

Atomic displacements around an impurity and three-body interactions in metals

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Two methods for calculating the asymptotic displacement of the ions around substitutional, homovalent impurities in a metal are compared. While the order of approximation in the method of homogeneous deformations coincides with the order of electronic response involved, this is not so in the direct calculation of local force and displacement fields. Consistency of the approximation requires that even the lowest-order structure-dependent calculation of the asymptotic and preasymptotic local displacements should include the nonlinear, third-order electronic response of the electron liquid.

INTRODUCTION

On dissolving a foreign atom, the elastic response of the host crystal always leads to a static displacement field which, for large distance from the impurity, goes like^{1,2}

$$\vec{u}(\vec{R}) \sim \vec{C}(\hat{R})/|\vec{R}|^2. \quad (1)$$

Here \hat{R} is the unit vector pointing to \vec{R} , and the relevant elastic properties of the host as well as the host-impurity interaction are contained in the amplitude vector \vec{C} . Macroscopic considerations² lead to a factorization of \vec{C} which, for cubic crystals, is

$$\vec{C} = \vec{A}(\hat{R}) \left(\frac{\delta \Omega_0}{\delta c} \right)_{\text{per}}. \quad (2)$$

Here the function \vec{A} is independent of the kind of impurity, being defined solely in terms of the elastic constants c_{ik} of the host, while the second factor has the meaning of variation of the atomic volume with concentration, with the proviso, however, that this derivative is taken by considering the crystal to expand (contract) uniformly, local deviations from *periodicity* being ignored.

Therefore, having a microscopic theory for the free energy of a dilute solid solution, e.g., that for simple metal alloys³ at $T=0$, we can determine \vec{C} in two ways; first, directly by calculating $\vec{u}(\vec{R})$ and looking for its asymptotics and second, by finding $(\delta \Omega_0 / \delta c)_{\text{per}}$ from the static equilibrium condition of the strictly regular lattice.

Besides showing that the perturbed-electron-liquid treatment of dilute, homovalent alloys actually involves the validity of (2), we will demonstrate the rather peculiar way the consistency of the theory is realized, via the nonlinear response of the electron liquid connected with three-body interactions⁴ in the alloy. As a result, it turns out that the necessity of taking into account nonlinear response is as unavoidable in calculating

asymptotical and preasymptotical displacements, as it is in finding long-wavelength-phonon characteristics⁴ in lattice dynamics.

By this we do not mean the fact that three-body interactions, while representing a different order of approximation in the *energy* of a *regular* crystal, may incidentally be still large enough not to be neglected besides the linear screening term, as found in the case of some pure metals.^{4,5} The point is that the contribution of the three-body interaction terms to the local *force* and *displacement fields*, even though associated with third-order electronic polarization, is in fact second order in *smallness* for long distances and without taking it into account, even the lowest-order structure-dependent approximation is incomplete.

RESULTS

The energy per atom of the dilute substitutional alloy can be expressed as³

$$E = E_h(\Omega_0) + \delta c(\Delta E_{\text{per}} + \Delta E_r) + \dots + O((\delta c)^2), \quad (3)$$

where the first term is the energy of the *pure* host at an actual volume per atom Ω_0 , $\delta c \Delta E_{\text{per}}$ would be the energy change if no local deformation of the periodic lattice were allowed and ΔE_r depends on the local ionic displacements,

$$\begin{aligned} \Delta E_r = & \frac{1}{N} \sum_{\vec{l}, \alpha} F(\vec{l})_{\alpha} u(\vec{l})_{\alpha} \\ & + \frac{1}{2N} \sum_{\vec{l}, \alpha} \sum_{\vec{l}', \beta} (\phi_{\vec{l}\alpha, \vec{l}'\beta} + \delta \phi_{\vec{l}\alpha, \vec{l}'\beta}) u(\vec{l})_{\alpha} u(\vec{l}')_{\beta}. \end{aligned} \quad (4)$$

In (4), ϕ is the dynamical matrix for the pure host, while the force field \vec{F} and the force-constant change matrix $\delta \phi$ arise due to the presence of the impurities; \vec{l} indicates the position of regular lattice sites. Equilibrium occurs at those $\vec{u}(\vec{l}) = \vec{u}(\vec{l})$ that minimize (3). Neglecting $\delta \phi$ one has

from (4)

$$\tilde{u}(\vec{l})_{\alpha} = - \sum_{\vec{l}'_{\beta}} g_{\vec{l}'_{\alpha}, \vec{l}'_{\beta}} F(\vec{l}')_{\beta}, \quad (5)$$

where the static Green's function $g = \phi^{-1}$ is given in terms of vibration frequencies ω , polarization vectors \vec{e} , and host atom mass M as an integral within the Brillouin zone and a sum over different polarizations λ ,

$$g_{\vec{l}'_{\alpha}, \vec{l}'_{\beta}} = \Omega_0 / (2\pi)^3 \int_{BZ} d\vec{q} \sum_{\lambda} \frac{e_{\alpha}^*(\vec{q}\lambda) e_{\beta}(\vec{q}\lambda)}{M\omega_{\vec{q}\lambda}^2} e^{i\vec{q} \cdot (\vec{l}' - \vec{l}')}.$$

For nontransition metals, E can be given as a series containing increasing powers of the electron-ion interaction⁴

$$E = E_M + E_0(n_0) + E^{(1)}(\Omega_0) + E^{(2)} + E^{(3)} + \dots \quad (6)$$

Here E_M is the Madelung energy, E_0 is the energy of the homogeneous electron liquid with density n_0 , $E^{(1)}$ is the average of the non-Coulombic part of the mean electron-ion potential \bar{v} ,

$$E^{(1)} = \frac{Z}{\Omega_0} \int \left(\bar{v}(\vec{r}) + \frac{Ze^2}{|\vec{r}|} \right) d\vec{r}, \quad (7)$$

where $Z = Z_h = Z_{imp}$ is the ionic charge, $E^{(2)}$ is connected with the linear response of the electrons and $E^{(n)}$ ($n > 2$) represent higher-order polarization terms responsible, in general, for many-body interactions among the ions.⁴ For the first two structure-dependent terms one has

$$E^{(2)} = -\frac{1}{2} \sum_{\vec{q}} \Omega_0 \frac{P_{\vec{q}}}{\epsilon_{\vec{q}}} |f_{\vec{q}}|^2 \quad (8)$$

and

$$E^{(3)} = \Omega_0 \sum_{\vec{q}\vec{q}'\vec{q}''} \Lambda^{(3)}(\vec{q}\vec{q}'\vec{q}'') \times \frac{f_{\vec{q}}}{\epsilon_{\vec{q}}} \frac{f_{\vec{q}'}}{\epsilon_{\vec{q}'}} \frac{f_{\vec{q}''}}{\epsilon_{\vec{q}''}} \delta(\vec{q} + \vec{q}' + \vec{q}''),$$

where the dielectric constant $\epsilon_{\vec{q}}$ is given by the linear polarizability function $P_{\vec{q}}$ as

$$\epsilon_{\vec{q}} = 1 + (4\pi e^2 / q^2) P_{\vec{q}}. \quad (8a)$$

$\Lambda^{(3)}$ is the third-order, irreducible response function⁴ of the electron liquid and, for a single impurity at $\vec{l} = \vec{l}$ the function $f_{\vec{q}}$ is

$$f_{\vec{q}} = v_{\vec{q}} \frac{1}{N} \sum_{\vec{l}} e^{i\vec{q} \cdot \vec{R}_{\vec{l}}} + \frac{1}{N} \Delta v_{\vec{q}} e^{i\vec{q} \cdot \vec{l}}. \quad (9)$$

Here $v_{\vec{q}}$ is the Fourier transform of the host-ion potential

$$v_{\vec{q}} = \frac{1}{\Omega_0} \int v(\vec{r}) e^{-i\vec{q} \cdot \vec{r}} d\vec{r}, \quad (10)$$

$\Delta v_{\vec{q}} = v_{\vec{q}}^{impurity} - v_{\vec{q}}$ and $\vec{R}_{\vec{q}}$ is the actual position of an ion originally at the regular position \vec{l} ,

$$\vec{R}_{\vec{q}} = \vec{l} + \vec{u}(\vec{l}).$$

Expanding $f_{\vec{q}}$ in powers of \vec{u} , the \vec{u} -independent energy change up to 2nd order, by (6)–(8), is³

$$\Delta E_{per} = \Delta E^{(1)} - \sum_{\vec{G} \neq 0} v_{\vec{G}} \Delta v_{\vec{G}} \Omega_0 \frac{P_{\vec{G}}}{\epsilon_{\vec{G}}} - \frac{1}{2N} \sum_{\vec{q}} |\Delta v_{\vec{q}}|^2 \Omega_0 \frac{P_{\vec{q}}}{\epsilon_{\vec{q}}}, \quad (11)$$

where $\Delta E^{(1)}$ is $E_{imp}^{(1)} - E_{host}^{(1)}$ and \vec{G} stands for reciprocal-lattice vectors. The linear terms in \vec{u} define, by (4), the force field \vec{F} tending to displace the ions from their regular sites. One gets subsequent contributions of increasing order according to (6)

$$\vec{F} = \vec{F}^{(2)} + \vec{F}^{(3)} + \dots$$

writing

$$F(\vec{l})_{\alpha} = \frac{i}{N} \sum_{\vec{k}} k_{\alpha} F(\vec{k}) e^{i\vec{k} \cdot (\vec{l} - \vec{l}')}, \quad (12)$$

we have³

$$F^{(2)}(\vec{k}) = -v_{\vec{k}} \Delta v_{\vec{k}} \Omega_0 (P_{\vec{k}} / \epsilon_{\vec{k}}) \quad (13)$$

and next,

$$F^{(3)}(\vec{k}) = 6\Omega_0 \frac{v_{\vec{k}}}{\epsilon_{\vec{k}}} \left(\frac{1}{2} \sum_{\vec{q}, -\vec{k}-\vec{q}} \Lambda_{\vec{k}, \vec{q}, -\vec{k}-\vec{q}}^{(3)} \frac{1}{N} \frac{\Delta v_{\vec{q}}}{\epsilon_{\vec{q}}} \frac{\Delta v_{-\vec{k}-\vec{q}}}{\epsilon_{-\vec{k}-\vec{q}}} + \sum_{\vec{G} \neq 0} \Lambda_{\vec{k}, \vec{G}, -\vec{k}-\vec{G}}^{(3)} \frac{v_{\vec{G}}}{\epsilon_{\vec{G}}} \frac{\Delta v_{-\vec{k}-\vec{G}}}{G_{-\vec{k}-\vec{G}}} \right). \quad (14)$$

It can be seen that higher-order terms have necessarily a factor of order $\sim v_{\vec{q}}/E_F$ or $\sim (\Delta v_{\vec{q}}/\epsilon_{\vec{q}} E_F)$ in comparison with those making up $F^{(2)}$ and $F^{(3)}$ (E_F is the Fermi energy), so that they can be neglected. [For a homovalent impurity ($\Delta v_{\vec{q}}/\epsilon_{\vec{q}} E_F \ll 1$ for large and small q values as well.) The physical significance of $F^{(3)}$ is clear; e.g., the second term represents three-body interactions among the impurity, the ion at \vec{l} and one of the other ions of the lattice.

Now, independent of the particular form for $F(k)$, one has generally, by (5) and (12),

$$\tilde{u}(\vec{l})_{\alpha} = -i \frac{\Omega_0}{(2\pi)^3} \int_{BZ} d\vec{q} \sum_{\lambda} \frac{e_{\alpha}^*(\vec{q}\lambda) e_{\beta}(\vec{q}\lambda)}{M\omega_{\vec{q}\lambda}^2} e^{i\vec{q} \cdot (\vec{l} - \vec{l}')} \times \left(\sum_{\vec{G}} (q_{\beta} + G_{\beta}) F(\vec{q} + \vec{G}) \right). \quad (15)$$

For the asymptotics of \vec{u} one has to look at the

small- \vec{q} expansion of the expression beside the exponential,⁶

$$\vec{\epsilon} = \vec{\epsilon}(0, \theta, \varphi, \lambda) + \dots + O(q^2),$$

$$\omega_{q\lambda}^2 = c_\lambda^2(\theta, \varphi)q^2 + \dots + O(q^4),$$

where θ, φ are the angles of the unit vector $\hat{q} = \vec{q}/|\vec{q}|$ and c_λ is the velocity of sound with a particular polarization. Further, for cubic crystals the expansion of F leads to (see Appendix)

$$\sum_{\vec{G}} (q_\beta + G_\beta)F(\vec{q} + \vec{G})$$

$$= q_\beta \lim_{\vec{q}=0} F(\vec{q}) + q_\beta \sum_{\vec{G} \neq 0} \left(F(\vec{G}) + \frac{1}{3} G_\gamma \frac{\partial F}{\partial G_\gamma} \right), \quad (16)$$

$$A(\vec{l})_\alpha = \frac{1}{4\pi\kappa} \frac{\Omega_0}{2\pi} \int_0^{2\pi} d\varphi \left[\frac{\partial}{\partial(\cos\theta)} \sum_\lambda \frac{e_\alpha^*(0, \theta, \varphi, \lambda) \cdot [\vec{\epsilon}(0, \theta, \varphi, \lambda) \cdot \hat{q}]}{M c_\lambda^2(\theta, \varphi)} \right]_{\theta=\pi/2} \quad (18)$$

Here the polar angle θ has to be measured with respect to \vec{l} and κ is the compressibility of the pure host. Obviously, \vec{A} is connected with the inverse Christoffel-matrix of the *host* and can be found, numerically in general, in any particular direction \vec{l} independently of the alloying problem (see Appendix). Comparison with the macroscopic theory² shows that \vec{A} so defined is precisely that entering Eq. (2), thus the bracket in (17) must equal $(\delta\Omega_0/\delta c)_{\text{per}}$.

Now, consider this bracket in the particular case of a metallic solution, with F given by (13), (14). The terms $F^{(3)}(\vec{G})$ in the sum in (17) can be neglected in comparison with $F^{(2)}(\vec{G})$ but the term $F^{(3)}(\vec{q}=0)$ is by no means small. In fact, due to the Coulombic behavior of v at large distance, Eqs. (8a) and (10) imply

$$\lim_{\vec{q}=0} \left(\frac{v\vec{q}}{\epsilon_{\vec{q}}} \right) = - \frac{Z}{\Omega_0 P(0)} \quad (19)$$

so that

$$\lim_{\vec{q}=0} F^{(3)}(\vec{q}) = - \frac{6Z}{P(0)} \left(\frac{1}{2N} \sum_{\vec{q}} \frac{\Lambda^{(3)}(0, \vec{q}, -\vec{q})}{(\epsilon_{\vec{q}})^2} |\Delta v_{\vec{q}}|^2 + \sum_{\vec{G} \neq 0} \frac{\Lambda^{(3)}(0, \vec{G}, -\vec{G})}{(\epsilon_{\vec{G}})^2} v_{\vec{G}} \Delta v_{\vec{G}} \right)$$

$$\vec{u}(\vec{l})_\alpha \sim \frac{A(\vec{l})_\alpha}{|\vec{l}|^2} \left[-\kappa\Omega_0 \frac{d(\Delta E^{(1)})}{d\Omega_0} + \kappa \sum_{\vec{G} \neq 0} \left(-\Omega_0 \frac{\partial}{\partial \Omega_0} + \frac{1}{3} G_\gamma \frac{\partial}{\partial G_\gamma} + n_0 \frac{\partial}{\partial n_0} \right) F^{(2)}(\vec{G}) - \kappa n_0 \frac{\partial}{\partial n_0} \frac{1}{N} \sum_{\vec{q}} |\Delta v_{\vec{q}}|^2 \Omega_0 \frac{P_{\vec{q}}}{\epsilon_{\vec{q}}} \right]. \quad (23)$$

The last term in the square brackets depends on Ω_0 only through n_0 , and the differential operator before $F^{(2)}(\vec{G})$ is actually $(-\Omega_0 d/d\Omega_0)$ for any function depending on Ω_0 explicitly and also through G_γ and n_0 .

with the repeated index γ implying summation. Evaluation of (15) for large $|\vec{l}|$ asymptotically gives, by choosing $\vec{l} = 0$,

$$\vec{u}(\vec{l})_\alpha = \frac{A(\vec{l})_\alpha}{|\vec{l}|^2} \left[\kappa \lim_{\vec{q}=0} F(\vec{q}) + \kappa \sum_{\vec{G} \neq 0} \left(F(\vec{G}) + \frac{1}{3} G_\gamma \frac{\partial F}{\partial G_\gamma} \right) \right] \quad (17)$$

with the "elastic amplitude vector" \vec{A} given by

or, equivalently, by using the identity due to Brovman and Kagan⁴

$$\frac{\Lambda^{(3)}(0, \vec{q}, -\vec{q})}{(\epsilon_{\vec{q}})^2} = \frac{P(0)}{6} \frac{d}{dn_0} \left(\frac{P_{\vec{q}}}{\epsilon_{\vec{q}}} \right), \quad (20)$$

($n_0 = Z/\Omega_0$ is the electron density) one has

$$\lim_{\vec{q}=0} F^{(3)}(\vec{q}) = -n_0 \frac{\partial}{\partial n_0} \left(\frac{1}{2N} \sum_{\vec{q}} |\Delta v_{\vec{q}}|^2 \Omega_0 \frac{P_{\vec{q}}}{\epsilon_{\vec{q}}} + \sum_{\vec{G} \neq 0} v_{\vec{G}} \Delta v_{\vec{G}} \Omega_0 \frac{P_{\vec{G}}}{\epsilon_{\vec{G}}} \right) \quad (21)$$

Further, by (13), (19), and (7) we have

$$\lim_{\vec{q}=0} F^{(2)}(\vec{q}) = Z \Delta v_{\vec{q}=0} = \Delta E^{(1)} = -\Omega_0 \frac{d(\Delta E^{(1)})}{d\Omega_0} \quad (22)$$

Since by (10), $v_{\vec{q}} \sim 1/\Omega_0$, $F^{(2)}(\vec{q})$ depends explicitly on the volume as $1/\Omega_0$, thus Eqs. (17), (21), and (22) give

We have therefore by (11) the asymptotic law

$$\vec{u}(\vec{l}) \sim \frac{\vec{A}(\vec{l})}{|\vec{l}|^2} \left(-\kappa\Omega_0 \frac{d(\Delta E_{\text{per}})}{d\Omega_0} \right). \quad (24)$$

The bracket in (24) has a very simple meaning. If the equilibrium atomic volume in the pure host is Ω_{oh} , and the minimum of (3) occurs at $\Omega_{oh} + \delta\Omega_0$, we have

$$\left(\frac{d^2 E_h}{d\Omega_0^2}\right)_{\Omega_{oh}} \delta\Omega_0 + \delta c \left(\frac{d(\Delta E_{per} + \Delta E_r)}{d\Omega_0}\right)_{\Omega_{oh}} = 0,$$

so that for the volume associated with the *homogeneous* expansion of the lattice we have

$$\left(\frac{\delta\Omega_0}{\delta c}\right)_{per} = -\kappa\Omega_0 \frac{d(\Delta E_{per})}{d\Omega_0}$$

which, with (24), leads to Eq. (2).

We emphasize that the contribution of third-order forces, consisting of the terms with $n_0(\partial/\partial n_0)$ in (23), is substantial in obtaining this result.

DISCUSSION

Two methods for the calculation of the asymptotical amplitude of the ionic displacements around an impurity have been compared and seen to give identical results, but the electronic response to be taken into account in the two cases is of different order. In particular, to reproduce the amplitude $(\delta\Omega_0/\delta c)_{per}$ derivable from the *second order* energy change of the *undistorted* lattice, we had to include both *second- and third-order* electronic response functions in the calculation of the force and displacement fields. Analogous result holds, in general, in any stage of approximation; the fact that the first-order (structure-independent) approximation $\Delta E^{(1)}$ in calculating $(\delta\Omega_0/\delta c)$ is consistent with the second-order "continuum" result for the local displacements [with $\vec{G} \neq 0$ terms in (17) neglected] has already been noticed.³

Higher-order electronic polarization, giving rise to many-body forces between the ions, appears in a similar way in the problem of phonons in pure metals,⁴ when one determines the longitudinal sound velocity by the method of long waves. There it turns out⁴ that to obtain the compressibility in *second order* [$\sim (v_{\vec{G}}/E_F)^2$] one has to account for *three- and even four-body* interactions in the small- \vec{q} expansion of the dynamical matrix. The physics in both the pure metal and the alloy cases lies in the fact that $E^{(n)}$ in the expansion (6) has a definite degree of smallness only for a *periodic* arrangement of the ions, whereas this is *not* so for a deformed crystal. The small quantity ensuring the decrease of subsequent terms in (6) in the case of periodicity is, however, different in the two problems: for the pure metal it is⁴ $v_{\vec{G}}/E_F$ while in the homovalent alloy, as seen from (8) and (9), it is either $v_{\vec{G}}/E_F$ or $\Delta v_{\vec{G}}/\epsilon_q E_F$. Since

$E^{(n)}$ consists of the *n*th-order response function and just *n* potential factors, and in the *periodic* case each of these must be either $v_{\vec{G}}$ or $\Delta v_{\vec{G}}$ [Eq. (9)], the term associated with the *n*th-order electronic response is automatically of *n*th order in *smallness*. If one calculates, however, the *force field* in the presence of the impurity (or in the phonon case, of the periodic distortion), a factor $v_{\vec{q}}(\vec{q} \neq \vec{G})$ appears, and $v_{\vec{q}}/\epsilon_q$ for small \vec{q} is by no means small, being instead of the order of E_F . Hence the force field $F^{(n+1)}$ derived from $E^{(n+1)}$ is for small \vec{q} 's actually of order *n* in smallness.

We see that, even in the lowest-order structure-dependent approximation, two- and three-body forces must be taken into account side by side in the calculation of the force and displacement field, otherwise the degree of approximation is not defined and hence the theory cannot be consistent.

Besides this principal question of consistency in describing the *asymptotics*, the result implies that any attempt to determine the *preasymptotic* displacements must also include third-order electronic polarization effects, since not too close to the foreign atom [small \vec{q} 's in $F^{(3)}(\vec{q})$] these contribute to $\vec{u}(\vec{R})$ in the same order as the linear screening terms.

Numerical results using the model parameters³ for a dilute Na(K) alloy show that leaving out $n_0\partial/\partial n_0$ terms in (23) leads to an about 8% overestimate of the asymptotical amplitude for the displacements.

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APPENDIX

(i) By inverting the transformation (12) we have, choosing $L = 0$

$$\sum_{\vec{G}} (k_{\alpha} + G_{\alpha}) F(\vec{k} + \vec{G}) = -i \sum_{\vec{l}} F(\vec{l})_{\alpha} e^{-i\vec{k}\cdot\vec{l}},$$

which, by differentiation with respect to k_{γ} gives at $\vec{k} = 0$

$$\delta_{\alpha\gamma} \sum_{\vec{G}} F(\vec{G}) + \sum_{\vec{G} \neq 0} G_{\alpha} \frac{\partial F}{\partial G_{\gamma}} = - \sum F(\vec{l})_{\alpha} l_{\gamma}.$$

Since the right-hand side of this equation shows the site symmetry of the lattice, we must have

$$\sum_{\vec{G}} G_{\alpha} \frac{\partial F}{\partial G_{\gamma}} = \delta_{\alpha\gamma} \times \frac{1}{3} \sum_{\gamma} \left(\sum_{\vec{G}} G_{\gamma} \frac{\partial F}{\partial G_{\gamma}} \right).$$

(ii) For cubic crystals $\vec{A}(\vec{1})$ was analytically obtained by Krivoglaz for the [100] direction²

$$A_x([100]) = \frac{c_{11} + 2c_{12}}{12\pi(c_{11} + c_{12})} \left(\xi + \frac{c_{11} + c_{12}(\xi + 1)}{c_{11} \left[1 + \frac{1}{4}\xi \left(1 + \frac{c_{12}}{c_{11}} \right) \right]^{1/2}} \right).$$

Here ξ is the anisotropy parameter

$$\xi = (c_{11} - c_{12} - 2c_{44})/c_{44}.$$

It is possible to obtain a relatively simple function also for the $\xi \parallel [110]$ -direction.

$$A_x([110]) = \frac{c_{11} + 2c_{12}}{12\pi c_{11}} \left(\frac{\alpha}{(1 + \frac{1}{2}\xi)^{1/2}} + I \right),$$

where

$$I = \frac{2}{\pi} \int_0^{\pi/2} \frac{\beta + \gamma \cos^2 \varphi}{E \cos^4 \varphi + F \cos^2 \varphi + 1} d\varphi,$$

and the constants α , β , γ , E , and F are combinations of ξ and $\lambda = c_{44}/c_{11}$ as

$$E = \xi \left[-\frac{3}{2} + \left(\xi + \frac{3}{2} \right) \lambda \right], \quad \gamma = -E \xi (\xi + 2) + \frac{1}{4} \xi^2 \left(\frac{1}{2} \xi - F \right)$$

$$F = \xi \left[\frac{3}{2} - (\xi + 2) \lambda \right], \quad \Delta = \frac{1}{4} \xi^2 + E - \frac{1}{2} \xi F$$

$$\alpha = \frac{1}{2} \xi^2 \left(\frac{\xi + 3}{\Delta} \right)$$

$$\beta = \frac{E(\xi + 1) - (\xi/2)(\xi + 1)F - (\xi^2/4)(\xi + 5)}{\Delta}$$

All other components of \vec{A} vanish in these cases. In highly anisotropic crystals, like the alkalis, one gets $A_x([100]) < 0$ and $A_x([110]) > 0$. Numerical results for the angular dependence of \vec{A} for a number of metals have been published very recently.⁷

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