Philos. Mag. **7**, 115 (1962).

[9] Our measurements here, as well as those of others, show that in Ag the value of p lies between 0.5 and 1 [see, e.g., K. L. Chopra, *Thin Film Phenomena* (McGraw-Hill, New York, 1969), table on p. 369]. We have, therefore, used $p = 0.7$ as an average value since the extraction of grain-boundary-scattering information does not require an exact value for p. We need p for two reasons here: (i) to determine l_0 and (ii) to subtract off the Fuchs size effect for the twinned sample. For (i) above, an exact value of p is not required since l_0 is very large and does not affect the final result in a significant way; for (ii), the size-effect resistivity is very small if $p = 0.5$ since other scattering mechanisms are so strong, and again the final result is only weakly dependent on p.

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Self-Consistent Screening in a Simple Model*

J. Rudnick and E. A. Stern

Department of Physics, University of Washington, Seattle, Washington 98195

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The self-consistent screening of a charged impurity by conduction electrons in a simple cubic metal is calculated in the tight-binding approximation. In order to satisfy screening it is not sufficient to add to the impurity-site potential an impurity-induced hopping perturbation, rather, perturbations on neighboring lattice sites must also be included. If the impurity potential is truncated a few lattice sites away from the impurity, the self-consistent Hartree screening problem can be reduced to a small set of simultaneous equations which can be solved numerically. Using techniques developed by Callaway and by Mann, Seeger, and co-workers, calculations are performed of the residual resistivity and specific heat of a dilute alloy for a set of self-consistent screening parameters. In addition, the forward-scattering amplitudes of electrons on the Fermi surface are calculated. The results show significant numerical differences from the non-self-consistent highly localized potential model used in current coherent-potential-approximation calculations of the properties of disordered binary alloys. The conclusion is that quantitatively accurate calculations of disordered alloys must include screening contributions to the potential. Predictions concerning the range of validity of the forward-scattering approximation introduced by Stern are also discussed. In addition, it is discovered that a new approximation, representing a hybrid between first-order perturbation theory and the highly localized potential model, can adequately describe self-consistent screening of the charged impurity investigated here.

I. INTRODUCTION

It has recently been shown that in the calculation of properties of disordered systems, the shielding requirement places a restriction on the random potential.[1] When applied to a model which has played a central role in the development of the coherent-potential approximation (CPA), the shielding restriction indicates that this localized-perturbation model is not applicable to real systems. Because this CPA model has been utilized with great expectations as the model that can explain the properties of real transition-metal alloys it is very important to pursue the implications of this shielding restriction further. Although the localized-perturbation model cannot satisfy the shielding restriction and remain physically interesting, it is still possible that by appropriately choosing the random potential, even though it violates the shielding restriction, the quantitative error made would not be serious. If such is the case then the shielding restriction, though physically correct, in practice would be of only academic interest. The purpose of this paper is to investigate numerically the implications of the shielding restriction and to determine whether it is quantitatively important. We find that, in general, the shielding requirement is quantitatively important.

In calculations of the effective potential of a localized impurity by the conduction electrons in a metal two approximations are commonly used. In the first, the density perturbation caused by the impurity is taken to be small relative to the unperturbed electron-gas density. In such a case, the response of the metal is accurately described by first-order perturbation theory. In a good many systems such an approximation greatly simplifies the solution of the self-consistent screening problem.[2] However, the large density perturbation in the immediate vicinity of the impurity generally causes the approximation to break down in that region. An example of such a breakdown will be exhibited explicitly later on in this paper. The second approximation, the localized-perturbation model, replaces the impurity potential by an effective δ function. The exact response to such a potential can be readily calculated, if the potential is assumed known and not calculated self-consistently. The approximation has been used to great advantage on CPA calculations of the properties of disordered binary alloys.[3,4] It has been pointed out, however,[1,5] that such a potential cannot be made self-consistent and yield perfect screening of a charged impurity via the Friedel sum rule.[6]

A third approximation has been introduced by Stern[7] as a generalization of perturbation theory. In it, the approximate single-electron eigenstates are taken to be Bloch states with an energy shifted from their unperturbed energy by the forward part of the scattering amplitude. Scattering out of the Bloch states is treated as a small perturbation. This forward-scattering approximation (FSA) is expected to be valid when the impurity potential is slowly varying in space. The validity of the FSA will be discussed later on.

A fourth approach that has proven very fruitful will be the one used in this paper. In this approach the impurity potential in the Wannier representation is taken to extend only a finite number of lattice sites beyond the central impurity site. Techniques for solving the shielding problem in such a model have been developed by Callaway[8] and Mann.[9] The techniques have been extended by Mann, Seeger, and co-workers to yield the transport properties of dilute alloys, such as the residual resistivity and thermoelectric power,[9,10] and the magnetoresistivity.[10–12] The attractive feature of the impurity potential of finite extent is that the scattering equation can be solved exactly without too much effort. A shortcoming of the model is that it neglects the long-range oscillations in the impurity potential associated with the Friedel oscillations[6] in the screening-charge cloud; aside from that, though, it should be a reasonably accurate representation of the strongly screened impurity potential. Further applications of this model are to the scattering of phonons[13] and spin waves[14] by localized imperfections, the problem of excitons in metals,[15] the magnetic properties of transition-metal alloys[16] and the response to impurities in semiconductors.[17]

One other approximation will also be discussed in this paper. In this approximation the scattering of the conduction electrons by the impurity potential on the site of the impurity is calculated to all orders in perturbation theory while the scattering on all other sites is calculated only to first order in perturbation theory and scattering both from the impurity site and a neighboring site is neglected. This approximation takes into account the long-range oscillations in the impurity potential and is correct to all orders in perturbation theory where the potential is strongest. Furthermore the approximation will be shown to give results close to those of the fourth approximation. In Appendix B the self-consistent screening equation in this model will be developed. An analogous approximation has been used recently in treating the effect of impurities on the phonon spectrum.[18]

An outline of the paper is as follows: In Sec. II the truncated-potential model (the fourth approximation mentioned above) will be presented, along with some results that can be obtained exactly in the model. The screening process will be discussed in detail, particularly with regard to the self-consistency of the screening potential. Parameters relating the impurity potential on a lattice site and the charge imbalance on that and neighboring sites will be introduced.

Section III presents the results of calculations. The screening charge and the impurity-potential strengths on the sites nearest a charged impurity are plotted versus a parameter describing the difference between the atomic energy of the impurity and the host atoms. The potential strengths are inserted into the equations for the total screening charge given by the various approximations mentioned in the introduction. The other approximations are discussed in terms of their accuracy in reproducing the results of the truncated-potential approximation. The residual resistivity and the change in specific heat of a dilute alloy in our model are also plotted in this section. It will be found that the residual resistivity is smallest when the impurity potential is smoothest. The specific heat will be compared to the rigid-band model and localized-perturbation model. A sensitive dependence on screening parameters will be found, contrary to predictions of the rigid-band model. The real and imaginary parts of the forward-scattering amplitude from the impurity potential will also be graphed. It is found that the FSA is most nearly correct when the potential is most spread out.

II. SCREENING MODEL

We shall treat the conduction electrons in a metal in the tight-binding approximation. Although this approach is by no means rigorous, the results we shall obtain can also be obtained by working in the Wannier representation.[8–9] What we are doing is making the approximation of neglecting interband matrix elements of the perturbing potential. On the other hand, the single band in the tight-binding approximation approximates the isolation of the conduction band from higher bands in noble metals, and we should thus obtain a not too unreasonable description of the screening of negatively charged impurities in noble metals.

The electrons are furthermore assumed to propagate in a simple-cubic lattice. This lattice, although it does not occur in pure metals, simplifies the calculation of Green's functions and has a reasonable looking density of states. We are in any case interested in quantitative comparisons within a given model with the CPA localized-perturbation model, and not to real systems. For the unperturbed Hamiltonian we assume the following:

$$H_0 = -\frac{W}{12} \sum_{n,n'}{}' a_n^\dagger a_{n'} \quad , \tag{1}$$

where a_n is the annihilation operator for an atomic orbital on the nth site. The prime on the summation indicates that it is restricted to nearest-neighbor sites. The band is centered at zero energy and its full width is W.

The eigenfunctions of H_0 are of the form

$$\Phi_{\vec{k}}(\vec{r}) = \sum_n e^{i\vec{k}\cdot\vec{R}_n} \psi(\vec{r} - \vec{R}_n) , \tag{2}$$

where $\psi(\vec{r} - \vec{R}_n)$ is the atomic orbital associated with the nth site and $\vec{R}_n$ is the position of the site. We have

$$\begin{aligned} H_0 \Phi_{\vec{k}} &= E(\vec{k}) \Phi_{\vec{k}} \\ &= -[\tfrac{1}{6} W(\cos k_x a + \cos k_y a + \cos k_z a)] \Phi_{\vec{k}}, \end{aligned} \tag{3}$$

where a is the interatomic spacing of the lattice. For convenience we can take $a = 1$. It is clear that in this model an electron wave function is completely specified by amplitudes associated with the various atomic orbitals. Similarly, the single-electron Green's function in coordinate space is completely described in terms of amplitudes associated with pairs of site indices. Because H_0 is invariant under any displacement that takes the crystal into itself (we neglect surface effects), the Green's function for H_0 will depend only on the relative positions of the two sites.

In the presence of a perturbing potential V, the Green's function is given by

$$\begin{aligned} G(E) &= (E - H_0 - V - i\delta)^{-1} \\ &= g(E) + g(E) V G(E); \end{aligned} \tag{4}$$

here

$$g(E) = (E - H_0 - i\delta)^{-1}$$

The site indices have been suppressed; they will be restored whenever it is found necessary or particularly useful. The infinitesimal $i\delta$ assures that the Green's function is causal. The last of equations (4) is Dyson's equation for the Green's function. Replacing $G(E)$ on the right hand side of (4) by $G_0(E)$ gives the solution of the equation to first order in the potential V.

A useful operator associated with the Green's function is the scattering or T matrix $T(E)$, which is defined by

$$T(E) = V + V g(E) T(E) \tag{5a}$$

or, from (4)

$$G = g(E) + g(E) T(E) g(E) \quad . \tag{5b}$$

An attractive property of $T(E)$ in our model is that it has matrix elements only between sites on which V has a nonzero projection. If V is taken to have matrix elements between a finite number of sites, therefore, there will exist only a finite number of matrix elements $T_{n,n'}(E)$, expressed in terms of each other and V and $g(E)$ through Eq. (5a). $T(E)$ is then obtained as a solution of a finite set of linear simultaneous equations. Equation (5b) then yields $G(E)$ immediately.

Knowing the Green's function we can find the change in the conduction-electron density at a given site due to the impurity potential, for we have

$$\rho_n = (2/\pi) \int_{-\infty}^{E_F} \mathrm{Im}\,[G_{n,n}(E)]\,dE \ , \tag{6}$$

where ρ_n is the conduction electron density on the nth site and E_F is the Fermi energy. We have multiplied by a factor of 2 to take account of spin. Equation (6) can be proved by expanding $G(E)$ in eigenfunctions of the full Hamiltonian.

We also obtain, by expanding $G(E)$ in terms of eigenfunctions $|j\rangle$ of the full Hamiltonian,

$$\begin{aligned} G_{n,n'}(E) &= \sum_j \frac{\langle n|j\rangle\langle j|n'\rangle}{E - E_j - i\delta} \\ &= \frac{\partial}{\partial E} \sum_j \langle n|j\rangle\langle j|n'\rangle \ln(E - E_j - i\delta) \\ &= -\frac{\partial}{\partial E} \langle n| \ln G(E) |n'\rangle \ . \end{aligned} \tag{7}$$

If we subtract from (6) the corresponding expression for the conduction-electron density in the unperturbed metal, sum over sites and use the relation

$$\mathrm{Tr}(\ln A) = \ln[\det(A)] \ , \tag{8}$$

where A is any matrix, we obtain

$$\begin{aligned} \sum_n \delta\rho_n &= \sum_n (\rho_n - \rho_n^{(0)}) \\ &= \frac{2}{\pi} \mathrm{Im}\left(\int_{-\infty}^{E_F} \frac{\partial}{\partial E} (\ln\{\det[g(E)]\} \right. \\ &\qquad \left. - \ln\{\det[G(E)]\}) dE \right) \qquad (9) \\ &= -\frac{2}{\pi} \mathrm{Im}\left\{ \ln\left[\det\left(\frac{G(E_F)}{g(E_F)} \right) \right] \right\} \\ &= \frac{2}{\pi} \mathrm{Im}(\ln\{\det[1 - g(E_F)V]\}). \end{aligned} \tag{10}$$

In going from the second to the third line of (10) we used the solution of (4), $G(E) = [1 - g(E)V]^{-1} g(E)$. The last line of (10) is a generalization of the Friedel sum rule. We note that if the matrix $1 - g(E)V$ is in the site representation and V is truncated then finding the determinant requires evaluating a finite number of terms.

We now make the simplifying assumption that the impurity potential has the equivalent of full rotational symmetry about a central ionic site. In particular, what we assume is that any rotation or rotation plus inversion about that site that takes the lattice into itself leaves the potential unchanged. Such symmetry, of course, is only characteristic of nonmagnetic impurities.

The Green's function and the T matrix can then be reduced in terms of irreducible representations of the point-symmetry group of the crystal.[8,19] The simplifications effected by such a reduction are substantial and are developed in detail by Mann, Seeger *et al.*,[9-12] and by Callaway.[8] For the purposes of this paper a brief description will suffice.

A useful orientation is gained by noting that the reduction of operators just described is the analogue of reducing the same operators in terms of angular momentum eigenstates in a isotropic system with a spherically symmetric potential. In the crystal case, however there are only a finite number of irreducible representations (10 for a cubic crystal) as opposed to an infinite number of possible angular momenta in the isotropic system. An equation in close correspondence with the Friedel sum rule can be obtained from Eq. (10) by reducing the matrix $1-g(E)V$. One obtains

$$\sum_n \delta\rho_n = -\frac{2}{\pi}\sum_{\Gamma_l} n_{\Gamma_l}\delta_{\Gamma_l}(E_F) , \tag{11}$$

where n_{Γ_l} is the dimension of the irreducible representation Γ_l (we use the notation of Bouckaert, Smolouchowski, and Wigner[20]) and $\delta_{\Gamma_l}(E)$ is the imaginary part of $\ln\{\det[1-G(E)V]\}$ corresponding to the Γ_l representation divided by n_{Γ_l}. We obtain in a similar fashion for the change in the density of states at the Fermi energy

$$\delta\sigma(E_F) = -\frac{N}{V}\,\frac{2}{\pi}\sum_{\Gamma_l} n_{\Gamma_l}\left.\frac{d\delta_{\Gamma_l}(E)}{dE}\right|_{E=E_F} , \tag{12}$$

where N is the number of impurities (in the dilute limit) and V is the volume of the crystal. Finally we note that the residual resistivity, as well as the other transport properties mentioned in the introduction, can be found using methods outlined by Mann.[10] For an impurity potential extending to the six nearest neighbors of a central impurity site one has to solve three simultaneous linear equations to obtain the resistivity, and for a potential extending to the twelve next-nearest neighbors one must solve fifteen such equations.[21]

We now require that the impurity potential be self-consistent with respect to the electron-electron interactions. A simple self-consistency requirement is that the total charge in the screening cloud be equal to minus the impurity charge. An equation embodying that requirement is obtained by substituting on the left-hand side of either Eq. (10) or (11) minus the charge on the impurity. The equation neglects the effects of the distortion induced in the ionic lattice by the impurity. Blatt[22] has estimated that distortion effects can reduce by up to 47% (Cd in Cu) the effective charge of an impurity with a valence one greater than the host as seen by the conduction electrons in a noble metal. Such an effect is beyond the scope of our work, but should be kept in mind when the results are applied to real situations.

The impurity potential in the Wannier representation will, in general, have diagonal and off-diagonal terms. The diagonal terms represent perturbations in the atomic energies and the off-diagonal terms represent perturbations in the hopping terms induced by the impurity. In the localized-perturbation model of the CPA the impurity perturbation is a single diagonal term on the impurity site. This simplest of potentials is not adequate when the screening requirement is added.[1] The next addition to the localized-perturbation model might be to add a perturbed hopping term to the nearest neighbors. As discussed in Appendix A this is also not adequate to satisfy screening. The minimum requirement to satisfy screening is to add perturbed diagonal terms to the neighboring atoms of the impurity. Since a perturbed hopping term does not aid in satisfying screening but adds another parameter, we simplify our model by assuming that the impurity potential is diagonal in the Wannier representation, i. e., it will contain no "hopping" terms such as those in the summation in Eq. (1). Furthermore, it will be truncated beyond the next-nearest neighbors to the central impurity site.

The potential will be nonzero on 19 sites. Because of the cubic symmetry of the surrounding lattice it will be described completely by three parameters: its strength on the central site, on a nearest neighbor, and on a next-nearest neighbor. The Friedel sum rule provides one relationship between the three potential strengths, so we only need two more self-consistency conditions to completely determine the impurity potential. The two we have chosen are

$$\begin{aligned} V_0 &= E_0 + \frac{\Delta_0}{e}\,(Q+\delta\rho_0) + \frac{\Delta_1}{e}\sum_{l\neq 0}\frac{\delta\rho_l}{|\vec{R}|} , \\ V_1 &= \frac{\Delta_0}{e}\,\delta\rho_1 + \frac{\Delta_1}{e|\vec{R}_1|}\,(Q+\delta\rho_0) + \frac{\Delta_1}{e}\sum_{l\neq 0,1}\frac{\delta\rho_l}{|\vec{R}_l-\vec{R}_1|} , \end{aligned} \tag{13}$$

where V_0 is the impurity potential on the central site and V_1 is the potential on a nearest neighbor. E_0 describes the difference between the atomic character of the impurity and the host atoms, and Δ_0 and Δ_1 are Hartree-like parameters[23] giving the potential energy on a site in terms of the charge imbalance on that and neighboring sites, respectively.

Δ_0 and Δ_1 should not be too large because it is known that for too strong a Coulomb interaction the ground state will be a spin ordered one, fundamentally different from the ground state in which we are interested.[24] We have chosen $\Delta_0/W=\frac{1}{3}$ and $|\vec{R}_1|\Delta_0/$

$\Delta_1 = 2.67$. The first ratio is significantly less than the "Hubbard ratio" that leads to ferromagnetic ordering of conduction electrons in a model similar to this one. The second ratio was chosen to satisfy the requirement that the potential energy be the same on both the central site and on the nearest neighbors due to a charge imbalance on the nearest neighbors. This requirement is what one obtains for spherical symmetry. With spherical symmetry any charge unbalance is in the form of a spherical shell. Such a shell contributes a potential which is constant on the shell and within it. In our simple-cubic lattice we do not of course have spherical symmetry but the potential for a given charge unbalance with the cubic lattice symmetry would not deviate greatly from that expected for spherical symmetry—hence the chosen ratio for Δ_0/Δ_1 to eliminate an additional parameter from the model.

Our calculations were for a half-filled band. There was therefore in the unperturbed metal one electron per atomic site. To simplify calculations, the impurity was taken to have one unit less of positive charge (rather than one unit more of positive charge) than the host atoms. The screening potential was then basically repulsive and no bound state was formed (except possibly for hole bound states above the top of the band). Because electron bound states lead to no special behavior in the electron gas,[25] except in the density of states below the bottom of the band, no important information was lost. The symmetry of the model allowed us to extract results for an impurity of plus a positive charge; all results in the next section will be for the latter case.

III. RESULTS AND DISCUSSION

The impurity-potential strengths and the conduction electron screening charge on the sites in the immediate vicinity of the impurity are plotted versus E_0/W, where W is the bandwidth, in Figs. 1 and 2, respectively. Also shown for comparison are the corresponding values for the localized-perturbation model (denoted by δ_{fun}). A useful result indicated by Fig. 1 is that the potential on the nearest- and next-nearest-neighbor sites is small enough to be treated by first-order perturbation theory. The same is not true of V_0, the potential strength on the impurity site. The change in sign of the screening-charge density from the impurity site to the nearest neighbor for $E_0/W \gtrsim 0.08$ is the first wiggle in the Friedel oscillations of the screening-charge density. Because of our truncation of the potential we cannot assess the self-consistent effect of that wiggle on the screening potential with any degree of certainty. Note that the localized-perturbation model is not self-consistent, nor can it be made so. By definition the potential perturbation is only on the impurity site yet charge perturbations exist on the neighboring atoms as shown in Fig. 2. Also shown in Fig. 2 are the charge distributions if the localized perturbation model is used, but the value of the potential on the impurity site is given by the self-consistent truncated model. In other words the value V_0 determined from the truncated self-consistent is used as the perturbing potential for the localized perturbation model in place of E_0. The charge on the impurity site is accurately given, in this case, by the localized-perturbation model but not for the neighboring sites. It is important to emphasize that using V_0 instead of E_0 is outside of the scope of the localized-perturbation model. V_0 is determined self-consistently and differs from E_0 because of the self-consistent potential induced by the charge distribution. It is impossible to calculate V_0 within the localized-perturbation model since this model cannot be treated self-consistently. However, the use of V_0 in the localized perturbation model and the close agreement for ρ_0 with the self-consistent theory has implications for the validity of the hybrid model discussed further on and in Appendix B.

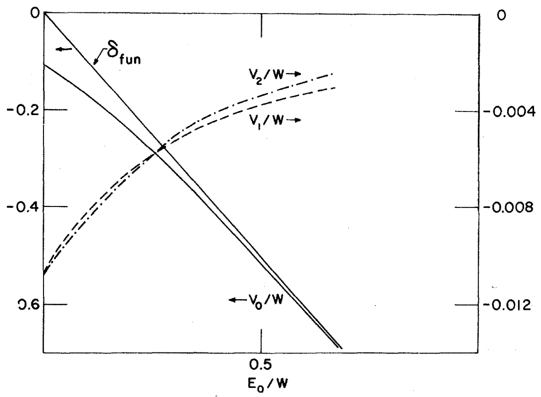

FIG. 1. Impurity potential in the immediate vicinity of an impurity of plus one unit of positive charge solved for self-consistently and plotted as a function of E_0. V_0 is the potential on the impurity site. V_1 and V_2 are the potentials on the nearest- and next-nearest-neighbor sites, respectively. W is the bandwidth. Also shown is the value of $V_0 = E_0$ for the localized-perturbation model, labeled by δ_{fun}. In this model both $V_1 = V_2 = 0$.

In Fig. 3 are plotted the total screening charge predicted by the various approximations discussed in the introduction.[26] A shielding charge of 1.0 represents the correct shielding. The curve denoted δ_{fun} is the localized-perturbation model. This model never completely shields the impurity. The curve denoted FSA is that calculated by the FSA to first order which is, in this case, formally the same as first-order perturbation theory, because the energy shift introduced by the single impurity is negligible. We note that the FSA gives correct shielding only when $E_0/W \simeq 0$. In that case we note

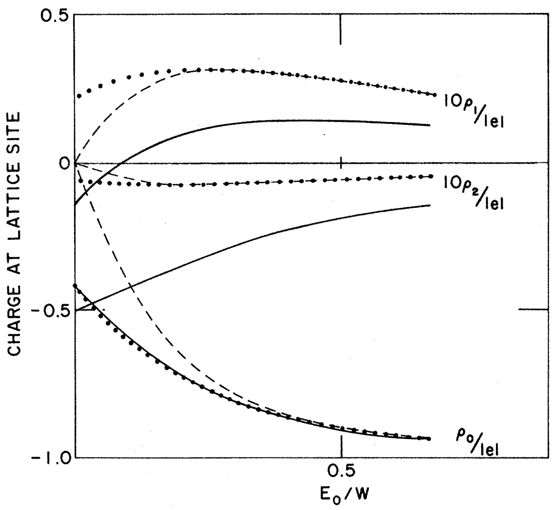

FIG. 2. Conduction-electron screening charge in the immediate vicinity of the impurity. ρ_0 is the change in the conduction-electron charge on the impurity site. ρ_1 and ρ_2 are the changes on the nearest- and next-nearest neighbor sites, respectively. The solid curves are the results for the truncated self-consistent model. The dashed curves are the results for the δ_{fun} model (localized-perturbation model). The dotted curves are the results of the localized-perturbation model if the self-consistent potential V_0 is used in place of E_0.

that $V_0/W = -0.11$ and V_1 and V_2 are much smaller. The expansion parameter of perturbation theory for the impurity site is in this case $(6V_0/W)I(E_F) = 0.6$. Here $I(E_F)$ is the imaginary part of $\frac{1}{6} W g_{00}(E_F)$ and is plotted in Fig. 8 as a function of E. This is not a small parameter and it is difficult to understand why the result is accurate to 2% viewed from ordinary perturbation theory. Viewed from the FSA, the expansion parameter is x^2, the ratio of the imaginary part of the energy shift to the real part—both terms have been plotted in Fig. 4. Near $E_0/W = 0$ this ratio has the value of 0.17 which is small and explains the good agreement of FSA curve there. The FSA deviates 20% from the correct shielding value when $x^2 = 0.44$, and the ordinary perturbation theory expansion parameter is 1.1—clearly too large to be applicable. It is of interest to note that at $E_0 = 0$, the potentials totaled over the six nearest neighbors and then twelve next-nearest neighbors are about the same as that on the impurity site, i.e., $6V_1/W = -0.065$, and $12V_2/W = -0.12$. The potential is appreciably spread out compared to the Fermi wavelength or lattice spacing, causing the scattering of an electron at the Fermi surface to be mainly in the forward direction. In this case the parameter x^2 is expected to be small[7] as found explicitly for this model. Finally plotted in Fig. 3 as FUN is the total screening charge obtained by using the FSA expression to first order but replacing the potential by the real part of the energy shift. These results agree with the FSA near $E_0/W = 0$ and do not deviate as much from the correct value at higher values of E_0/W. However, there is no physical justification for the FUN approximation.

The highly localized potential model, labeled δ_{fun} in Fig. 3, assumes that the impurity potential is zero except on the central site. The total screening charge predicted when that approximation is made in Eq. (10) or (11), as plotted on Fig. 3, is a consistent underestimate of the correct value. The prediction becomes more nearly correct as the potential becomes more concentrated on the central site, although for the range of the parameter E_0 that we have taken it is never greater than 83% of the screening charge.

In sharp contrast to the above, the hybrid approximation, described in Appendix B, gives the

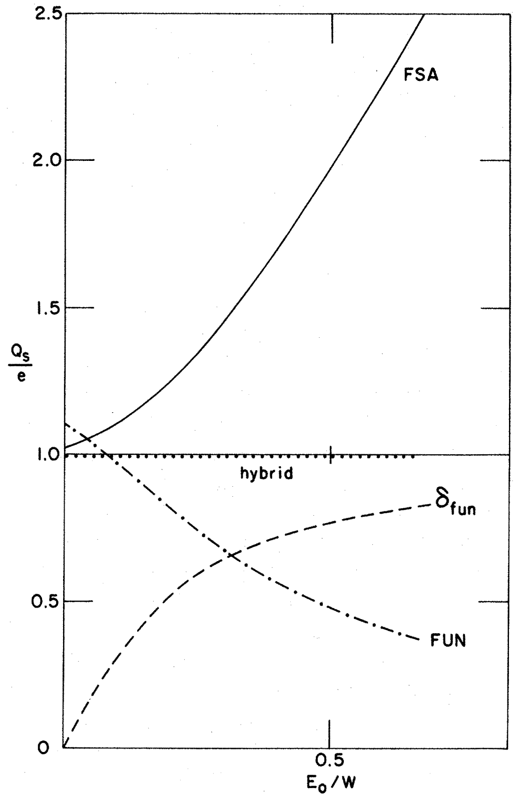

FIG. 3. Total screening charge as given by various models. For perfect screening the result should be 1.0 for all values of E_0/W. This result is obtained for the self-consistent truncated model shown by the horizontal line through 1.0. The hybrid model results are shown by the dotted curve. The forward-scattering approximation result to first order is shown by the curve labeled FSA. The localized-perturbation model results of the CPA are shown by the dashed curves labeled δ_{fun}. The results denoted by the dashed-dot curve and labeled by FUN are those obtained from the real part of the energy shift substituted in the expression for the FSA in place of the potential.

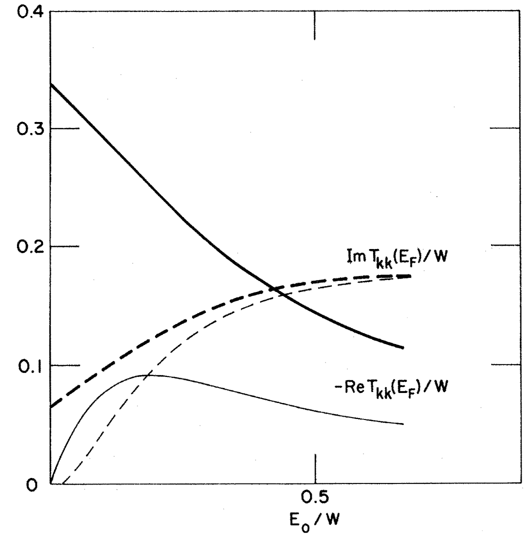

FIG. 4. Real (solid curves) and imaginary (dashed curves) parts of the forward scattering amplitude at the Fermi energy. These are proportional to the real and imaginary parts, respectively, of the energy shift caused by alloying to first order in the concentration. The thick curves are for the self-consistent truncated model while the thin curves are for the localized-perturbation model of the CPA.

total screening charge to within better than 1% for the entire range of E_0. The hybrid model is correct to all orders in strength on the central site and to first order in the rest of the potential, except for scattering terms coupling the central and neighboring sites. Although to obtain the results for the hybrid approximation in Fig. 3 the potential strengths obtained from the truncated potential approximation were used, one can solve a self-consistent screening completely within the hybrid model, including an impurity potential without truncation. The equation and its formal solution are developed in Appendix B.

We note in Fig. 4 that the $\mathrm{Im}T_{kk}(E_F)$ is accurately given in the localized perturbation model when $E_0/W \gtrsim 0.5$. However, the $\mathrm{Re}T_{kk}(E_F)$ is never given accurately by the localized-perturbation model. This is a direct consequence of the neglect of the potentials outside of the impurity site.

The residual resistivity due to a dilute concentration of impurities is plotted in Fig. 5. The impurity potential at the next-nearest neighbors was neglected to simplify the calculation though including it should not change the result by much since the neglected potential gives negligible large angle scattering. The rise in the resistivity with the increasing potential at the central site is due to the increase in s-like scattering by the impurity at the expense of higher-angular-momentum-type terms[27] as the potential becomes more strongly peaked.

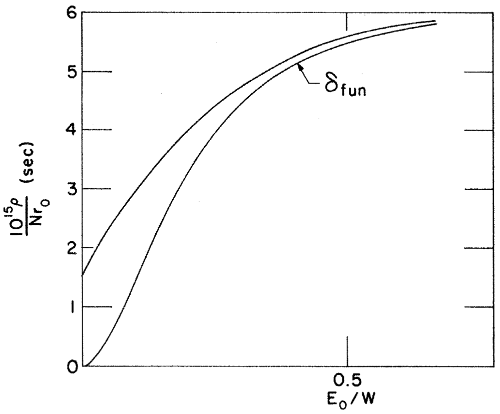

FIG. 5. Residual resistivity ρ due to a dilute concentration of impurities, divided by the number of impurities N and by r_0, the interatomic spacing in units of the Bohr radius. The curve labeled δ_{fun} is for the localized-perturbation model of the CPA while the other curve is for the self-consistent truncated model.

The scattering phase shifts for the various irreducible representations are shown in Fig. 6.

We note that the resistivity for the localized-perturbation model, denoted by δ_{fun}, differs from that of the self-consistent model mainly for small values of E_0/W. Most of this variation is caused by the difference in the impurity potential introduced by self-consistency, i.e., the difference between V_0 and E_0 in Fig. 1. If the potential at the impurity site is assumed to be V_0 in place of E_0 for the lighly localized model, close agreement with the self-consistent model is found. This is be-

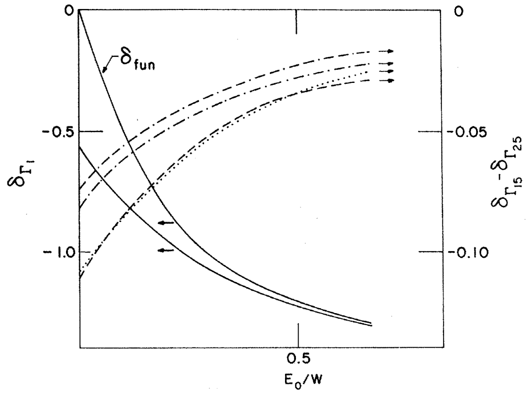

FIG. 6. Scattering phase shifts associated with the impurity potential. The correspondence between the curves and the phase shifts is as follows: δ_{Γ_1}, solid line; $\delta_{\Gamma_{12}}$, dashed line; $\delta_{\Gamma_{25}}$, double-dashed—dot line; $\delta_{\Gamma_{15}}$, dashed-dot line; $\delta_{\Gamma_{25'}}$, dotted line. The curve labeled δ_{fun} is for the localized-perturbation model of the CPA. The other curves are for the self-consistent truncated model. The localized-perturbation model has only one phase shift δ_{Γ_1}.

cause the resistivity is dominated by the s-wave scattering coming from the impurity site.

Figure 7 shows the logarithmic derivative of the low-temperature electronic specific heat with respect to the concentration of impurities for a dilute concentration. The prediction of the rigid band model is that it should be proportional to the energy derivative of the density of states, independent of screening parameters. The density of states in our model has a zero derivative on the middle of the band, so our result is in clear contradiction to that prediction. It is useful to note in this respect that experiments on dilute noble metal alloys[28] also disagree with the prediction of the rigid-band model. The hybrid model here is, at its worst, off by only slightly more than 1%.

As in the case for resistivity, the difference in Fig. 7 between the localized-perturbation model and the self-consistent model is mainly caused by the difference between E_0 and the self-consistent V_0. In this particular case V_1 and V_2 do not contribute to the γ changes because the derivative of the unperturbed density of states at E_f is zero. In the more general case where the derivative of the unperturbed density of states is nonzero, V_1 and V_2 do contribute to γ and the full self-consistent problem must be solved for quantitative results. The localized-perturbation model of the CPA would nowhere be accurate in this more general case, in contrast to the result shown in Fig. 7 where it is accurate above $E_0/W \simeq 0.4$.

IV. CONCLUSION

A calculation has been performed of the self-consistent screening of a charged impurity in the tight-binding approximation with the further approximation that the impurity potential is truncated beyond the second nearest neighbors to the impurity. This approximation was taken to be fairly accurate and used as a standard to compare with other approximations to the impurity screening problem. An approximation representing a hybrid between first order perturbation theory and a highly localized impurity potential model was found to very closely replicate the predictions of the truncated potential model. Furthermore, the self-consistent screening problem in that approximation is straightforward in principle to solve. First order perturbation theory, was found not to hold at all while first-order FSA was valid only when the potential was appreciably spread out over more than one lattice site. The rigid band model never was appropriate. The highly localized potential model is also not accurate, a result that casts doubt on the usefulness of CPA calculations that rely on it. There is hope that the hybrid model can be easily incorporated into a coherent potential formalism; work in that direction is presently in progress.

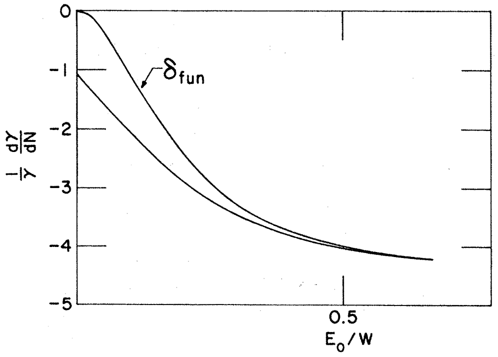

FIG. 7. Logarithmic derivative with respect to the number of impurities, N, of the electronic specific heat γ. The curve labeled δ_{fun} is the result for the localized-perturbation model of the CPA while the other curve is for the self-consistent truncated model.

APPENDIX A: IMPURITY HOPPING PERTURBATION

As mentioned in the text, perturbations induced by the impurity in the "hopping" matrix elements were neglected. This neglect was partially motivated by the fact that simply adding the hopping perturbation to the impurity site perturbation still does not adequately satisfy the perfect shielding requirement. In this appendix we prove this result. The highly localized potential approximation in our single band model, has the unphysical feature that for a band half full one can only have perfect screening of an impurity of $Z = 1$ when $|V_0| = \infty$. The question arises whether adding a hopping perturbation will correct this screening difficulty. Such a question is relevant because of the many recent CPA calculations using the highly localized approximation enhanced by such off-diagonal terms.[29]

We consider the response of the conduction-electron system to the impurity potential

$$V = V_0 a_0^\dagger a_0 + \sum_n{}' (t a_0^\dagger a_n + t^* a_n^\dagger a_0)$$

where, as before, a_n is the destruction operator for an atomic orbital on the nth site. The prime on the summation means that it is to be only over sites that are nearest neighbors to the central impurity site. For such a potential one obtains the following expression for the phase shift at the Fermi energy $E = 0$:

$$\delta(0) = \tan^{-1}[-v_0 I(0)/T] , \tag{A1}$$

where $I(0)$ is the imaginary part of $\frac{1}{6}W$ times the Green's function $g_{00}(E)$, $v_0 = 6V_0/W$, and W is the full bandwidth. T is given by

$$T = (1 - 12t/W)(1 - 12t^*/W). \tag{A2}$$

$I(E)$ and $R(E)$, the real part of $\frac{1}{6}Wg_{00}(E)$, are plotted in Fig. 8.

In obtaining (A1) we used the relationship that

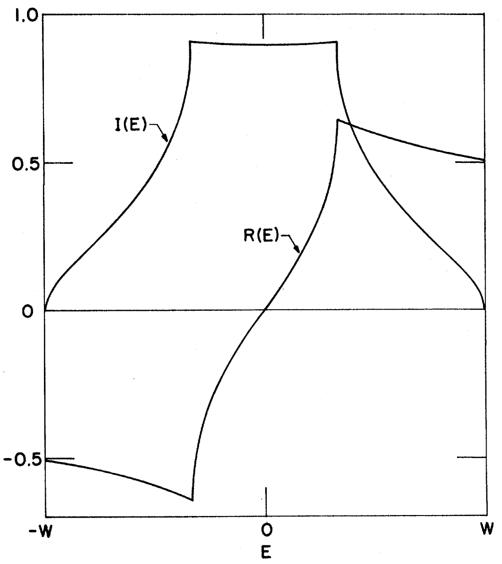

FIG. 8. Real [$R(E)$] and imaginary [$I(E)$] parts of $\frac{1}{6}Wg_{00}(E)$ plotted as a function of energy E.

$g_0(0)+g_4(0)+4g_2(0)=0$, where the subscript denotes the difference in the number of neighbors between the site locations of the matrix elements. Thus a subscript 0 denotes a diagonal element g_{00} while 2 denotes a matrix element between Wannier states centered at sites a distance 2 nearest neighbors apart, and 4 denotes a matrix element between Wannier states centered at sites a distance 4 nearest neighbors apart. By assuming $E_F=0$ to obtain (A1) we have chosen the only physically interesting case where the band is half-filled. This corresponds to a pure host of one electron per atom. A pure host of zero or two electrons per atom would correspond to an empty or full band, neither case being of interest because it is not metallic. Perfect screening of an impurity with plus or minus the charge of an electron requires $|\delta|=\frac{1}{2}\pi$. In the highly localized potential model ($T=1$) one can have perfect screening of either a positively or negatively charged impurity only when $|V_0|\rightarrow\infty$.

In (A1) we can have $|\delta|=\frac{1}{2}\pi$ only under two conditions; we must either have $|V_0|\rightarrow\infty$ or $T=0$. The second case, as one can see from (A2) and (1) corresponds to an off-diagonal impurity potential that exactly cancels out the hopping terms connecting the central impurity site with its neighbors. The atomic orbital on the impurity atom is completely isolated from all the other atoms in the host. $T=0$ is then an additional unphysical feature and the addition of a hopping perturbation alone does not give a physical solution to the perfect shielding requirement.

Within the one-band model the above discussion exhausts all physically interesting cases. However, one can envision a case of degenerate bands, such as d-bands, where an integer number of electrons per atom can be accommodated by distributing over the bands such that each band accommodates a noninteger number of states per atom. For such a case it is useful to discuss the shielding requirement for a less than half-filled or more than half-filled band in addition to an exactly half-filled band as above. In this more general case the phase shift of (11) will have the value

$$\delta(E)=\mathrm{Im}(\ln\{(\epsilon-v_0)G_0(E)-T[\epsilon G_0(E)-1]\}), \quad (A3)$$

where $G_0(E)=\frac{1}{6}Wg_0(E)$ and $\epsilon=6E/W$. To obtain (A3) we used the relations

$$g_1(E)=\tfrac{1}{3}[Eg_0(E)-1],$$

$$g_0(E)+4g_2(E)+g_4(E)=\tfrac{2}{3}E[Eg_0(E)-1].$$

Equation (A3) can be written as

$$\delta(E)=\tan^{-1}\left(\frac{(\epsilon-v_0-\epsilon T)I(E)}{(\epsilon-v_0)R(E)-[\epsilon R(E)-1]T}\right) . \quad (A4)$$

Applying the screening requirement to (A4) and using the functional forms of $I(E)$ and $R(E)$ illustrated in Fig. 8, one obtains the same unphysical restrictions as found for the case of the highly localized potential ($T=1$), namely the following: In the case of the screening of an impurity of unit charge, an impurity of positive charge (valence one less than the host) can only be screened by a less than half-filled band; by symmetry an impurity of valence one more than the host can only be screened by a more than half-filled band. (ii) There can be no screening of an impurity with a charge of $|2e|$, $|3e|$, etc.

The only improvement over the highly localized model introduced by the hopping perturbation is that of an isovalent impurity in a less than or more than half-filled band. In that case V_0 can be finite instead of zero. However, even in this case there is some question whether a one-band model with fractional occupation is a valid representation of overlapping degenerate bands, and deserves further study. All in all, the addition of simply a hopping perturbation does not give a very satisfactory improvement to the screening difficulty encountered in the highly localized perturbation model.

APPENDIX B: HYBRID APPROXIMATIONS

The numerical results of the paper indicate that V_1 and V_2 are always small enough to be treated by perturbation theory while V_0 in general must be treated to all order. We divide the solution for the Green's function in two steps. In the first step we solve for the Green's function with only V_0 present and treat it to all orders. We next calculate the correction to the Green's function added by V_1 and V_2 using perturbation theory.

We solve the Dyson equation (4) where V in the Wannier representation is nonzero only for the diagonal element on the impurity site:

$$G'_{n,n'}(E)=g_{n,n'}(E)+\frac{g_{n,n'}(E)\,V_0 g_{0,n}(E)}{1-V_0 g_{00}(E)} \;. \tag{B1}$$

Adding V_1 and V_2 in perturbation theory, (4) becomes

$$G_{n,n'}(E)=G'_{n,n'}+\sum_{n''}{}' G'_{n,n''}(E)V_{n''}G'_{n'',n'}(E) \;, \tag{B2}$$

where the prime is added to the sum to indicate that the term $n''=0$ is not included.

Numerical calculations indicate that in the second term on the right side of (B2), cross terms between V_0 and $V_{n''}\neq V_0$ are always negligible in the model of this paper, permitting the substitution of g for G' in that term. Thus (B2) simplifies, with the aid of (B1), to

$$G_{n,n'}(E)=g_{n,n'}(E)+\sum_{n''} g_{n,n''}(E)V_{n''}g_{n'',n'}(E) +\frac{g_{n,0}(E)g_{0,n}(E)V_0^2 g_{0,0}(E)}{1-V_0 g_{0,0}(E)} \;, \tag{B3}$$

where now the sum is over all sites including the impurity site ($n=0$). Now, using (6) we obtain for the change in the electronic density at the nth site

$$\delta\rho_n \equiv \sum_{n'} K(\vec{R}_n-\vec{R}_{n'})\,V_{n'}+F(\vec{R}'_n V_0) \;, \tag{B4a}$$

$K(\vec{R}_n)$ and $f(R_n, V_0)$ are obtained directly from (B3) and (6). We have used the fact that the unperturbed Green's function depends only on the relative positions of two sites. We now generalize (13) to obtain a relation between the impurity potential and the perturbed charge density.

$$V_n=\frac{\Delta_0}{e}\,\delta\rho_n+\frac{\Delta_1}{e}\sum_{n'\neq n}\frac{\delta\rho_{n'}}{|\vec{R}_n-\vec{R}_{n'}|}+(1-\delta_{n,0})\,\frac{\Delta_1}{|\vec{R}_n|}\,\frac{Q}{e} +\delta_{n,0}\left(Q\,\frac{\Delta_0}{e}+E_0\right) . \tag{B5a}$$

Taking the Fourier transforms of (B4a) and (B5a), we obtain

$$\sum_n \delta\rho_n e^{i\vec{q}\cdot\vec{R}_n}\equiv \Delta\rho(q)=k(q)v(q)+f(q, V_0) \;, \tag{B4b}$$

$$v(q)=E_0+A(q)[Q+\Delta\rho(q)] \;, \tag{B5b}$$

where $k(q)$, $v(q)$, and $f(q, V_0)$ are obtained by taking suitable Fourier transforms of the corresponding quantities in (B4a) and (B5a). $A(q)$ is given by

$$\sum_{n=0} e^{i\vec{q}\cdot\vec{R}_n}\left(\frac{\Delta_1}{e|\vec{R}_n|}\right)+\frac{\Delta_0}{e} \;.$$

An important feature of $A(q)$ is

$$A(q)\to\frac{4\pi}{q^2}\,\frac{\Delta_1}{e}\ \text{as}\ q\to 0. \tag{B6}$$

On the other hand $k(q)$ approaches a constant, and $f(q, V_0)$ has no singularity as $q\to 0$.

Substituting (B5b) into (B4b) we obtain

$$\Delta\rho(q)=-\frac{k(q)A(q)\,Q}{1+k(q)A(q)}-\frac{k(q)E_0}{1+k(q)A(q)} +\frac{f(q, V_0)}{1+k(q)A(q)} \;. \tag{B7}$$

Taking the limit $q\to 0$ and remembering the comments just made we obtain

$$\sum_n \delta\rho_n=\lim_{q\to 0}\Delta\rho(q)=-\,Q \,.$$

So we obtain perfect screening on this model. Using (B5b) and (B7) to find $v(q)$ and taking the inverse Fourier transform yields

$$V_n=\frac{1}{(2\pi)^3}\int v(q)e^{-i\vec{q}\cdot\vec{R}_n}\,d^3q =\frac{1}{(2\pi)^3}\int\frac{[A(q)Q+E_0+A(q)f(q, V_0)]e^{-i\vec{q}\cdot\vec{R}_n}}{1+k(q)A(q)}\,d^3q \,. \tag{B8}$$

Numerically solving this implicit equation for V_n completes the solution of the self-consistent screening problem in the hybrid model.

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Temperature Dependence of the Electron Relaxation Time in Thallium Measured by the Radio-Frequency Size Effect*

James E. Bradfield† and Julian B. Coon
Department of Physics, University of Houston, Houston, Texas 77004

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The temperature dependence of the electron scattering time τ averaged over an orbit has been investigated in thallium using the radio-frequency size effect. It was found that τ fit an expression of the form $1/\tau = a + bT^n$. For closed orbits the temperature exponent varied from $n = 3$ at low magnetic fields to $n = 5$ at high values of the magnetic field. A scattering-effectiveness criterion was introduced and was used to predict a magnetic field dependence for n in agreement with experiment. The value of the deformation potential averaged over an orbit was obtained for orbits with $n = 3$.

I. INTRODUCTION

The temperature dependence of the relaxation time for electrons in metals has been the subject of several recent investigations. Various techniques including radio-frequency size effects (RFSE),[1–7] ultrasonic attenuation,[8–15] cyclotron resonance,[16] bulk-resistivity measurements,[17–20] and magnetic-surface-state resonance[21–27] have been employed by experimenters, yielding a variety of results. Generally, however, it is found that the relaxation time τ varies according to $1/\tau = a + bT^n$ for temperatures in the range 0 to 10 °K, where n assumes values between $n = 2$ and $n = 7$.

The experimental results may be understood by assuming that an electron on a resonant orbit undergoes a scattering event in an average time τ which removes the electron from the resonant orbit. If one also assumes that collisions with impurities and with the lattice (in the form of electron-phonon interactions) contribute to the total scattering rate independently, the expression for τ may be written as $1/\tau = 1/\tau_i + 1/\tau_p$, where $1/\tau_i$ is the average scattering frequency due to impurities and $1/\tau_p$ is the electron-phonon scattering frequency. τ_i is temperature independent over the range of temperatures investigated.

A model for electron-phonon scattering in which it is assumed that every electron-phonon collision is effective in removing the electron from the resonant orbit results in an expression of the form

$$1/\tau_p = \frac{|C_0|^2}{8\pi^2 NMC_s}\int [n_{\vec{q}}(1 - f_{\vec{k}+\vec{q}})\delta(E_{\vec{k}+\vec{q}} - h\omega_{\vec{q}} - E_{\vec{k}}) + (n_{\vec{q}} + 1)(1 - f_{\vec{k}-\vec{q}})\delta(E_{\vec{k}-\vec{q}} + h\omega_{\vec{q}} - E_{\vec{k}})] q\, d^3q \ ,$$

corresponding to processes of emission and absorption of a phonon of wave vector $\vec{q}$. (M is the ion mass, C_s is the velocity of sound, and C_0 is the average deformation potential.) In the Debye approximation and at low temperatures the integral may be evaluated and one finds $1/\tau_p = \Gamma T^3$ where

$$\Gamma = 2.4 \times 10^7 (|C_0|^2/k_D)(m_c/m)$$

for thallium where $|C_0|$ is measured in eV and k_D in units of 10^8 cm^{-1}. Thus a temperature dependence for $1/\tau$ of the form $1/\tau = a + \Gamma T^3$ is predicted. If $n = 3$ experimentally, as occurs for many orbits observed in this experiment and others, a value for the average value of the deformation potential over the orbit can be determined.

In this experiment, as well as in the work of