

## Electron-Phonon Interaction via the Augmented-Plane-Wave Method\*

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A form of electron-phonon matrix element is presented and justified. The integrals in the matrix element are then reduced to sums of quantities appearing in existing augmented-plane-wave computer programs. The method holds special promise for the practical numerical evaluation of the electron-phonon interaction for the transition metals.

### INTRODUCTION

A FIRST-PRINCIPLES calculation of the electron-phonon interaction has long been a major problem of solid-state theory. There are two questions which must be answered. In principle, what should one consider as the electron-phonon matrix element? Then, once the basic form has been agreed upon, how can one calculate the matrix element in practice? The entire problem is especially difficult for the transition metals where one must consider both highly mobile *s*-like electrons and semimobile *d*-like electrons. (In this paper we shall loosely refer to both *s* and *d* electrons as conduction electrons.)

We give here an answer to these questions based on the augmented plane-wave (APW) method of energy-band calculation. Our first concern is the presentation and justification of the basic electron-phonon matrix element which is to be calculated. We then proceed to reduce this matrix element to a form in which all quantities are those generated in the APW computer calculations of energy bands and wave functions for the periodic lattice.

Thus, our method is a direct extension of already existing APW programs to the calculation of the electron-phonon interaction. Since present APW work has achieved considerable accuracy and reliability and included studies of many transition elements, its application to the electron-phonon interaction is very attractive.

### THE INTERACTION MATRIX ELEMENT

The appropriate form of the electron-phonon matrix element has been extensively studied. General reviews have been given by Ziman,<sup>1</sup> Sham and Ziman,<sup>2</sup> and Schrieffer.<sup>3</sup> Here we take the matrix element to be

$$\mathfrak{M}(n', \mathbf{k}'; n, \mathbf{k}) = \langle \Psi_{n'\mathbf{k}'} | \sum_j \delta \mathbf{R}_j \cdot \frac{\partial U}{\partial \mathbf{R}_j} \Big|_{\mathbf{R}_j = \mathbf{R}_j^0} | \Psi_{n\mathbf{k}} \rangle, \quad (1)$$

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<sup>1</sup> J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960).

<sup>2</sup> L. J. Sham and J. M. Ziman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 15.

<sup>3</sup> J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964).

where the integration is taken over the entire crystal (considered to be of unit volume in this paper).  $\Psi_{n\mathbf{k}}$  is the APW<sup>4</sup> wave function of crystal momentum  $\mathbf{k}$  and band index *n* for the ions in their equilibrium positions,  $\mathbf{R}_j$  is the ionic coordinate and  $\mathbf{R}_j^0$  is the equilibrium position. We consider only elements with one atom per unit cell for which  $\delta \mathbf{R}_j$ , the deviation from the equilibrium position, is related to phonon coordinates by<sup>3</sup>

$$\delta \mathbf{R}_j = \sum_{\mathbf{q}, \lambda} \left( \frac{\hbar}{NM2\omega_{\mathbf{q}, \lambda}} \right)^{1/2} \boldsymbol{\epsilon}_{\mathbf{q}, \lambda} \exp(i\mathbf{q} \cdot \mathbf{R}_j^0) (a_{-\mathbf{q}, \lambda}^\dagger + a_{\mathbf{q}, \lambda}). \quad (2)$$

*M* is the ionic mass,  $\omega_{\mathbf{q}, \lambda}$  is the phonon frequency of momentum  $\mathbf{q}$  and polarization  $\lambda$ , *N* is the number of atoms in unit volume, and  $\boldsymbol{\epsilon}_{\mathbf{q}, \lambda}$  is a unit polarization vector. Alternatively, we may express  $\delta \mathbf{R}_j$  in terms of the normal-mode amplitude

$$\varphi_{\mathbf{q}, \lambda} = (\hbar/2\omega_{\mathbf{q}, \lambda})^{1/2} (a_{\mathbf{q}, \lambda} + a_{-\mathbf{q}, \lambda}^\dagger). \quad (3)$$

For the sake of convenient adaptation to already existing APW programs, we take *U* to be the conventional APW potential. It consists of spherically symmetric "muffin tin" potentials around each atomic site. The method by which the APW potential is constructed<sup>4</sup> accounts for the average screening of the ionic potential by the conduction electrons. A more accurate description of true dynamical screening effects could be accomplished in a number of ways. One could restrict the potential to be used in (1) to that of the bare ions. Later, the resulting bare electron-phonon interaction could be altered by explicitly considering true many-body interactions among conduction electrons. Alternatively, one could calculate  $\mathfrak{M}(n', \mathbf{k}'; n, \mathbf{k})$  by using a bare ion potential reduced by the conduction electron dielectric constant.

Our basic assumption in this calculation is that the lattice perturbed by phonons may be adequately described by an appropriate displacement of the "muffin tin" potentials. One could then readily deduce (1) by considering the scattering of conduction electrons (described by wave functions for the unperturbed lattice) resulting from the change in potential. Such an approach would violate the Pauli principle. The APW

<sup>4</sup> J. C. Slater, Solid State and Molecular Theory Group, M.I.T., Quarterly Progress Report No. 51, 1964 (unpublished). This article is a general review of the APW method and references all but the most recent work.

potential is essentially a Hartree-Fock field describing the influence of the core and conduction electrons through the exclusion principle as well as the true Coulomb potentials. The effect of the core electrons required by the Pauli principle is further accounted for in the very construction of the APW basis functions. Calculation of a matrix element of the displaced potential with respect to wave functions for the undisplaced cores is inconsistent. The proper procedure is to consider the conduction wave functions for the perturbed lattice based on a set of displaced APW functions; that is, one must solve the unperiodic lattice problem. The derivation of (1) by this approach is presented in detail in the Appendix.

### EVALUATION OF THE MATRIX ELEMENT I

We first evaluate the matrix element using simple APW basis functions. This will clearly illustrate the essentials of the calculation. Then in the following section lattice-symmetry considerations will be introduced.

The form of the APW potential, namely,

$$U(\mathbf{r}) = \begin{cases} U(|\mathbf{r}-\mathbf{R}_j|) & \text{inside the } j\text{th muffin tin} \\ \text{constant} & \text{elsewhere,} \end{cases} \quad (4)$$

leads to

$$\frac{\partial U(\mathbf{r})}{\partial \mathbf{R}_j} = \begin{cases} -\frac{\partial U}{\partial \mathbf{r}} = -\nabla U & \text{inside the } j\text{th muffin tin} \\ 0 & \text{elsewhere.} \end{cases} \quad (5)$$

In cases of interest, the electron-phonon scattering occurs between states near the Fermi surface. The initial and final states of course differ in energy by the amount of the emitted phonon energy. Since phonon energies are small compared to the Fermi energy we will make the approximation that both states have the Fermi energy.  $\Psi_{n\mathbf{k}}$  is an implicit function of energy which for the remainder of this paper will be fixed at the Fermi energy. For reasons to become clear it is convenient to use the spherical components of a vector defined by

$$V_{\pm 1} = \mp(1/\sqrt{2})(V_x \pm iV_y) \quad V_0 = V_z. \quad (6)$$

The scalar product is given by

$$\mathbf{V} \cdot \mathbf{V}' = \sum_{\mu=-1}^{+1} (-1)^\mu V_\mu V'_{-\mu}. \quad (7)$$

With these additional facts taken into account, the matrix element is written

$$\mathfrak{M}(n', \mathbf{k}'; n, \mathbf{k}) = -\sum_{j, \mu} (-1)^\mu \delta \mathbf{R}_{j, \mu} \int \Psi_{n' \mathbf{k}'}^* (\nabla_{-\mu} U) \Psi_{n \mathbf{k}} d\mathbf{r}, \quad (8)$$

where the integration includes the volume of only the  $j$ th muffin tin.  $\Psi_{n\mathbf{k}}$  is of course the equilibrium lattice wave function.

The APW wave function is given by

$$\Psi_{n\mathbf{k}} = \sum_{\mathbf{g}} A_{n\mathbf{g}} \varphi_{\mathbf{g}}. \quad (9)$$

For one atom per unit cell, the APW basis function within the primary cell is

$$\varphi_{\mathbf{g}}(\mathbf{r}) = \sum_{l, m} 4\pi i^l j_l(gR_s) \frac{Y_l^{m*}(\theta_{\mathbf{g}}, \varphi_{\mathbf{g}})}{u_l(R_s)} u_l(r) Y_l^m(\theta, \varphi) \quad r < R_s \\ = \exp(i\mathbf{g} \cdot \mathbf{r}) \quad r > R_s \quad (10)$$

(Outside the primary cell  $\varphi_{\mathbf{g}}$  is obtained simply by multiplying by the factor  $e^{i\mathbf{g} \cdot \mathbf{R}_j}$ .)  $Y_l^m$  is a spherical harmonic,  $\theta$  and  $\varphi$  are the coordinates of  $\mathbf{r}$  and  $\theta_{\mathbf{g}}$  and  $\varphi_{\mathbf{g}}$  are the coordinates of  $\mathbf{g}$ ,  $R_s$  is the radius of the APW sphere,  $\mathbf{g} = \mathbf{k} + \mathbf{K}$ ,  $\mathbf{k}$  is a wave vector in the first Brillouin zone, and  $\mathbf{K}$  is a reciprocal lattice vector.  $u_l(r)$  is the solution of the radial Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{du_l}{dr} \right) + \left[ \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} + U(r) \right] u_l = E u_l, \quad (11)$$

which is regular at the origin. Substituting the wave function into (8), we obtain

$$\mathfrak{M}(n', \mathbf{k}'; n, \mathbf{k}) = - \sum_{j, \mu, \mathbf{g}, \mathbf{g}', l, l', m, m'} (-1)^\mu \delta R_{j, \mu} A_{n' \mathbf{g}'}^* A_{n \mathbf{g}} \\ \times 4\pi (-i)^l j_l(g'R_s) \frac{Y_l^{m'}(\theta_{\mathbf{g}'}, \varphi_{\mathbf{g}'})}{u_l^*(R_s)} 4\pi (i)^{l'} j_{l'}(gR_s) \\ \times \frac{Y_l^{m*}(\theta_{\mathbf{g}}, \varphi_{\mathbf{g}})}{u_l(R_s)} \int_{\text{sphere}} u_l^* Y_{l', m'}^* \\ \times (\nabla_{-\mu} U) u_l Y_l^m d\mathbf{r}. \quad (12)$$

Thus the problem immediately reduces to the evaluation of the integrals,

$$\int_{\text{sphere}} u_l^* Y_{l', m'}^* (\nabla_{\mu} U) u_l Y_l^m d\mathbf{r}.$$

We note and emphasize the important fact that these integrals do not depend on the choice of initial and final states in the matrix element and consequently they need be calculated only once. Let us now proceed to the crucial step of reducing these integrals to a sum of constants which are found in standard APW calculations.

The function  $u_l Y_l^m$  satisfies the Schrödinger equation

$$[-(\hbar^2/2m)\nabla^2 + U] u_l Y_l^m = E_f u_l Y_l^m, \quad (13)$$

where  $E_f$  is the Fermi energy. We differentiate this and rearrange to obtain

$$(\nabla_{\mu} U) u_l Y_l^m = [E_f + (\hbar^2 \nabla^2 / 2m) - U] \nabla_{\mu} (u_l Y_l^m). \quad (14)$$

Using this result, the integral can be re-expressed as

$$\begin{aligned} & \int_{\text{sphere}} u_{l'}^* Y_{l', m'}^* (\nabla_{\mu} U) u_l Y_{l, m} d\mathbf{r} \\ &= \frac{\hbar^2}{2m} \int \nabla \cdot [u_{l'}^* Y_{l', m'}^* \nabla (\nabla_{\mu} u_l Y_{l, m}) - (\nabla u_{l'}^* Y_{l', m'}^*) \nabla_{\mu} u_l Y_{l, m}] d\mathbf{r} + \int \left( \frac{\hbar^2}{2m} \nabla^2 u_{l'}^* Y_{l', m'}^* \right) \nabla_{\mu} u_l Y_{l, m} d\mathbf{r} \\ & \quad + \int u_{l'}^* Y_{l', m'}^* (E_f - U) \nabla_{\mu} u_l Y_{l, m} d\mathbf{r}. \quad (15) \end{aligned}$$

The sum of the last two integrals is zero by virtue of (13). The first integral can be transformed by the divergence theorem to yield

$$\begin{aligned} & \int_{\text{sphere}} u_{l'}^* Y_{l', m'}^* (\nabla_{\mu} U) u_l Y_{l, m} d\mathbf{r} \\ &= \frac{\hbar^2}{2m} \int d\mathbf{S} \cdot [u_{l'}^* Y_{l', m'}^* \nabla (\nabla_{\mu} u_l Y_{l, m}) - (\nabla u_{l'}^* Y_{l', m'}^*) \nabla_{\mu} u_l Y_{l, m}], \\ &= \frac{\hbar^2 R_s^2}{2m} \int_{r=R_s} d\Omega \left[ u_{l'}^* Y_{l', m'}^* \frac{d}{dr} (\nabla_{\mu} u_l Y_{l, m}) - \frac{du_{l'}^*}{dr} Y_{l', m'}^* \nabla_{\mu} u_l Y_{l, m} \right], \quad (16) \\ &= \frac{\hbar^2 R_s^2}{2m} u_{l'}^*(R_s) \frac{d}{dr} \int d\Omega Y_{l', m'}^* \nabla_{\mu} u_l Y_{l, m} - \frac{\hbar^2 R_s^2}{2m} \frac{du_{l'}^*}{dr} \Big|_{r=R_s} \int d\Omega Y_{l', m'}^* \nabla_{\mu} u_l Y_{l, m}. \end{aligned}$$

The integrals  $\int d\Omega Y_{l', m'}^* \nabla_{\mu} u_l Y_{l, m}$  have been evaluated<sup>5</sup> with the help of the Wigner-Eckhart theorem. Non-vanishing results are obtained only for the cases where  $m' = m + \mu$  and  $l' = \pm 1$ .

$$\int d\Omega Y_{l+1, m+\mu}^* \nabla_{\mu} u_l Y_{l, m} = \frac{(-1)^{l+m} A_{\mu}^+}{[2(2l+3)(2l+1)]^{1/2}} \left( \frac{d}{dr} - \frac{l}{r} \right) u_l, \quad (17)$$

where

$$A_{1^+} = [(l+m+1)(l+m+2)]^{1/2}, \quad A_{0^+} = -[2(l+m+1)(l-m+1)]^{1/2}, \quad A_{-1^+} = [(l-m+1)(l-m+2)]^{1/2},$$

$$\int d\Omega Y_{l-1, m+\mu}^* \nabla_{\mu} u_l Y_{l, m} = \frac{(-1)^{l+m} A_{\mu}^-}{[2(2l+1)(2l-1)]^{1/2}} \left( \frac{d}{dr} + \frac{l+1}{r} \right) u_l(r), \quad (18)$$

where

$$A_{1^-} = [(l-m-1)(l-m)]^{1/2}, \quad A_{0^-} = [2(l+m)(l-m)]^{1/2}, \quad A_{-1^-} = [(l+m-1)(l+m)]^{1/2}.$$

Substituting (17) and (18) into (16) and eliminating the second derivative of  $u_l$  by (11), we finally obtain

$$\begin{aligned} \int d\Omega u_{l+1}^* Y_{l+1, m+\mu}^* \nabla_{\mu} u_l Y_{l, m} &= \frac{\hbar^2 R_s^2}{2m} \frac{(-1)^{l+m} A_{\mu}^+}{[2(2l+3)(2l+1)]^{1/2}} u_{l+1}^* u_l \left\{ \frac{2m}{\hbar^2} [U(R_s) - E_f] + \frac{l(l+2)}{R_s^2} - \frac{u_l'(l+2)}{u_l R_s} \right. \\ & \quad \left. + \frac{u_{l+1}^* l}{u_{l+1}^* R_s} - \frac{u_{l+1}^* u_l'}{u_{l+1} u_l} \right\}, \quad (19) \end{aligned}$$

$$\begin{aligned} \int d\Omega u_{l-1}^* Y_{l-1, m+\mu}^* \nabla_{\mu} u_l Y_{l, m} &= \frac{\hbar^2 R_s^2}{2m} \frac{(-1)^{l+m} A_{\mu}^-}{[2(2l+1)(2l-1)]^{1/2}} u_{l-1}^* u_l \left\{ \frac{2m}{\hbar^2} [U(R_s) - E_f] + \frac{(l+1)(l-1)}{R_s^2} \right. \\ & \quad \left. + \frac{u_l'(l-1)}{u_l R_s} - \frac{u_{l-1}^* (l+1)}{u_{l-1}^* R_s} - \frac{u_{l-1}^* u_l'}{u_{l-1}^* u_l} \right\}, \quad (20) \end{aligned}$$

where  $u_l = u_l(R_s)$  and  $u_l' = (du_l/dr)|_{r=R_s}$ .

<sup>5</sup> A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), p. 80.

## EVALUATION OF THE MATRIX ELEMENT II

Actual calculations with the APW method rely heavily on the lattice symmetry.<sup>6,7</sup> Instead of labeling by a band index  $n$ , the wave functions are labeled as  $\Psi_{pk}^\alpha$  which transforms irreducibly as the  $p$ th partner in the  $\alpha$ th representation of the group of the wave vector. In addition, the wave functions developed by the computer calculations are not normalized, and we must account for this.

The matrix element is now written as

$$\begin{aligned} \mathfrak{M}(p', \alpha', \mathbf{k}'; p, \alpha, \mathbf{k}) \\ = - \sum_{j, \mu} (-1)^\mu \delta R_{j, \mu} \int_{j\text{th sphere}} \Psi_{p'k'}^{\alpha'*} (\nabla_\mu U) \Psi_{pk}^\alpha d\mathbf{r} / \\ \langle \Psi_{p'k'}^{\alpha'} | \Psi_{p'k'}^{\alpha'} \rangle^{1/2} \langle \Psi_{pk}^\alpha | \Psi_{pk}^\alpha \rangle^{1/2}. \end{aligned} \quad (21)$$

$$\begin{aligned} \int \Psi_{p'k'}^{\alpha'*} (\nabla_\mu U) \Psi_{pk}^\alpha d\mathbf{r} = \sum_{\substack{\mathbf{g}, \mathbf{g}', \mathbf{q}, \mathbf{q}', R, R', \\ l, l', m, m', m', m''}} A_{\mathbf{g}'\mathbf{q}'}^{\alpha'*} A_{\mathbf{g}\mathbf{q}}^\alpha \Gamma_{p'\mathbf{q}'}^{\alpha'}(R') \Gamma_{p\mathbf{q}}^\alpha(R) 4\pi (-i)^{l'} j_{l'}(g'R_s) \frac{Y_{l'm'}(\theta_{\mathbf{g}', \varphi_{\mathbf{g}'}})}{u_{l'}^*(R_s)} 4\pi (i)^l j_l(gR_s) \\ \times \frac{Y_{l'm}(\theta_{\mathbf{g}, \varphi_{\mathbf{g}}})}{u_l(R_s)} G_{m''m'}^{l''}(R') G_{m''m}^l(R) \int u_{l'}^* Y_{l'm''}(\nabla_\mu U) u_l Y_{l'm} d\mathbf{r}. \end{aligned} \quad (25)$$

The integrals  $\int u_{l'}^* Y_{l'm''}(\nabla_\mu U) u_l Y_{l'm} d\mathbf{r}$  were evaluated in terms of quantities in the computer calculation in the last section. The only quantities appearing in (25) which are not already in the programs are the standard rotation matrices  $G^l(R)$ .

Finally it is necessary to evaluate the normalization integral. By group-theoretical arguments this integral

$$\langle \Psi_{pk}^\alpha | \Psi_{pk}^\alpha \rangle = \sum_{\mathbf{g}, \mathbf{g}', \mathbf{q}, \mathbf{q}'} A_{\mathbf{g}'\mathbf{q}'}^{\alpha*} A_{\mathbf{g}\mathbf{q}}^\alpha \times \langle \sum_{R'} \Gamma_{p\mathbf{q}'}^{\alpha*} R' \varphi_{\mathbf{g}'} | \sum_R \Gamma_{p\mathbf{q}}^\alpha R \varphi_{\mathbf{g}} \rangle \quad (26)$$

is reduced to

$$\langle \Psi_{pk}^\alpha | \Psi_{pk}^\alpha \rangle = \frac{G}{n_\alpha} \sum_{\mathbf{g}, \mathbf{g}', \mathbf{q}, \mathbf{q}', R} A_{\mathbf{g}'\mathbf{q}'}^{\alpha*} A_{\mathbf{g}\mathbf{q}}^\alpha \Gamma_{\mathbf{q}'\mathbf{q}}^{\alpha*} \times \langle \varphi_{\mathbf{g}'} | R \varphi_{\mathbf{g}} \rangle, \quad (27)$$

where  $G$  is the order of the group and  $n_\alpha$  is the dimension of the  $\alpha$ th representation. The APW functions have the translational property

$$\varphi_{\mathbf{g}}(\mathbf{r} + \mathbf{R}_j) = e^{i\mathbf{g} \cdot \mathbf{R}_j} \varphi_{\mathbf{g}}(\mathbf{r}), \quad (28)$$

which allows us to reduce the integral over the entire crystal to one over a unit cell.

$$\langle \varphi_{\mathbf{g}'} | R \varphi_{\mathbf{g}} \rangle = N \int_{\text{unit cell}} d\mathbf{r} \varphi_{\mathbf{g}'} R \varphi_{\mathbf{g}}. \quad (29)$$

The wave function  $\Psi_{pk}^\alpha$  is given by

$$\Psi_{pk}^\alpha = \sum_{\mathbf{g}, \mathbf{q}} A_{\mathbf{g}\mathbf{q}}^\alpha (\varphi_{\mathbf{g}})_{p\mathbf{q}}^\alpha. \quad (22)$$

$(\varphi_{\mathbf{g}})_{p\mathbf{q}}^\alpha$  is a symmetrized augmented plane wave (SAPW).

$$(\varphi_{\mathbf{g}})_{p\mathbf{q}}^\alpha = \sum_R \Gamma_{p\mathbf{q}}^{\alpha*}(R) R \varphi_{\mathbf{g}}. \quad (23)$$

Here the summation is over all the operators of the group of the wave vector and  $\Gamma_{p\mathbf{q}}^\alpha(R)$  is the  $p$ th row,  $q$ th column element of the matrix  $\Gamma^\alpha(R)$  which gives the transformation properties of the  $\alpha$ th representation.

Evaluation of the integral in the numerator of (21) is straightforward. We first substitute (22), (23), and (10) into the integral. Next we eliminate the rotation operators  $R$  with the help of the matrices  $G^l(R)$  defined by

$$R Y_{l'm} = \sum_{m'} G_{m''m'}^l(R) Y_{l'm''}. \quad (24)$$

Immediately we obtain our result.

Here  $N$  is the number of atoms in unit volume of the crystal and we have used the fact that  $R\mathbf{g}$  and  $\mathbf{g}'$  differ by a reciprocal lattice vector.

The integral of the plane-wave product over the entire cell is given by

$$\int_{\text{cell}} d\mathbf{r} e^{-i(\mathbf{g}' - R\mathbf{g}) \cdot \mathbf{r}} = \Omega \delta_{R\mathbf{g}, \mathbf{g}'}, \quad (30)$$

where  $\Omega$  is the volume of the unit cell. From this we subtract the integral of the plane-wave product over the APW sphere. Expanding the plane wave in spherical harmonics one easily finds

$$\int_{\text{sphere}} e^{-i(\mathbf{g}' - R\mathbf{g}) \cdot \mathbf{r}} d\mathbf{r} = 4\pi R_s^2 \frac{j_1(|R\mathbf{g} - \mathbf{g}'| R_s)}{|R\mathbf{g} - \mathbf{g}'|}. \quad (31)$$

We again use the rotation properties of the spherical harmonics (24) as well as their orthogonality properties to reduce the integral over the sphere of the non-plane-wave part of the APW function

$$\begin{aligned} \int_{\text{sphere}} \varphi_{\mathbf{g}'} R \varphi_{\mathbf{g}} d\mathbf{r} = \sum_{l, m, m'} 4\pi (-i)^l j_l(g'R_s) \\ \times \frac{Y_{l'm'}(\theta_{\mathbf{g}', \varphi_{\mathbf{g}'}})}{u_{l'}^*(R_s)} 4\pi (i)^l j_l(gR_s) \frac{Y_{l'm}(\theta_{\mathbf{g}, \varphi_{\mathbf{g}}})}{u_l(R_s)} \\ \times G_{m''m'}^l(R) \int_0^{R_s} |u_l|^2 r^2 dr. \end{aligned} \quad (32)$$

<sup>6</sup> J. H. Wood, Phys. Rev. 126, 517 (1962).

<sup>7</sup> W. E. Rudge, Solid State and Molecular Theory Group, M.I.T., Quarterly Progress Report No. 59, 1966 (unpublished).

TABLE I. The electron-phonon matrix element in terms of quantities generated in APW programs.

$$\begin{aligned}
\mathfrak{M}(\rho', \alpha', \mathbf{k}'; \rho, \alpha, \mathbf{k}) &= -\sum_{j, \mu} (-1)^{\mu} \delta R_{j, \mu} \frac{\int_{j\text{th sphere}} \Psi_{\rho' \mathbf{k}'}^{\alpha'} (\nabla_{-\mu} U) \Psi_{\rho \mathbf{k}}^{\alpha} d\mathbf{r}}{\langle \Psi_{\rho' \mathbf{k}'}^{\alpha'} | \Psi_{\rho' \mathbf{k}'}^{\alpha'} \rangle^{1/2} \langle \Psi_{\rho \mathbf{k}}^{\alpha} | \Psi_{\rho \mathbf{k}}^{\alpha} \rangle^{1/2}} \quad (34) \\
\int \Psi_{\rho' \mathbf{k}'}^{\alpha'} (\nabla_{\mu} U) \Psi_{\rho \mathbf{k}}^{\alpha} d\mathbf{r} &= \sum_{\substack{\mathbf{g}, \mathbf{g}', \mathbf{q}, \mathbf{q}', R, R', \\ l, l', m', m, m'', m'''}} A_{\mathbf{g}' \mathbf{q}'}^{\alpha'} A_{\mathbf{g} \mathbf{q}}^{\alpha} \Gamma_{\rho' \mathbf{q}'}^{\alpha'} (R') \Gamma_{\rho \mathbf{q}}^{\alpha} (R) 4\pi (-i)^{l'} j_{l'}(g'R_s) \frac{Y_{l', m'}(\theta_{\mathbf{g}', \varphi_{\mathbf{g}'})}}{u_{l'}^*(R_s)} 4\pi (i)^l j_l(gR_s) \frac{Y_{l, m}(\theta_{\mathbf{g}, \varphi_{\mathbf{g}}})}{u_l(R_s)} \\
&\quad \times G_{m'' m'}^{l'}(R') G_{m' m}^l(R) \int u_{l'}^* Y_{l', m''} (\nabla_{\mu} U) u_l Y_{l, m'} d\mathbf{r} \quad (35) \\
\int u_{l'}^* Y_{l', m'} (\nabla_{\mu} U) u_l Y_{l, m} d\mathbf{r} &= \frac{\hbar^2 R_s^2}{2m} \frac{(-1)^{l+m} A_{\mu}^+}{[2(2l+3)(2l+1)]^{1/2}} u_{l+1}^* u_l \left\{ \frac{2m}{\hbar^2} [U(R_s) - E_f] + \frac{l(l+2)}{R_s^2} \frac{u_l'(l+2)}{u_l} \frac{u_{l+1}^* l}{u_{l+1}^* R_s} + \frac{u_{l+1}^* u_l'}{u_{l+1}^* u_l} \right\} \\
&\quad \text{if } l' = l+1, m' = m+\mu; \quad (36) \\
&= \frac{\hbar^2 R_s^2}{2m} \frac{(-1)^{l+m} A_{\mu}^-}{[2(2l+1)(2l-1)]^{1/2}} u_{l-1}^* u_l \left\{ \frac{2m}{\hbar^2} [U(R_s) - E_f] + \frac{(l+1)(l-1)}{R_s^2} \frac{u_l'(l-1)}{u_l} \frac{u_{l-1}^* (l+1)}{u_{l-1}^* R_s} + \frac{u_{l-1}^* u_l'}{u_{l-1}^* u_l} \right\} \\
&\quad \text{if } l' = l-1, m' = m+\mu; \\
&= 0 \quad \text{otherwise;} \\
\text{where} & \quad A_1^+ = [(l+m+1)(l+m+2)]^{1/2} \quad A_1^- = [(l-m-1)(l-m)]^{1/2}, \\
& \quad A_0^+ = [2(l+m+1)(l-m+1)]^{1/2} \quad A_0^- = [2(l+m)(l-m)]^{1/2}, \\
& \quad A_{-1}^+ = [(l-m+1)(l-m+2)]^{1/2} \quad A_{-1}^- = [(l+m-1)(l+m)]^{1/2}. \\
\langle \Psi_{\rho \mathbf{k}}^{\alpha} | \Psi_{\rho \mathbf{k}}^{\alpha} \rangle &= \frac{G}{n_{\alpha}} \sum_{\mathbf{g}, \mathbf{g}', \mathbf{q}, \mathbf{q}', R} A_{\mathbf{g}' \mathbf{q}'}^{\alpha} A_{\mathbf{g} \mathbf{q}}^{\alpha} \Gamma_{\mathbf{q}'}^{\alpha} \Gamma_{\mathbf{q}}^{\alpha} \left\{ \delta_{R\mathbf{g}, \mathbf{g}'} - 4\pi N R_s^2 \frac{j_1(|R\mathbf{g} - \mathbf{g}'| R_s)}{|R\mathbf{g} - \mathbf{g}'|} + N \sum_{l, m, m'} 4\pi (-i)^l j_l(g'R_s) \frac{Y_{l, m}(\theta_{\mathbf{g}, \varphi_{\mathbf{g}}})}{u_l^*(R_s)} \right. \\
&\quad \left. \times 4\pi (i)^l j_l(gR_s) \frac{Y_{l, m}(\theta_{\mathbf{g}, \varphi_{\mathbf{g}}})}{u_l(R_s)} G_{m' m}^l(R) \int_0^{R_s} |u_l|^2 r^2 dr \right\}. \quad (37)
\end{aligned}$$

Adding the contributions from (30) and (32) and subtracting the contribution given by (31), multiplying by  $N$ , and substituting the sum into (27), we obtain for the normalization integral

$$\begin{aligned}
\langle \Psi_{\rho \mathbf{k}}^{\alpha} | \Psi_{\rho \mathbf{k}}^{\alpha} \rangle &= \frac{G}{n_{\alpha}} \sum_{\mathbf{q}, \mathbf{q}', \mathbf{q}, \mathbf{q}', R} A_{\mathbf{g}' \mathbf{q}'}^{\alpha} A_{\mathbf{g} \mathbf{q}}^{\alpha} \Gamma_{\mathbf{q}'}^{\alpha} \Gamma_{\mathbf{q}}^{\alpha} \left\{ \delta_{R\mathbf{g}, \mathbf{g}'} - 4\pi N R_s^2 \frac{j_1(|R\mathbf{g} - \mathbf{g}'| R_s)}{|R\mathbf{g} - \mathbf{g}'|} + N \sum_{l, m, m'} 4\pi (-i)^l j_l(g'R_s) \right. \\
&\quad \left. \times \frac{Y_{l, m}(\theta_{\mathbf{g}', \varphi_{\mathbf{g}'})}}{u_{l'}^*(R_s)} 4\pi (i)^l j_l(gR_s) \frac{Y_{l, m}(\theta_{\mathbf{g}, \varphi_{\mathbf{g}}})}{u_l(R_s)} G_{m' m}^l(R) \int_0^{R_s} |u_l|^2 r^2 dr \right\}. \quad (33)
\end{aligned}$$

The radial integrals need be evaluated only once since the  $u_l$ 's for all matrix elements in our restricted calculation are the solutions of (11) with  $E = E_f$ . In Table I we present a convenient summary of our results in a form suitable for programming.

## DISCUSSION

Let us briefly consider the practical numerical evaluation of the matrix element. Again we note that the integrals  $\int u_{l'}^* Y_{l', m'} (\nabla_{\mu} U) u_l Y_{l, m} d\mathbf{r}$  given by (36) are independent of initial and final states and need be evaluated only once. The same is true of the radial integrals  $\int_0^{R_s} |u_l|^2 r^2 dr$ . The only quantity appearing in (35) and (37) which does not also appear in the APW energy band and wave-function program is the standard rotation matrix  $G^l(R)$ . The sum over  $q$  in (35) and (37) is inconsequential since this parameter usually takes only

one value and at most two or three. On examination of Rudge's<sup>7</sup> published values of  $A_{\mathbf{g}, \mathbf{q}}^{\alpha}$  for Na, it appears that approximately four terms in the sum over  $\mathbf{g}$  will be sufficient for 1% accuracy. The sum over  $l$  in (35) and (37) will be rapidly cut off by the decrease of the spherical Bessel functions with increasing order for fixed argument.

The major difficulty in the method proposed here is the calculation of the eigenvector components  $A_{\mathbf{g}, \mathbf{q}}^{\alpha}$ . As a result of the considerable amount of calculation required, a general evaluation of the interaction over the entire Fermi surface appears prohibitive at this time. However, a careful choice of a limited number of matrix elements should give an accurate picture of the strength of the interaction.

It is hoped that the method will find application for the many transition elements for which APW programs have already been written. One outstanding problem

which could be resolved is the extent of phonon renormalization of the density of states in palladium.

### ACKNOWLEDGMENTS

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### APPENDIX

In this appendix we present the derivation of the matrix element. Consider the lattice in which the ions have been displaced from their equilibrium positions. We assume that the potential seen by the electrons in this situation can be described simply by displacing the original "muffin tin" potentials. The conduction wave function for the distorted lattice is given approximately by

$$\Psi_{nk} \cong \Psi_{nk}^0 + \sum_{n', \mathbf{k}'} M(n', \mathbf{k}'; n, \mathbf{k}) \Psi_{n'k'}^0, \quad (\text{A1})$$

where the summation here is over all states including both conduction and core electrons. We demand that  $M$  be a linear function of the ionic displacements as appropriate to the phonon approximation. (Throughout this Appendix a superscript 0 will refer to the unperturbed lattice, a prime will refer to the difference between the perturbed and unperturbed states to first order, and the absence of a superscript will refer to the distorted lattice.)

$$\begin{aligned} \Psi_{nk} \cong \sum_{\mathbf{K}} A_n^0(\mathbf{k}, \mathbf{k} + \mathbf{K}) \varphi_{\mathbf{k} + \mathbf{K}}^0 + \sum_{\mathbf{K}} A_n^0(\mathbf{k}, \mathbf{k} + \mathbf{K}) \varphi'_{\mathbf{k} + \mathbf{K}} + \sum_{\mathbf{K}} A_n'(\mathbf{k}, \mathbf{k} + \mathbf{K}) \varphi_{\mathbf{k} + \mathbf{K}}^0 \\ + \sum_{\mathbf{k}' \neq \mathbf{k} + \mathbf{K}} A_n'(\mathbf{k}, \mathbf{k}') \varphi_{\mathbf{k}'}^0 = \Psi_{nk}^0 + \sum_{\text{all } \mathbf{k}'} A_n'(\mathbf{k}, \mathbf{k}') \varphi_{\mathbf{k}'}^0 + \sum_{\mathbf{K}} A_n^0(\mathbf{k}, \mathbf{k} + \mathbf{K}) \varphi'_{\mathbf{k} + \mathbf{K}}. \end{aligned} \quad (\text{A6})$$

For convenience we define

$$\theta_{nk} = \sum_{\text{all } \mathbf{k}'} A_n'(\mathbf{k}, \mathbf{k}') \varphi_{\mathbf{k}'}^0 \quad (\text{A7})$$

and

$$\zeta_{nk} = \sum_{\mathbf{K}} A_n^0(\mathbf{k}, \mathbf{k} + \mathbf{K}) \varphi'_{\mathbf{k} + \mathbf{K}}. \quad (\text{A8})$$

We see that the effect of allowing the APW basis functions to follow the cores is incorporated in  $\zeta_{nk}$ .

Our problem now is to calculate  $\theta_{nk}$  and  $\zeta_{nk}$  which are related to  $M(n', \mathbf{k}'; n, \mathbf{k})$  by

$$M(n', \mathbf{k}'; n, \mathbf{k}) = \langle \Psi_{n'k'}^0 | \theta_{nk} \rangle + \langle \Psi_{n'k'}^0 | \zeta_{nk} \rangle. \quad (\text{A9})$$

Consider the one-electron Schrödinger equation

$$-(\hbar^2/2m)\nabla^2 \Psi_{nk} + U \Psi_{nk} = E_{nk} \Psi_{nk}, \quad (\text{A10})$$

where  $U$  is the modified APW potential in which the muffin tin potentials have been displaced. We expand all quantities in powers of the lattice displacements and

We visualize the problem from a scattering point of view. It is known that the outgoing scattered wave is given by

$$\Psi_{nk} = \Psi_{nk}^0 + \sum_{n', \mathbf{k}'} \frac{T(n', \mathbf{k}'; n, \mathbf{k})}{E_{nk}^0 - E_{n'k'}^0 + i\delta} \Psi_{n'k'}^0, \quad (\text{A2})$$

where  $T$  is the appropriate transition matrix. We now define the electron-phonon matrix element as

$$\mathfrak{M}(n', \mathbf{k}'; n, \mathbf{k}) = (E_{nk}^0 - E_{n'k'}^0) M(n', \mathbf{k}'; n, \mathbf{k}). \quad (\text{A3})$$

This is seen to be just that part of the  $T$  matrix linear in phonon coordinates.

The unperturbed conduction-electron wave function is written as

$$\Psi_{nk}^0 = \sum_{\mathbf{K}} A_n^0(\mathbf{k}, \mathbf{k} + \mathbf{K}) \varphi_{\mathbf{k} + \mathbf{K}}^0, \quad (\text{A4})$$

where  $\varphi_{\mathbf{k}}^0$  is the APW basis function for the unperturbed lattice and  $\mathbf{K}$  is a reciprocal lattice vector.  $\Psi_{nk}^0$  is a periodic function and thus only APW basis functions differing by a reciprocal lattice vector are included in the sum. In the perturbed case we have

$$\Psi_{nk} = \sum_{\mathbf{K}} A_n(\mathbf{k}, \mathbf{k} + \mathbf{K}) \varphi_{\mathbf{k} + \mathbf{K}} + \sum_{\mathbf{k}' \neq \mathbf{k} + \mathbf{K}} A_n(\mathbf{k}, \mathbf{k}') \varphi_{\mathbf{k}'}, \quad (\text{A5})$$

where  $\varphi_{\mathbf{k}}$  is the APW basis function for the distorted lattice. Expanding all factors in powers of the ion displacements and retaining only linear terms, we obtain

examine the equation relating first-order quantities, namely,

$$\mathfrak{H}^0(\theta_{nk} + \zeta_{nk}) + U' \Psi_{nk}^0 = E_{nk}^0(\theta_{nk} + \zeta_{nk}). \quad (\text{A11})$$

where

$$\mathfrak{H}^0 = -(\hbar^2/2m)\nabla^2 + U^0, \quad (\text{A12})$$

$$\mathfrak{H}^0 \Psi_{nk}^0 = E_{nk}^0 \Psi_{nk}^0, \quad (\text{A13})$$

and

$$U' = \sum_j \delta \mathbf{R}_j \cdot (\partial U / \partial \mathbf{R}_j) |_{\mathbf{R}_j = \mathbf{R}_j^0}. \quad (\text{A14})$$

We now write

$$\theta_{nk} = \sum_{n'k'} b(n', \mathbf{k}'; n, \mathbf{k}) \Psi_{n'k'}^0, \quad (\text{A15})$$

where the sum includes only conduction-electron states. Then

$$M(n', \mathbf{k}'; n, \mathbf{k}) = b(n', \mathbf{k}'; n, \mathbf{k}) + \langle \Psi_{n'k'}^0 | \zeta_{nk} \rangle \quad (\text{A16})$$

and we proceed to find  $b(n', \mathbf{k}'; n, \mathbf{k})$ . From (A11) we have

$$(\mathfrak{E}^0 - E_{n\mathbf{k}}^0)\theta_{n\mathbf{k}} = (E_{n\mathbf{k}}^0 - \mathfrak{E}^0)\zeta_{n\mathbf{k}} - U'\Psi_{n\mathbf{k}}^0. \quad (\text{A17})$$

Taking the scalar product with  $\Psi_{n'\mathbf{k}'^0}$  gives

$$(E_{n'\mathbf{k}'^0} - E_{n\mathbf{k}}^0)b(n', \mathbf{k}'; n, \mathbf{k}) = (E_{n\mathbf{k}}^0 - E_{n'\mathbf{k}'^0})\langle \Psi_{n'\mathbf{k}'^0} | \zeta_{n\mathbf{k}} \rangle - \langle \Psi_{n'\mathbf{k}'^0} | U' | \Psi_{n\mathbf{k}}^0 \rangle, \quad (\text{A18})$$

or

$$b(n', \mathbf{k}'; n, \mathbf{k}) = -\langle \Psi_{n'\mathbf{k}'^0} | \zeta_{n\mathbf{k}} \rangle + \frac{\langle \Psi_{n'\mathbf{k}'^0} | U' | \Psi_{n\mathbf{k}}^0 \rangle}{E_{n\mathbf{k}}^0 - E_{n'\mathbf{k}'^0}}. \quad (\text{A19})$$

Substituting the expression into (A16) and using (A3), we have

$$\mathfrak{M}(n', \mathbf{k}'; n, \mathbf{k}) = \langle \Psi_{n'\mathbf{k}'^0} | U' | \Psi_{n\mathbf{k}}^0 \rangle. \quad (\text{A20})$$

The effect of the core motion is identically cancelled out. This is seen to be consequence of the first-order perturbation nature of the argument which in turn is a consequence of the phonon approximation. There is no communication among the two scattered states and the other states as would occur in higher order.

## Evidence for Interstitial Cobalt in Indium by Mössbauer Spectroscopy

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The Mössbauer effect for  $\text{Fe}^{57}$  in indium was measured from helium temperature to near the melting point. Contrary to a previous report, we found no evidence for large anharmonic effects. The high Debye-Waller factor indicates interstitial solution of  $\text{Co}^{57}$  in indium metal.

IN the early period of Mössbauer investigations, the resonance effect for  $\text{Fe}^{57}$  believed to be dissolved in indium was investigated<sup>1,2</sup> and an anomalous result reported: The Debye-Waller factor was quite small ( $\approx 0.5$ ) at low temperature, and showed very little temperature dependence over the temperature range from near absolute zero to the melting point of indium. Since this result has been widely accepted and quoted as evidence for extreme anharmonic behavior,<sup>3</sup> we felt it desirable to reinvestigate the question. Our results, in contrast to the original ones, show a normal tempera-

ture dependence for the Debye-Waller factor, and hence no indications of large anharmonicity. The large Debye-Waller factor at elevated temperature is consistent with the assumption that the cobalt (and its daughter iron) are in interstitial positions in indium.

Since the solid solubility of iron and cobalt<sup>4</sup> in indium is extremely small (not measurable by conventional methods), the Mössbauer effect can be studied only by a "source" experiment, i.e., by dissolving carrier-free  $\text{Co}^{57}$  in indium and studying the  $\gamma$  rays of the  $\text{Fe}^{57}$  arising from the decay of the  $\text{Co}^{57}$ . To ensure that the  $\text{Co}^{57}$  was indeed in solution, we used a method of preparation different from that of the original investigators.  $\text{Co}^{57}$  was electroplated onto an indium foil, which was then compacted and heated to  $900^\circ\text{C}$  in hydrogen to ensure reduction of any oxide and the formation of a homogeneous liquid solution.<sup>5</sup> The sample was then cooled quickly, and again converted to foil by compression between steel plates followed by cold rolling. The ratio of 14-keV  $\gamma$  rays to  $\text{Fe} K$  x rays was consistent with the assumption that the cobalt was indeed homogeneously distributed through the material.

The Mössbauer spectrum observed for this source ( $\text{Co}^{57}$  in indium at  $80^\circ\text{K}$ ) versus a quadrupole-split absorber of  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$  at room temperature is shown in Fig. 1. From the spectrum the following values can be deduced: isomer shift  $\delta = -0.91 \pm 0.01$  mm/sec and quadrupole splitting (peak separation) for

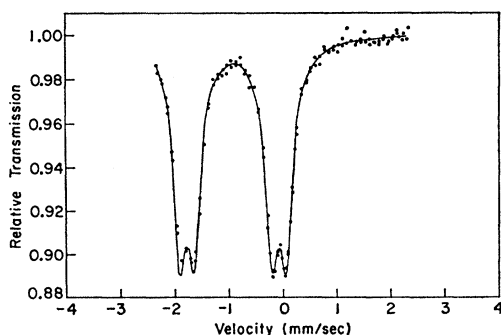


FIG. 1. Mössbauer absorption spectrum of a  $\text{Co}^{57}$  in In source at  $80^\circ\text{K}$ , and an absorber of  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$  at room temperature.

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<sup>5</sup> The  $\text{Co}^{57}$ -In source was prepared by Nuclear Science and Engineering Corporation, Pittsburgh, Pennsylvania.