(da/dc)$, which indicates that $\mathbf{u}(\mathbf{r})$ may play a significant role in explaining the electric field gradient in these alloys.

IV. DISCUSSION

The generalized Kanzaki method[14] has been applied to evaluate the strain field due to substitutional impurities in metallic crystals with bcc structure. The expressions for the dynamical matrix, impurity-induced force, and the atomic displacements, taking into account the interactions up to the 2NN's, have been derived for the bcc symmetry. The formalism has been applied to evaluate $\mathbf{u}(\mathbf{r})$ in V-based metallic alloys with 3d, 4d, and 5d TM impurities.

In a TM the atomic d shells are distorted by the crystal field,[21] which give two contributions. First, the distortion shifts the center of the d band, and second, it broadens the d state into bands with finite bandwidth. Wills and Harrison[16] have proposed an effective ion-ion interaction which takes care of both these contributions and further have suggested its generalization to the alloys. It is found that both $\phi_{HH}(r)$ and $\Delta\phi(r)$ (Figs. 1 and 2) are very small and vary smoothly beyond the 2NN distance. Therefore the contributions to $\phi_{\alpha\beta}(\mathbf{q})$ and $F_\alpha(\mathbf{q})$ are expected to be negligibly small beyond the 2NN site. In the present investigations, $\mathbf{u}(\mathbf{r})$ has been calculated for Ti, Cr, Mn, Fe, Nb, Mo, Ta, and W impurities in the V metal. It has been found that the strength and range of $\mathbf{u}(\mathbf{r})$ is proportional to the magnitude and range, respectively, of $\Delta\phi(r)$. The direct comparison of $a^{-1}(da/dc)$ with oscillatory $\mathbf{u}(\mathbf{r})$ is not possible because the x-ray study gives some sort of average value of $a^{-1}(da/dc)$. But it is found that $\mathbf{u}(\mathbf{r})$ for all impurities, at a particular NN, is approximately proportional to $a^{-1}(da/dc)$. Further, the averaged value of atomic displacement, $\langle u(\mathbf{r})\rangle$, for all the impurities is proportional to $a^{-1}(da/dc)$ both in magnitude and sign except W.

The lattice static method, formulated in Sec. II, is based on the harmonic approximation, which neglects the angular forces in the TM's. The study of lattice dynamics of the TM's,[18–20,28,29] in the harmonic approximation, yields reasonably good agreement between the calculated and experimental values of phonon frequencies, which shows that this approximation works reasonably well in the TM's. The angular forces can be taken care of partially in the evaluation of effective ion-ion interaction by using the dielectric tensor approach (see the Appendix). But the numerical evaluation of the local field effect [see Eq. (A21)], which describes angular forces, is complicated and consumes lot of computer time[30] as it involves the exact electronic band structure. We want to point out that the effective ion-ion interaction potential proposed by Wills and Harrison[16] uses $Z_s = 1.5$, and this value has been taken from the self-consistent calculations done by Pettifor[31] and Moriarty.[32] As the TM impurity is dissolved in a different TM host, the value of Z_s may further become different as a result of charge transfer. Therefore some residual electrostatic interaction, although very small in the dilute alloys under investigation, might have been left. To improve upon the present results, one should investigate in detail the electronic band structure of the TM in the presence of the TM impurity and calculate self-consistently the effective value of the d charge on the impurity.

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APPENDIX

In the TM's the conduction electrons possess both s and d characters. The d conduction electrons are quasilocalized and anisotropic and give rise to a nonuniform component of conduction-electron density, which is responsible for the existence of local fields (LF's), in addition to the uniform s-conduction-electron density. The overall conduction-electron density in the TM's becomes nonuniform, which makes the dielectric function a matrix, $\epsilon_H(\mathbf{K},\mathbf{K}')$, and the off-diagonal elements of it are manifestations of the LF effects. **K** and **K**′ are wave vectors in Fourier space, and the subscript "H" indicates that the dielectric matrix is of the host metal.

The general expression for $\epsilon_H(\mathbf{K},\mathbf{K}')$ is[33]

$$\epsilon_H(\mathbf{K},\mathbf{K}')=\delta_{\mathbf{K},\mathbf{K}'}-v(\mathbf{K})\chi_H(\mathbf{K},\mathbf{K}') , \tag{A1}$$

where

$$v(\mathbf{K})=\frac{4\pi e^2}{K^2}\left[1-f_{xc}(\mathbf{K})\right] , \tag{A2}$$

$$\chi_H(\mathbf{K},\mathbf{K}')=\sum_{\lambda,\lambda'}\sum_{\mathbf{k},\mathbf{K}''}\left[\frac{f_0(E^{\lambda}_{\mathbf{k}})-f_0(E^{\lambda'}_{\mathbf{k}+\mathbf{K}''})}{E^{\lambda}_{\mathbf{k}}-E^{\lambda'}_{\mathbf{k}+\mathbf{K}''}}\right]\langle \psi'_{\mathbf{k}}(\mathbf{r})|e^{-i\mathbf{K}\cdot\mathbf{r}}|\psi^{\lambda'}_{\mathbf{k}+\mathbf{K}''}(\mathbf{r})\rangle\langle \psi^{\lambda'}_{\mathbf{k}+\mathbf{K}''}(\mathbf{r})|e^{i\mathbf{K}'\cdot\mathbf{r}}|\psi^{\lambda}_{\mathbf{k}}(\mathbf{r})\rangle . \tag{A3}$$

Here $f_0(E^{\lambda}_{\mathbf{k}})$ is the Fermi-Dirac distribution function. $E^{\lambda}_{\mathbf{k}}$ is the energy eigenvalue for the electron wave function $\psi^{\lambda}_{\mathbf{k}}(\mathbf{r})$, where **k** and λ are the electron wave vector and band index, respectively. The function $v(\mathbf{K})$ is the electron-electron interaction potential, which includes the exchange interactions through the function $f_{xc}(\mathbf{K})$. $\chi_H(\mathbf{K},\mathbf{K}')$ is the polarizability matrix which is the product of the band structure part (in square brackets) and the overlap matrix element part. The periodicity of the electron charge distribution requires $\epsilon_H(\mathbf{K},\mathbf{K}')$ to be nonzero when $\mathbf{K}'=\mathbf{K}+\mathbf{G}$, where **G** is the reciprocal lattice vector.

In the TM's the formalism for the effective ion-ion interaction should include the effect of anisotropic and nonuniform density of *d* electrons,[34,35] which gives rise to LF's and is responsible for the existence of angular forces.[18–20,29] Rattan *et al.*[14] have derived the expression for $\Delta\phi(r)$ due to a substitutional impurity in a TM, which is given as

$$\Delta\phi(\mathbf{r})=\frac{\Delta Z\, Z_H e^2}{|\mathbf{r}|}+\frac{2}{N}\sum_{\mathbf{K}}{}'\Delta F(\mathbf{K})e^{-i\mathbf{K}\cdot\mathbf{r}} , \tag{A4}$$

where the excess impurity valency $\Delta Z=Z_I-Z_H$ and N is the total number of lattice points in the lattice. The prime over the summation sign excludes the $r=0$ term. The first term gives the change in the direct ion-ion Coulomb interaction due to the presence of the impurity. The second term represents the change in the ion-ion interaction via electrons and is equal to twice the Fourier transform of the change in the energy wave number characteristic function $\Delta F(\mathbf{K})$. The function $\Delta F(\mathbf{K})$ takes care of the LF effects and hence the angular forces in the TM's. The general expression for $\Delta F(\mathbf{K})$ is given as[14]

$$\Delta F(\mathbf{K})=\frac{\Omega_0 K^2}{8\pi e^2}\sum_{\mathbf{G}}\Delta V^b(\mathbf{K})\left[\epsilon_H^{-1}(\mathbf{K},\mathbf{K}+\mathbf{G})-\delta_{\mathbf{K},\mathbf{K}+\mathbf{G}}\right]\times V^b_H(\mathbf{K}+\mathbf{G}) , \tag{A5}$$

where

$$\Delta V^b(\mathbf{K})=V^b_I(\mathbf{K})-V^b_H(\mathbf{K}) . \tag{A6}$$

Here we have used the periodicity condition. $V^b_H(\mathbf{K})$ and $V^b_I(K)$ are the Fourier transforms of the bare electron-ion potentials for the host and impurity ions, and Ω_0 is the atomic volume. Nonlinear effects arising from the exchange and correlation interactions are included. If the function $\Delta F(\mathbf{K})$ is assumed to be spherically symmetric, Eq. (A4) becomes

$$\Delta\phi(r)=\frac{\Delta Z\, Z_H e^2}{|\mathbf{r}|}+\frac{\Omega_0}{\pi^2}\int\Delta F(\mathbf{K})\frac{\sin(Kr)}{Kr}K^2 dK , \tag{A7}$$

which is the usual expression for the free-electron metals.[6] From Eqs. (A4)–(A7) it is evident that $\Delta\phi(\mathbf{r})$ can be estimated with the knowledge of $\epsilon_H^{-1}(\mathbf{K},\mathbf{K}')$, $V^b_I(\mathbf{K})$, and $V^b_H(\mathbf{K})$.

The inversion of the dielectric function is a difficult problem as it is an infinite-dimensional matrix. Therefore one has to resort to some simplifications. It is convenient to evaluate the inverse dielectric matrix in the mixed-band scheme[18–20] in which the *s* conduction electrons are represented by plane waves and the *d* conduction electrons by a local representation, i.e.,

$$\psi^s_{\mathbf{k}}(\mathbf{r})=\frac{1}{\sqrt{\Omega}}\exp(i\mathbf{k}\cdot\mathbf{r}) , \tag{A8}$$

$$\psi^d_{\mathbf{k}}(\mathbf{r})=\frac{1}{\sqrt{N}}\sum_n\exp(i\mathbf{k}\cdot\mathbf{R}^0_n)\phi_\lambda(\mathbf{r}-\mathbf{R}^0_n) . \tag{A9}$$

$\Omega=N\Omega_0$ is the volume of the crystal, and $\mathbf{R}^0_n$ are the direct lattice vectors of the crystal structure. $\phi_\lambda(\mathbf{r}-\mathbf{R}^0_n)$ are the atomic wave functions centered at the $\mathbf{R}^0_n$ site. Equation (A9) gives one of the local representations, and one can also use Wannier functions in place of the atomic wave functions. In such a mixed-band scheme, $\epsilon_H(\mathbf{K},\mathbf{K}')$ can be split into two parts. First is the purely diagonal part $\epsilon_0(\mathbf{K})$ arising from the intraband transitions in the *s* band and is just the Lindhard function. The second contribution arises from the intraband and interband transitions between the partially filled *s* and *d* subbands and contains both the diagonal and nondiagonal contributions. Therefore $\epsilon_H(\mathbf{K},\mathbf{K}+\mathbf{G})$ can be written as[18,19,30]

$$\epsilon_{\mathrm{H}}(\mathbf{K},\mathbf{K}+\mathbf{G})=\epsilon_0(\mathbf{K})\delta_{\mathbf{K},\mathbf{K}+\mathbf{G}} -v(\mathbf{K})\sum_{s,s'} A_s(\mathbf{K})f_{ss'}(\mathbf{K})A_{s'}^{*}(\mathbf{K}+\mathbf{G}) , \tag{A10}$$

where

$$A_s(\mathbf{K})=\int \phi_{l\lambda}^{*}(\mathbf{r})e^{-i\mathbf{K}\cdot\mathbf{r}}\phi_{l\lambda'}(\mathbf{r}+\mathbf{R}_n^0)d\mathbf{r} , \tag{A11}$$

$$f_{ss'}(\mathbf{K})=\sum_{\mathbf{k}\le\mathbf{k}_{\mathrm{FH}}} \frac{f_0(E_{\mathbf{k}}^{l\lambda})-f_0(E_{\mathbf{k}+\mathbf{K}}^{l\lambda})}{E_{\mathbf{k}}^{l\lambda}-E_{\mathbf{k}+\mathbf{K}}^{l\lambda}} \times\exp[-i(\mathbf{k}+\mathbf{K})\cdot(\mathbf{R}_n^0-\mathbf{R}_{n'}^0)] . \tag{A12}$$

The subscript s denotes $\{nl\lambda\lambda'\}$, where l is the orbital quantum number.

The inverse dielectric matrix can now be obtained easily from Eq. (A10) and is written as

$$\epsilon_{\mathrm{H}}^{-1}(\mathbf{K},\mathbf{K}+\mathbf{G})=\frac{1}{\epsilon_0(\mathbf{K}+\mathbf{G})}\left[\delta_{\mathbf{K},\mathbf{K}+\mathbf{G}}+\frac{v(\mathbf{K})}{\epsilon_0(\mathbf{K})}\sum_{ss'} A_s(\mathbf{K})F_{ss'}(\mathbf{K})A_{s'}^{*}(\mathbf{K}+\mathbf{G})\right] , \tag{A13}$$

where

$$F_{ss'}(\mathbf{K})=[f_{ss'}^{-1}(\mathbf{K})-f_{ss'}^{d}(\mathbf{K})]^{-1} =\left[f_{ss'}^{-1}(\mathbf{K})-\sum_{\mathbf{G}'} A_s(\mathbf{K}+\mathbf{G}')A_{s'}^{*}(\mathbf{K}+\mathbf{G}')\frac{v(\mathbf{K}+\mathbf{G}')}{\epsilon_0(\mathbf{K}+\mathbf{G}')}\right]^{-1} . \tag{A14}$$

In the TM's the crystal field polarizes the d-electron charge, producing monopoles and dipoles at the lattice positions which are screened by the s conduction electrons. Thus the present model of the mixed-band scheme is similar to the breathing shell model.[36] For the intraband transitions, $A_s(\mathbf{K})/\epsilon_0(\mathbf{K})$ gives the screened form factor for the monopoles, while for the interband transitions it gives the screened form factor for the dipoles. Putting $\epsilon_0(\mathbf{K})=1$ for the ideal insulators, Eq. (A13) gives screened dipolar model of screening.[28] Equation (A13) includes all sorts of interactions between the screened monopoles and dipoles mediated by the resonant function $F_{ss'}(\mathbf{K})$.

Substituting Eq. (A13) in Eq. (A5), we get

$$\Delta F(\mathbf{K})=\Delta F^{(0)}(\mathbf{K})+\sum_{s'}\sum_{\mathbf{G}} X_{s'}(\mathbf{K})U_{s'}(\mathbf{K}+\mathbf{G}) , \tag{A15}$$

where

$$\Delta F^{(0)}(\mathbf{K})=\frac{\Omega_0 K^2}{8\pi e^2}\Delta V^b(\mathbf{K})\left[\frac{1}{\epsilon_0(\mathbf{K})}-1\right]V_{\mathrm{H}}^b(\mathbf{K}) , \tag{A16}$$

$$X_{s'}(\mathbf{K})=\frac{\Omega_0 K^2}{8\pi e^2}v(\mathbf{K})\sum_{s}\Delta V^b(\mathbf{K})\frac{A_s(\mathbf{K})}{\epsilon_0(\mathbf{K})}F_{ss'}(\mathbf{K}) , \tag{A17}$$

$$U_{s'}(\mathbf{K}+\mathbf{G})=\frac{A_{s'}^{*}(\mathbf{K}+\mathbf{G})}{\epsilon_0(\mathbf{K}+\mathbf{G})}V_{\mathrm{H}}^b(\mathbf{K}+\mathbf{G}) . \tag{A18}$$

Taking the Fourier transform of Eq. (A15) and using the identity

$$\sum_{n} U(\mathbf{R}_n^0)\exp(i\mathbf{K}\cdot\mathbf{R}_n^0)=\sum_{\mathbf{G}} U(\mathbf{K}+\mathbf{G}) , \tag{A19}$$

we obtain

$$\Delta F(\mathbf{r})=\Delta F^{(0)}(\mathbf{r})+\sum_{n}\sum_{s'} U_{s'}(\mathbf{R}_n^0)X_{s'}(\mathbf{r}-\mathbf{R}_n^0) . \tag{A20}$$

$\Delta F(\mathbf{r})$, $\Delta F^{(0)}(\mathbf{r})$, $U_s(\mathbf{r})$, and $X_s(\mathbf{r})$ are the Fourier transforms of $\Delta F(\mathbf{K})$, $\Delta F^{(0)}(\mathbf{K})$, $U_s(\mathbf{K})$, and $X_s(\mathbf{K})$, respectively. Equation (A20) gives the exact expression for the change in the energy wave number characteristic function in $\mathbf{r}$ space.

Substituting the values of $\Delta F(\mathbf{K})$ in Eq. (A4), one can obtain

$$\Delta\phi(\mathbf{r})=\frac{\Delta Z\, Z_{\mathrm{H}}e^2}{|\mathbf{r}|}+2\Delta F(\mathbf{r}) =\frac{\Delta Z\, Z_{\mathrm{H}}e^2}{|\mathbf{r}|}+2\Delta F^{(0)}(\mathbf{r}) +2\sum_{n}\sum_{s'} U_{s'}(\mathbf{R}_n^0)X_{s'}(\mathbf{r}-\mathbf{R}_n^0) , \tag{A21}$$

which gives the exact expression for $\Delta\phi(\mathbf{r})$ in the mixed-band scheme. Both $\Delta F(\mathbf{r})$ and $\Delta\phi(\mathbf{r})$ depend upon the electronic band structure through $X_{s'}(\mathbf{r}-\mathbf{R}_n^0)$ and the crystal structure through the lattice sum. The first two terms in Eq. (A21) are isotropic and correspond to the free-electron-like contribution. The last term represents the interaction of monopoles and dipoles arising from the distortion (polarization) of the d-electron charge on the TM ions. Therefore this term incorporates the effect of angular forces or LF's, which is anisotropic in nature. The comparison of Eqs. (37) and (A21) shows that the effects of $\Delta\phi^c(r)$ and $\Delta\phi^b(r)$ are included in the last term of Eq. (A21) more precisely. But the numerical calculation of Eq. (A21) is too difficult as it requires first-principles calculations of the electronic band structure, which in itself is a separate problem. But if one neglects the d-band contribution in Eq. (A21), a simple metal expression for $\Delta\phi(\mathbf{r})$ is retrieved.[14]

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