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Correlation of the Mössbauer Isomer Shift and the Residual Electrical Resistivity for ^{197}Au Alloys*

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The Mössbauer isomer shift, which is simply related to the charge density at the Mössbauer nucleus, has been measured for pure ^{197}Au and for ^{197}Au as an impurity in Cu, Ag, Ni, Pd, and Pt. Since the isomer shift associated with an impurity and the residual electrical resistance due to that impurity are properties of a common conduction-band wave function, one may expect a correlation of the residual resistance with the isomer shift through a suitable model. We have thus made residual-resistance as well as isomer-shift measurements at 4.2°K for the above dilute gold alloys. These measurements have been correlated through a theoretical model using (a) the residual electrical resistivity and the Friedel sum rule to specify the asymptotic wave function at the Fermi level and (b) a pseudopotential which will produce this asymptotic wave function and which is used to continue the s partial wave inward to the gold nucleus at the origin. The correlation of our experimental results using the theoretical model is good if we assume that a gold impurity presents an attractive potential to the s partial wave of the host s-band conduction electrons, and if we assume the s-band fillings to have the values 1, 1, 0.58, and 0.37 for Cu, Ag, Pd, and Pt.

I. INTRODUCTION

In the theory of metals, it is often convenient to think of the whole metallic sample as a single potential well for the conduction electrons. The Bloch wave functions, which give an approximate solution to the corresponding quantum-mechanical problem extend throughout the entire sample. If an impurity is dissolved in the metal, these electron wave functions again will in general extend throughout the sample. One will then expect a correlation between the properties of the electron wave function in the region near the impurity and its properties in the far region. Correspondingly one will expect a correlation between different physical phenomena associated with the impurity which depend dominantly on the different regions of the wave function.

When an impurity atom is dissolved in a host metal, it may have an affinity for electrons different from that of the host and as is implied above this may result in a redistribution of the electron charge density. For a suitable impurity, this change of charge density at the impurity nucleus may be measured through the use of the isomer shift of the Mössbauer effect. Other consequences of this charge displacement appear, for example, in the Knight shifts[1,2] and quadrupole line broadening effects in NMR[3,4] of the components of the alloy, in the heat of formation of an alloy,[5] and in the residual electrical resistivity of the alloy due to the impurity.[5–8] Thus, there will be a correlation between all these quantities through the electron wave functions associated with the charge displacement. In the following we give both electrical resistance and isomer shift measurements for gold in several noble metal and transition metal alloys. We then present through a simple model a correlation between our measured isomer shifts for several dilute gold alloys and the residual electrical resistivity per atomic percent, $\Delta\rho/c$, introduced by the gold in these alloys.

Because of their relatively simple electronic configurations, the noble elements copper, silver, and gold have played a prominent role in the development of the theory of metals. Copper and silver, unfortunately, do not have gamma rays convenient for Mössbauer effect studies. Gold, however, does have a suitable gamma ray, and if it is assumed that the gold $5d$ shell, as well as all the other inner shells, remains full and relatively little modified in the alloying process, measurements of the gold isomer shift may be interpreted to give some information about the valence s-state wave function in gold alloy systems.

To give an idea of the kind of information we would like to obtain from the isomer shift, let us consider two examples which indicate some of the interesting questions concerning the electronic distribution in alloys.

Silver and gold, in addition to having the same valence and crystal structure (fcc), have virtually the same lattice constant. Thus the alloys of these elements with each other should be favorable cases to discuss

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theoretically. Mott[8] had already concluded in 1936 that, in dilute alloys of gold in silver, gold with the larger ionization energy should present a more attractive potential than silver for the conduction-band electron charge. This difference of potentials would lead to the qualitative suggestion that a gold atom in silver would be negatively charged compared to a gold atom in gold. Theoretical studies employing the Fermi-Thomas semiclassical potential,[6,8] as well as quantum-mechanical partial-wave calculations beginning with that of Huang,[5,6] indicate that the "screening" charge density falls off very rapidly with distance, but little experimental information has been available.

In the case of alloys of the noble metals with the transition metals, investigations of the dependence on composition of the magnetic, electric, and thermal properties have provided important information on the *s* and *d* bands of the transition metals. For example, the alloys Ni(Cu), Pd(Ag), and Pt(Au), in which the components adjoin each other in the periodic table, reveal rather sharp changes of behavior of these properties near 55–65% of noble metals.[9] A well known interpretation of these data involves overlapping *s* and *d* bands, where for pure Ni and Pd it is thought that the fillings are about 0.6 electron/atom in the *s* band and 0.6 hole/atom in the *d* band. In the alloys the quantum states of the noble metal atoms should be included in the discussion of the alloy properties. However, as compared with the information obtained about the *d*-character of the transition metal, little is directly known about the role which the noble metal plays in producing the interesting alloy behavior observed. In a discussion of say the specific heat or the paramagnetic susceptibility of Pt-Au it may perhaps be assumed that charge is transferred in some degree from the *s* shell of the gold to the *d* shell of the platinum. This single process alone would tend to make the gold atom in the alloy electrically positive relative to a gold atom in gold. As with the Ag-Au alloys mentioned above, however, there may also be an effect due to the different attractive potentials of the gold and of the platinum for the valence charge. In considering alloys in which the components have different atomic volumes it is clear[7] that differences in atomic sizes also play an important role. A study of the correlation to be expected between the isomer shift of an impurity and the residual electrical resistivity which it introduces should give information on subjects such as those indicated above.

We conclude this introduction by recalling how the electronic charge density at the nucleus is obtained from the measured isomer shift.[10,11] The isomer shift arises from the interaction between electrons and the Mössbauer nucleus. As a consequence of this interaction, each level of a nucleus which is penetrated by electrons has a slightly different energy than it would have if the nucleus were "bare", i.e., if it had no electrons penetrating it. The Coulomb (electrostatic monopole) term in the interaction gives the dominant contribution to this energy shift. In first-order perturbation theory, the Coulombic energy shift, of a bare nuclear state χ produced by a single Dirac *s* electron is $D|\psi_s(0)|^2 \times\langle\chi|r^{2\sigma}|\chi\rangle$. Here D is a constant, $\sigma=(1-\alpha^2z^2)^{1/2}$ where z is the nuclear charge and α is the fine structure constant, and $|\psi_s(0)|^2$ is the nonrelativistic electron density at the origin.

If the matrix elements $\langle\chi|r^{2\sigma}|\chi\rangle$ are different for the nuclear ground and excited states involved in a gamma-ray transition, the penetration of the nucleus by all the *s* electrons will modify the gamma-ray energy by $D\rho_s(0)[\langle r^{2\sigma}\rangle_e-\langle r^{2\sigma}\rangle_g]$, where g and e refer to the ground and excited nuclear states and

$$\rho_s(0)=\sum_i|\psi_{si}(0)|^2$$

is the total nonrelativistic probability density of all the *s* electrons. By the use of the Mössbauer method, one may study the resonant emission and absorption of a gamma ray under the circumstance that $\rho_s(0)$ is different at the gamma-ray source and absorber nuclei. There will then be an energy ΔE, the isomer shift, which must be added to the emitted gamma ray energy E_γ to bring about resonance with the absorber nuclei, namely

$$\Delta E=D[\rho_{s,\text{abs.}}(0)-\rho_{s,\text{source}}(0)][\langle r^{2\sigma}\rangle_e-\langle r^{2\sigma}\rangle_g]\,. \quad (1)$$

Instead of the isomer shift ΔE relative to the experimental gamma-ray source, it is convenient to consider the shift relative to pure gold,

$$\Delta E_I=(\Delta E_{\text{alloy}}-\Delta E_{\text{pure gold}}) \propto[\rho_{s,\text{alloy}}(0)-\rho_{s,\text{Au}}(0)]. \quad (2)$$

The corresponding mechanically supplied Doppler velocity of the source toward the absorber, the experimentally measured quantity, is $v_I=c\Delta E_I/E_\gamma$, where here c is the velocity of light. Measurements of v_I may yield information either about the nuclear size change between ground and excited states or about the electronic densities at nuclei in solids.

II. RESULTS OF ISOMER SHIFT AND RESIDUAL ELECTRICAL RESISTIVITY MEASUREMENTS

Measurements of v_I have been made for the 77-keV resonant gamma ray of ^{197}Au, where the gold has been placed in a variety of alloy environments.[11–13] The gamma-ray source was prepared by neutron activation of 50-mg samples of ^{196}Pt metal in the Oak Ridge

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TABLE I. Parameters used in the correlation of the isomer shift with the residual resistance for Au. The phase shifts δ_0 and δ_1 are given for the case of a potential attractive for s waves and for the valence η_A, also given below, which results in the best correlation, Fig. 6. The quantity $k_0^2/2$ is the corresponding well depth in eV.

Host metal	Experimental residual resistivity $\Delta\rho/c$ ($\mu\Omega$ cm/at.%)	Experimental isomer shift v_I (mm/sec)	$\frac{\delta a}{a}$	Poisson's ratio σ	$1+\frac{3}{\gamma^{\text{h}}}\frac{\delta a}{a}$	Host valence used η_A	Phase shifts δ_0	Phase shifts δ_1	Well depth $k_0^2/2$ (eV)
Cu	0.52±0.02	4.4±0.2	0.157[a]	0.364[f]	1.337	1.0	0.0562	−0.1951	0.305
Ag	0.36±0.02	2.1±0.2	−0.00735[b]	0.37[f]	0.984	1.0	0.2155	−0.06343	1.07
Ni	0.38±0.02	5.4±0.2	0.209[c]	0.31[f]	1.397	0.6	0.2872	−0.01113	1.407
Pd	0.70±0.02	2.4±0.2	0.0528[b,d]	0.39[g]	1.120	0.58	0.423	+0.0425	1.933
Pt	1.55±0.02	1.4±0.2	0.040[e]	0.39[f]	1.091	0.37	0.624	+0.102	2.597

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[h] $\gamma=3(1-\sigma)/(1+\sigma)$.

research reactor to form some ^{197}Pt. Following a beta decay to ^{197}Au, this source gives the desired 77-keV gamma ray. The absorbers were prepared either from pure gold or from arc-melted gold alloys. All measurements were made at 4.2°K. Details of the equipment and the treatment of the data have been described previously.[12]

The results of our isomer-shift measurements, in units of mm/sec and as a function of the Au concentration c in atomic percent, for binary alloys of Au with Ni, Pd, Ag, and Cu are shown in Fig. 1. The curve for Au-Ni has been presented previously[12] but is reproduced in Fig. 1 for reference. In Fig. 2 results are given for the isomer shift of Au in the ternary alloy $Au_{0.01}Cu_{(x-1)/100}Ni_{(100-x)/100}$.

As was noted in Sec. I, alloys like Cu-Ni, Ag-Pd, and Au-Pt have a sharp change in some of their properties as a function of composition near 55–65 at.% of the noble metal and it is of interest to see whether the gold isomer shift also displays any exceptional behavior in this composition region. The results given in Figs. 1 and 2 show that for the gold-transition metal alloys studied thus far, v_I may be described within experimental error as a nearly linear function of composition. Although more refined measurements may perhaps show some curvature of $v_I(c)$, it seems reasonable to conclude that there is no dramatic change of slope, dv_I/dc, near 55–65 at.% gold, and hence no obvious correlation of v_I with the filling of the d band.

In studies of dilute alloys, one often considers the variation of some property of the system when a variety of impurities are dissolved in a single host metal. Here we study the isomer shift associated with a single-impurity type when the latter is dissolved in a number of different host metals. For the values of the isomer shifts at infinite dilution we take the intercepts of the straight lines in Fig. 1 at 0 at.% noble metal. As was mentioned above, it is probable that more refined measurements will show that the correct description of $v_I(c)$ will not be given by a straight line. For example, near infinite dilution dv_I/dc may be very close to zero. However, for our present purpose the

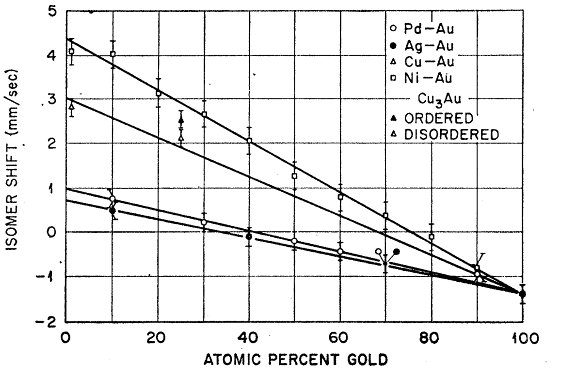

FIG. 1. Isomer shift v in mm/sec as a function of composition for alloys of gold with palladium, silver, copper, and nickel. Here v is measured relative to a source consisting of ^{197}Au in Pt metal and is given by $v=c\Delta E/E_\gamma$ where ΔE is defined by Eq. (1).

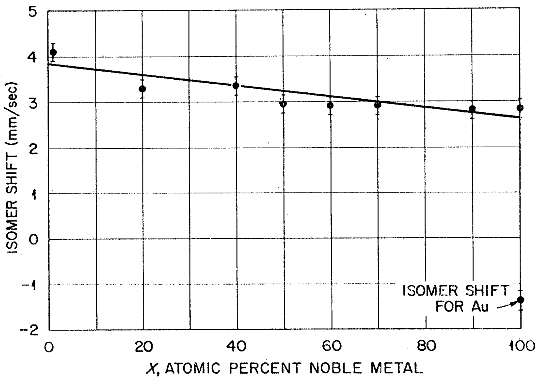

FIG. 2. Isomer shift v of gold in the ternary alloy $Au_{0.01}Cu_{(x-1)/100}$-$Ni_{(100-x)/100}$ as a function of the total atomic percent x of the noble metals. Here v is defined as in the caption of Fig. 1.

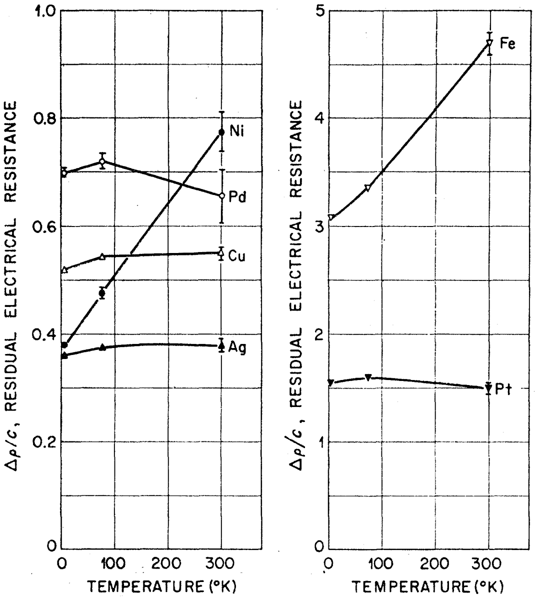

FIG. 3. Impurity electrical resistivity per atomic percent of impurity, $\Delta\rho/c$, as obtained from solid solutions containing 0.50, 1.00, and 2.00 atomic percent of gold in silver, copper, palladium, nickel, platinum, and iron.

use of the intercept should give a sufficiently precise value of $v_I(0)$. Experimental values for $v_I(0)$ obtained from these intercepts are given in Table I.

From Figs. 1 and 2 and Table I it may be observed that v_I is positive for all of the alloys reported here. It is in fact true that all of the gold isomer shifts which have been observed[11–13] for alloys of gold have $v_I > 0$. In Sec. I it was noted that in Au-Pt a transfer of charge from the s-shell of the gold to the d-shell of the platinum would tend to give the gold a positive charge, while, on the basis of the model given by Mott,[8] mentioned in the introduction, gold alloyed in silver would tend to assume a negative charge. The fact that the isomer shifts are of the same sign for both of these alloys—as well as for the other gold-transition metal alloys discussed here—suggests that either the picture with regard to the Au-Ag or that relative to the transition element alloys, Au-Pt, for example, is insufficient. Because of the evident inability of the qualitative models presented above to give a satisfactory interpretation of the Mössbauer measurements, we have sought to correlate these isomer shift measurements with some other alloy property which would also be related to the modification in the electric charge distribution produced by the impurity.

In Sec. III a theoretical model is presented which gives a mechanism for the description of these isomer shift measurements for dilute alloys. In this treatment, information about the essential parameters of the model is drawn from measurements of $\Delta\rho/c$, the residual electrical resistivity per atomic percent of impurity. In that our isomer shift measurements were made at 4.2°K, it seemed appropriate to use values of $\Delta\rho/c$ measured at this temperature also. Earlier studies[14,15] of the residual electrical resistivity of dilute Au alloys have not usually included measurements at such low temperatures. For this reason we have made measurements of $\Delta\rho/c$ for the alloys of interest at 4.2, 77, and 298°K. These results, given in Fig. 3, were obtained from measurements on alloys containing 0.5, 1, and 2 at.% of gold and are in good agreement with earlier measurements at the two higher temperatures where they are available.

The measured values of $\Delta\rho/c$ for the dilute ferromagnetic alloys Au-Ni and Au-Fe show an exceptionally strong temperature dependence which is attributed to magnetic scattering effects.[16] Because of this behavior, we have extended these measurements to temperatures well above the Curie point for an alloy containing 2 at.% of gold in nickel and for an alloy of 0.50 at.% of gold in iron. At the concentration used, gold forms a solid solution with nickel over the entire temperature range.[17] For the iron alloy, however, the limited solubility of gold precluded measurements on a true solid solution below about 1030°K,[17] although measurements on quenched samples were made at temperatures near 300°K and below. Due to the complications introduced by the ferromagnetism of these alloys, the theoretical treatment of $\Delta\rho/c$ is more complex here than for the other alloys. For the purposes of this paper we assume that $\Delta\rho/c$ at 4.2°K gives the appropriate measure of the transport cross section for the Au impurity in Ni to be used in the theory of the isomer shift. Further study may require that this assumption be modified.

III. THEORETICAL DISCUSSION OF THE ISOMER SHIFT OF THE IMPURITY IN A DILUTE ALLOY

Significant progress has been made in the theory of dilute alloys using a variety of theoretical methods. Here we present a simple theoretical model for the correlation of the isomer shift of an impurity in an alloy with the residual electrical resistivity through the conduction band wave functions of the infinitely dilute alloy.[18] Our calculation is based on the use of an impurity potential using methods similar to those introduced by Mott[8] and Friedel.[6] We adopt this approach because it gives a convenient treatment of both the residual electrical resistivity and the charge at an impurity site in terms of the same approximate band theory.

Basically, the gamma-ray isomer shift of an impurity in an alloy may be viewed as an aspect of the screening

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of the impurity. We shall assume that the impurity is a noble metal, i.e., gold, and we shall consider cases in which the impurity is dissolved in another noble metal or in a transition metal. In the case where the noble metal impurity is dissolved in another noble metal the screening will presumably be predominantly by the conduction s band of the host. In the case where the host is a transition metal, however, the situation may be more complex. We shall take the usual view that the eigenstates of the outer electrons in a transition metal host may be described by two bands, one of dominantly s and the other of dominantly d character. For dilute gold alloys with the transition metals we further assume (a) that the states of gold other than than the $6s$ state, in particular the $5d$ states, are not sufficiently modified, relative to pure gold, to significantly alter their screening of the gold s shells, (b) that only the s band contributes to the isomer shift, e.g., we neglect any hybridization of gold s and $p_{1/2}$ states into the d band, (c) that in a gold cell, the hybridization of gold p and d functions into the s band is nearly the same as in pure gold, and (d) that the residual resistivity is attributable entirely to the s band, because of the high effective mass of the d band holes.

The interaction of the impurity atom with the electrons of the s band of the host metal will be described by associating a perturbing pseudopotential with the impurity atom. The pseudopotential will give rise to a transport cross section σ_{tr} for the conduction electrons and will thus produce a residual electrical resistivity per atomic percent, $\Delta\rho/c$. From a measurement of $\Delta\rho/c$, σ_{tr} for electrons at the Fermi level may be obtained. Then from σ_{tr} and the requirement that the impurity atom must be screened in an electrically conducting alloy, the effective potential for the $l=0$ component of Bloch waves in the s band may be estimated. Using this well, one may obtain a calculated value of

$$\rho_s(0)=\sum_i|\psi_{si,\text{abs.}}(0)|^2,$$

and thus of the isomer shift to within a constant which depends on the nuclear size change. The details of this calculation, which are given below, differ from previous applications of the impurity potential method in several respects, which will be discussed as they occur.

We consider the substitution of an impurity atom B for an atom A of the host metal. The Wigner-Seitz approximation of replacing the atomic cell by a sphere of equal volume will be made. At the bottom of the conduction band at energy E_A in the pure host metal, there will be a wave function $U_A(r)$, which is a solution to the Schrödinger equation,

$$\nabla^2U_A+2(E_A-V_A)U_A=0,\quad r\leqq r_A,\qquad dU_A/dr|_{r=r_A}=0,\tag{3a}$$

containing the potential V_A of the lattice, where atomic units are used. For pure metal B and at the bottom of the band, one would similarly have the wave equation,

$$\nabla^2U_B+2(E_B-V_B)U_B=0,\quad r\leqq r_B,\qquad dU_B/dr|_{r=r_B}=0.\tag{3b}$$

In the above, r_A and r_B are the radii of the Wigner-Seitz spheres in the pure metals A and B, respectively.

In the alloy the radius R of the impurity sphere may in general be expected to differ slightly from that in pure gold, r_B. This radius R is not directly measurable physically. Furthermore, for small variations of R the result of the approximate calculation given below is not very sensitive to the value of R assumed. We therefore assume $R=r_B$, i.e., we take the radius of the gold atom in the alloy to be the same as its radius in pure gold. The pseudopotential within the impurity sphere, $V_{\text{alloy}}(r)=V_B(r)+V_S(r)$, $(r\leqq R)$, will in general differ from that within the Wigner-Seitz sphere of pure metal B, V_B, by the additional term V_S, which consists mainly of a screening potential and an orthogonality potential.[19] Outside the impurity sphere there will be a potential of similar form, $V_{\text{alloy}}(r)=V_A(r)+V_S(r)$, $(r>R)$. Here, however, as the screening charge falls off fairly rapidly with increasing r, $V_S(r)$ may be much smaller relative to $V_{\text{alloy}}(r)$ than it is within the impurity sphere. Thus we assume $V_{\text{alloy}}(r)=V_A(r)$, $(r>R)$.

The wave function $\psi_{\mathbf{k}}$ for an s-band electron in the alloy with energy E_k will be written as

$$\psi_{\mathbf{k}}(\mathbf{r})=\Phi_{\mathbf{k}}(\mathbf{r})U(r),\tag{4a}$$

where

$$\begin{aligned}U(r)&=U_B(r),\quad r\leqq R;\\&=U_A(r),\quad r>R,\end{aligned}\tag{4b}$$

is independent of k.[20] The Schrödinger equation for the alloy,

$$\nabla^2\psi_{\mathbf{k}}+2(E_k-V_{\text{alloy}}(r))\psi_{\mathbf{k}}=0,\tag{5}$$

then becomes

$$[\nabla^2\Phi_{\mathbf{k}}+2(E_k-E_B-V_S(r))\Phi_{\mathbf{k}}]U_B+2\boldsymbol{\nabla}\Phi_{\mathbf{k}}\cdot\boldsymbol{\nabla}U_B=0,\quad r\leqq R\tag{6a}$$

and

$$[\nabla^2\Phi_{\mathbf{k}}+2(E_k-E_A)\Phi_{\mathbf{k}}]U_A+2\boldsymbol{\nabla}\Phi_{\mathbf{k}}\cdot\boldsymbol{\nabla}U_A=0,\quad r>R.\tag{6b}$$

Friedel[6] and Daniel[2] have argued that, in the various regions of the alloy, either $\boldsymbol{\nabla}\Phi_{\mathbf{k}}$ or $\boldsymbol{\nabla}U$ or both will be small and that the term $\boldsymbol{\nabla}\Phi_{\mathbf{k}}\cdot\boldsymbol{\nabla}U$ may be neglected. In the case of a pure metal this approximation leads to approximate Bloch waves of the form $\psi_{\mathbf{k}}(\mathbf{r})=U_0(r)e^{i\mathbf{k}\cdot\mathbf{r}}$; for the alloy, Eqs. (5) and (6) are reduced to the simple

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[20] For pure metals one often uses the alternative form, $\psi_{\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}U_{\mathbf{k}}(\mathbf{r})$, but in the presence of a scattering potential the form chosen above is more convenient. Also $U_B(r)$ is the function for the actual pure metal, not for the fictitious pure metal discussed by Daniel (Ref. 2).

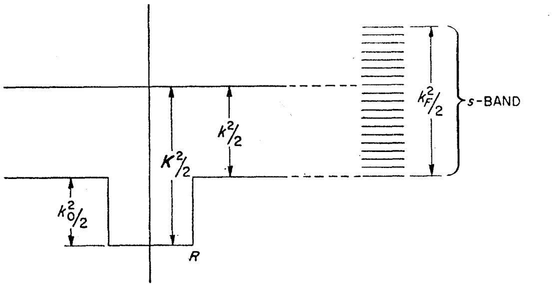

FIG. 4. Potential well parameters used for $l=0$ partial wave.

form,

$$\nabla^2\Phi_{\mathbf{k}}(\mathbf{r})+[k^2-2V(r)]\Phi_{\mathbf{k}}(\mathbf{r})=0 \tag{7a}$$

with

$$k=(2(E_k-E_A))^{1/2}, \tag{7b}$$

and[21]

$$\begin{aligned} V(r)&=(E_B-E_A)+V_S(r), & r\leq R \\ &=0, & r>R. \end{aligned} \tag{7c}$$

Equation (7a) is mathematically the same as the equation for the scattering of a plane wave with wave number $\mathbf{k}$ from the potential $V(r)$. As usual, one expands $\Phi_{\mathbf{k}}$ in partial waves. The asymptotic form of $\Phi_{\mathbf{k}}$ is then specified by phase shifts $\delta_l(k)$. Very little direct information is known about the perturbing potential $V(r)$, but information about the phase shifts produced by $V(r)$ for $k=k_F$, the Fermi wave number, is available from the residual resistivity together with a sum rule as described below. These phase shifts specify the approximate wave functions for $k=k_F$ in the asymptotic region outside the impurity. Only the $l=0$ partial wave contributes to the isomer shift as only this partial wave is finite at the gold nucleus, $r=0$. We need to use $V(r)$ explicitly only in continuing the $l=0$ partial wave from the asymptotic region to the origin for those states with the Fermi momentum k_F and also for all lower momentum values down to the bottom of the s-band.

In some cases a considerable part of $V(r)$ will be due to the energy difference E_B-E_A, which is of square-well shape.[8] In the absence of detailed information about $V_S(r)$ we shall assume, specifically for calculating the $l=0$ partial wave amplitude as a function of k and r, that $V(r)$ may be approximated by a square well of radius R and a depth $k_0^2/2$ adjusted to give the s-wave phase shift at the Fermi surface as calculated below from $\nabla\rho/c$. This amounts to assuming only that, in its effect on s-waves over a limited range of energy, $V_S(r)$ may be replaced by a roughly equivalent square well.

Different partial waves feel different regions of the potential more strongly. Consequently it is to be expected that if the effective potential acting on p waves, for example, is also represented by a square well of radius R, then the depth of this well will be different from that for the s wave. The present application does not require, however, an assumption concerning the effect of V_S on any part of the wave function other than the $l=0$ partial wave.

Although $U_A(R)$ will not in general precisely equal $U_B(R)$, nevertheless, because

$$\left.\frac{dU_A}{dr}\right|_R=0=\left.\frac{dU_B}{dr}\right|_R,$$

the logarithmic derivative of $\Phi_{\mathbf{k}}$ will be continuous.[22] Thus, in a partial-wave description of the scattering process, the phase shifts produced by the potential[2] will be the same as those for the scattering of a free electron of the same energy and satisfying the continuity conditions at $r=R$. However, there will be a discontinuity in $\Phi_{\mathbf{k}}$ at R required to compensate the discontinuity in U.

We now estimate the charge polarization[2] using the square well (Fig. 4). The radial s-wave equations corresponding to Eq. (7a) are

$$d^2(r\phi_k)/dr^2+k^2(r\phi_k)=0 \quad \text{for} \quad r>R, \tag{8a}$$

$$d^2(r\phi_k)/dr^2+K^2(r\phi_k)=0 \quad \text{for} \quad r\leqslant R. \tag{8b}$$

Here, $K^2=k_0^2+k^2$. The solution outside the well is

$$\phi_k=\sin(kr+\delta_0)/kr. \tag{9}$$

The solution inside the well may be written conveniently in the form

$$\phi_k=[U_A(R)/U_B(R)]C_k\sin(Kr)/kr. \tag{10}$$

The continuity of the logarithmic derivative at $r=R$ yields the equation

$$K\tan(kR+\delta_0)=k\tan KR. \tag{11}$$

The continuity of $\phi_k U$ at R gives

$$C_k\sin KR=\sin(kR+\delta_0). \tag{12}$$

The constant C_k needed in Eq. (10) can be obtained from Eqs. (11) and (12) [cf. Eq. (21)].

Before being able to calculate the charge density, we must specify the normalization of the single-electron wave functions. We consider first the approximate Bloch wave function for a pure metal, for example metal B,

$$\psi_{B\mathbf{k}}(\mathbf{r})=U_B(r)e^{i\mathbf{k}\cdot\mathbf{r}}/(\Omega_B)^{1/2}. \tag{13}$$

Here, as before, $U_B(r)$ is the wave function within the Wigner-Seitz cell at the bottom of the band, that is,

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[21] In the alternative formulation (Ref. 2) in which $U(r)$ inside the impurity cell is taken to be the wave function for the fictitious metal in which the lattice potential is V_B+V_S, the scattering pseudopotential $V(r)$ is simply E_B-E_A. Inasmuch as one does not know V_S accurately and cannot calculate the required U function, we feel that this approach hides the difficulty which is explicit in our formulation through the presence of V_S in $V(r)$.

[22] Small deviations of the derivatives of U_A and U_B from zero would in principle occur when R differs from r_A or r_B. As U_A and U_B are quite flat near the surfaces of the Wigner-Seitz spheres, we shall assume that the deviations are negligible.

at $k=0$, and Ω_B is the volume of the metal sample. The average value of $|U_B(r)|^2$ is taken as unity over the volume $v_B=(4\pi/3)r_B^3$ of the W-S cell,

$$v_B^{-1}\int_{v_B}|U_B(r)|^2d\tau=1. \tag{14}$$

Then

$$\int_{v_B}|\psi_{B\mathbf{k}}(r)|^2d\tau=\frac{v_B}{\Omega_B}, \tag{15}$$

and

$$\int_{\Omega_B}|\psi_{B\mathbf{k}}(r)|^2d\tau=1. \tag{16}$$

This normalization is such that one electron of each spin projection is associated with each $\mathbf{k}$ state. The charge at $\mathbf{r}$, $\rho_{B\mathbf{k}}(\mathbf{r})$, associated with each $\mathbf{k}$ state and with a given spin projection is then

$$\rho_{B\mathbf{k}}(\mathbf{r})=|U_B(\mathbf{r})|^2/\Omega_B. \tag{17}$$

Next we consider the alloy. A prime will be used on quantities which refer to the alloy. In Eq. (9), ϕ_k was given the same normalization as the s-wave part of the plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$. In the alloy the wave function $\psi_{B\mathbf{k}}'(\mathbf{r})$, normalized in the same way as $\psi_{B\mathbf{k}}(\mathbf{r})$ for the pure metal [Eq. (13)], is, therefore, for $r=0$,

$$\psi_{B\mathbf{k}}'(0)=U_B(0)\phi_k(0)/(\Omega')^{1/2} \tag{18}$$

or

$$\psi_{B\mathbf{k}}'(0)=U_B(0)[U_A(R)C_k\sin Kr/U_B(R)kr(\Omega')^{1/2}]_{r=0}. \tag{19}$$

The probability density $\rho_{Bk}'(0)$ at the origin, that is, at the nucleus of an impurity atom B in the alloy, arising from a given $\mathbf{k}$ state is then

$$\rho_{Bk}'(0)=\frac{|U_B(0)|^2}{\Omega'}\left|\frac{U_A(R)}{U_B(R)}\right|^2P(kR), \tag{20}$$

where the charge modification factor for a given $\mathbf{k}$ state, $P(kR)$, is

$$\begin{aligned}P(kR)&=[C_k(k_0^2+k^2)^{1/2}R/kR]^2\\&=\{1-[k_0^2R^2/(k_0^2+k^2)R^2]\\&\qquad\times\sin^2[(k_0^2+k^2)^{1/2}R]\}^{-1},\end{aligned} \tag{21}$$

where C_k is obtained from Eqs. (11) and (12). This square-well estimate for the charge enhancement of a $\mathbf{k}$ state at the origin has been used by Daniel[2] for electrons at the Fermi surface in connection with the Knight shift. Now $P(k_Fr_B)$ differs little from unity, but for smaller values of k, $P(kr_B)$ deviates appreciably from one. Thus the isomer shift is more strongly influenced by the impurity potential than is the Knight shift.

To obtain the charge density at a B nucleus arising from all the conduction electrons, either in the pure metal B or in the alloy, one must sum the partial probability density $\rho_{Bk}(0)$ over the two spin projections and over all $\mathbf{k}$ states up to the Fermi energy, E_F. Letting $n(\mathbf{k})$ be the density of the states, including a factor of two for the spin multiplicity, one has in the pure metal B

$$\begin{aligned}\rho_B(0)&=\frac{|U_B(0)|^2}{\Omega_B}\int_{E\leq E_F}n_B(\mathbf{k})d^3k\\&=\frac{|U_B(0)|^2}{v_B}\eta_B=\frac{3}{4\pi r_B^3}|U_B(0)|^2\eta_B,\end{aligned} \tag{22}$$

where η_B is the number of s-band electrons per atom. In the alloy one has at a B nucleus located at the origin

$$\rho_B'(0)=\frac{|U_B(0)|^2}{\Omega'}\left|\frac{U_A(R)}{U_B(R)}\right|^2\times\int_{E\leq E_F'}n'(\mathbf{k})P(kR)d^3k \tag{23}$$

where $n'(\mathbf{k})$ is the density of states in the alloy. In the simple free-electron-like band model with spherical energy surfaces and $E(k)=k^2/2$, the density of states is

$$n'(\mathbf{k})=2\Omega'/(2\pi)^3, \tag{24}$$

so that

$$\rho_B'(0)=|U_B(0)|^2\left|\frac{U_A(R)}{U_B(R)}\right|^2\frac{1}{\pi^2R^3}\int_0^{k_F'R}P(w)w^2dw. \tag{25}$$

With $R=r_B$, and using Eq. (22) this may be written

$$\rho_B'(0)=\rho_B(0)\left|\frac{U_A(R)}{U_B(R)}\right|^2\frac{\bar{P}(k_F'r_B)}{\eta_B}, \tag{26}$$

where

$$\bar{P}(k_F'r_B)=\frac{4}{3\pi}\int_0^{k_F'r_B}P(w)w^2dw. \tag{27}$$

The convenient quantity $\bar{P}$ is closely related to the average value of $P(k_Fr_B)$ over the filled states, which is

$$P_{\text{av}}=\frac{3}{(k_F'r_B)^3}\int_0^{k_F'r_B}P(w)w^2dw. \tag{28}$$

If the alloy were infinitely dilute, the Fermi momentum k_F' would be equal to the Fermi momentum in the pure host metal, k_{FA}, which is related to the radius of the Wigner-Seitz sphere r_A through the equation

$$k_{FA}r_A=(9\pi\eta_A/4)^{1/3}\approx1.92\eta_A^{1/3}, \tag{29}$$

which follows from Eqs. (22) and (24) as applied to the metal A. Thus for a very dilute alloy, the relevant charge modification factor is given by

$$\frac{\bar{P}(w_F)}{\eta_B}=\frac{\eta_A}{\eta_B}\left(\frac{r_B}{r_A}\right)^3P_{\text{av}}, \tag{30a}$$

where

$$w_F=k_{FA}r_B=1.92\eta_A^{1/3}r_B/r_A. \tag{30b}$$

If, as for gold in transition metals, the number of conduction electrons per atom is smaller in the host than in metal B, then this "valence" difference tends to reduce $\bar{P}/\eta_B$. If the host atoms are smaller than the impurity atoms, as is the case for Au in Cu, Ni, Pd, and Pt (but not in Ag), the size difference tends to increase $\bar{P}/\eta_B$. The remaining factor, P_{av} is greater than unity for an attractive impurity potential and less than unity for a repulsive potential.

Referring back to Eq. (2), the isomer shift ΔE_I is seen to be proportional to the difference between the probability densities $\rho_B'(0)$ and $\rho_B(0)$, that is for an infinitely dilute alloy

$$\begin{aligned}\Delta E_I&=\alpha[\rho_B'(0)-\rho_B(0)]\\&=\alpha\rho_B(0)\left\{\left|\frac{U_A(r_B)}{U_B(r_B)}\right|^2\frac{\bar{P}(w_F)}{\eta_B}-1\right\},\end{aligned}\qquad(31)$$

where[23] the proportionality constant α equals $D[\langle r^{2\sigma}\rangle_e-\langle r^{2\sigma}\rangle_g]$ in Eq. (1).

Detailed information about the ratio $|U_A(r_B)/U_B(r_B)|^2$ is not available. By our choice of normalization[24] the average values of $|U_A(r)|^2$ and $|U_B(r)|^2$ are unity, independent of v_A and v_B. We may expect, therefore, that $|U_A(r_B)/U_B(r_B)|^2$ will be close to unity. The ratio will be set equal to unity in our comparisons with experiment. Thus the equation we shall use for gold isomer shifts ($\eta_B=1$) is

$$v_I=G[\bar{P}(w_F)-1],\qquad(32)$$

where the constant G is given by

$$G=\alpha\rho_B(0)c/E_\gamma$$

and where in this expression c is the velocity of light.

In order to calculate $P(kr_B)$ from Eq. (21), we must know the well-depth parameter k_0. As was indicated earlier we shall obtain an estimate of k_0 from the experimental value of $\Delta\rho/c$ and the Friedel sum rule.[6]

The residual resistivity per atomic percent impurity, $\Delta\rho/c$, should be given sufficiently accurately for our purposes by the first-order solution to the Boltzmann transport equation. If $\Delta\rho/c$ is in $\mu\Omega$ cm/at.%, k_F, $\hbar$ and e in cgs units, and the transport cross section σ_{tr} in cm^2, then

$$\Delta\rho/c=9.00\times10^{15}(\hbar k_F/e^2)\sigma_{\text{tr}}(k_{FA}).\qquad(33)$$

Huang[5] has expressed σ_{tr} in terms of the phase shifts of the partial waves scattered by a spherically symmetric potential as

$$\sigma_{\text{tr}}(k_{FA})=\frac{4\pi}{k_{FA}^2}\sum_{l=0}^{\infty}(l+1)\sin^2[\delta_l(k_{FA})-\delta_{l+1}(k_{FA})].\qquad(34)$$

Hence, using Eq. (29),

$$\begin{aligned}\sum_{l=0}^{\infty}(l+1)&\sin^2[\delta_l(k_{FA})-\delta_{l+1}(k_{FA})]\\&=(0.703\eta_A^{1/3}/r_A)(\Delta\rho/c),\end{aligned}\qquad(35)$$

where now r_A is in atomic units. Thus the residual resistivity provides one condition on the phase shifts at the Fermi surface.

Another condition is provided by the Friedel sum rule.[6] When a neutral impurity atom is substituted for a host atom, the metal as a whole remains neutral. However the impurity atom furnishes to the conduction band, in general, an amount of electronic charge different from that furnished by a host atom. The ionic core of the impurity atom has a correspondingly different net charge from that of the core of a host atom. The conductivity of a metal insures that the excess core charge on the impurity is screened within a relatively short distance by the conduction electrons. The excess conduction electron charge within a sphere about the impurity of radius large enough that the wave functions have attained their asymptotic forms, must just compensate the extra ionic charge within this sphere. Friedel's sum rule is an expression of this in terms of the phase shifts of the conduction electrons, namely,[6] for a single band,

$$\tfrac{1}{2}\pi Z=\textstyle\sum_{l=0}^{\infty}(2l+1)[\delta_l(k_{FA})-\delta_l(0)],\qquad(36)$$

where Z is the excess ionic charge and $\delta_l(0)$ is zero unless the impurity potential is strong enough to support a bound state for that partial wave. The sum rule has been generalized to apply to the scattering of Bloch waves and to bands with nonspherical Fermi surfaces by Blandin.[25]

In the case of gold in transition metals, screening may occur in both the s and d bands. One would then have a self-consistency requirement to satisfy, relating the charge to be screened by each band to the electronic charge distribution in the other band. We do not attempt to solve this difficult problem, but assume, Sec. I, that to a good approximation the $5d$ shell of each gold impurity atom is full. Then the ionic charge presented by a gold ion to the s band is the same as in pure gold, namely η_B, which is unity. When occupied by a host atom the impurity site has an ionic charge for s band electrons equal to η_A. Consequently, if the host and impurity atoms are of the same size, the charge to be screened by the s band per impurity ion is $Z=\eta_B-\eta_A$.

Size differences between host and impurity atoms introduce complications into the determination of the charge to be screened. Blatt[7] has investigated the effect of size differences on residual resistivities. His discussion was phrased in terms of the change in ionic charge within the volume occupied by an impurity

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[23] In $U_A(r_B)$ the argument is r_B relative to the center of the impurity cell. Translated to the neighboring host cell the argument would be approximately r_A.

[24] If we had normalized U_A and U_B to unity in their respective Wigner-Seitz spheres, then the factor $(r_B/r_A)^3$ which appears in Eq. (30a) would be absorbed into the ratio $|U_A(r_B)/U_B(r_B)|^2$.

[25] A. Blandin, J. Phys. Radium 22, 507 (1961).

atom. He did not explicitly consider modifications in the ionic charge density outside the impurity cell, although the Friedel sum rule involves the total change in ionic charge within a large sphere about an impurity.[6] We show in the appendix, however, that consideration of the alteration in ionic charge within a Friedel sphere of radius not much greater than a mean free path yields the same result as Blatt's.[7] Letting $f=c/100$ be the atomic fraction of impurities, and writing the fractional change in lattice parameter due to the impurities as $\Delta a/a=(\delta a/a)f+0(f^2)$, then Blatt's formula takes the form

$$Z=(\eta_B-\eta_A)-[(1+\sigma)/(1-\sigma)](\delta a/a)\eta_A. \qquad (37)$$

Values for Poisson's ratio σ and $\delta a/a$ are given in Table I. We note that this formula does not refer explicitly to the volume of the impurity cell but refers only to expansion of the crystal as a whole. In our derivation of this formula, elasticity theory is used to relate the expansion of the material originally inside a Friedel sphere to the expansion of the crystal. This would seem to be better justified than using it to predict the expansion of an impurity cell.

In order to calculate the residual resistivity Friedel *et al.*[6] and Blatt[7] assumed that the impurity potential could be approximated by a square well of range equal to the impurity sphere radius. They varied the depth until the sum rule was satisfied to within reasonable accuracy. This entailed using the first four phase shifts, $l=0$ to 3, in Blatt's work. Blatt's phase shifts have been used by Blandin and Daniel[1] in calculating the Knight shift of the host nuclei and by Flynn and Seymour[4] in calculating effects of electric field gradients in NMR. On the other hand, Kohn and Vosko,[3] who also calculated quadrupole effects in NMR, used the sum rule together with the experimental residual resistivity and the assumption that only the first two partial waves were non-negligible. This yields values for the s and p wave phase shifts at the Fermi surface. We adopt Kohn and Vosko's procedure largely for two reasons. First, the Friedel-Blatt procedure gives a relatively poor estimate of the residual resistivity for alloys such as Ag(Au) for which Z is very small. This results from the fact that the Friedel-Blatt potential is determined by valence and size differences, but does not include any effect of the orthogonality term in V_S. Second, the spatial dependence of the impurity pseudo-potential is not very well known, so that it is advantageous not to have to assume a specific form for it in obtaining the phase shifts. The Kohn-Vosko procedure would lead to erroneous s and p wave phase shifts if higher phase shifts are important. However, since the d and f wave phase shifts in Blatt's calculations are relatively small, the error in neglecting them may not be very great, especially for small Z.

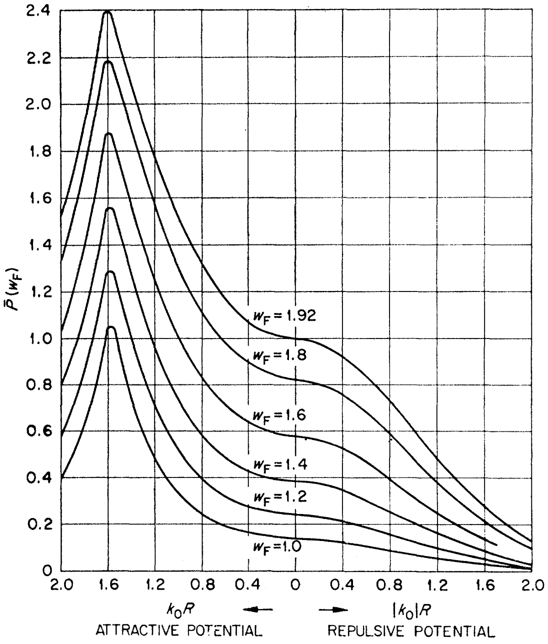

FIG. 5. Modification factor $\bar{P}$, Eq. (27), for the electronic probability density at the nucleus of an impurity in an alloy. This was computed with the use of a square well, Fig. 4, as the effective impurity potential acting on s-partial waves; $\bar{P}$ is a function of well depth or barrier height through the parameter $|k_0|R$ and of the s-band filling through the parameter $\omega_F=k_{FA}R$.

In obtaining $\delta_0(k_F)$ and $\delta_1(k_F)$ from $\Delta\rho/c$ and the sum rule, there are in general two sets of solutions because Eq. (34) involves the squares of the sine functions. We give below the results of the calculations for both sets of solutions. For the cases we have treated, one value of $\delta_0(k_F)$ is positive and the other negative. If the potential is weak, a positive $\delta_0(k_F)$ corresponds to an attractive potential for s waves, and a negative $\delta_0(k_F)$ arises from a repulsive potential. Consequently the two solutions give strikingly different results for the isomer shift. We note also that if Z is close to zero while $\Delta\rho/c$ is not small, then for each set of phase shifts, $\delta_1(k_F)$ is of the opposite sign from $\delta_0(k_F)$.[26] Instead of producing moderately large s and p wave phase shifts of opposite sign, the Friedel-Blatt procedure gives very small phase shifts of the same sign in such cases. The isomer-shift predictions turn out to be much better when one uses $\Delta\rho/c$ than when one uses only the sum rule and an assumed square well.

Having obtained $\delta_0(k_F)$ we proceed, as explained earlier, to employ a square-well potential to extend *the s wave* inward to the origin. The well depth parameter may be found from Eq. (11) which for $k=k_F$ may be written in the form.

$$v_F\cot v_F=\frac{w_F[\cot w_F-\tan\delta_0(k_F)]}{1+\cot w_F\tan\delta_0(k_F)}, \qquad (38)$$

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[26] For the solution with $\delta_0(k_F)$ negative and $\delta_1(k_F)$ positive, one may speculate that the orthogonality term in the pseudopotential is more repulsive at larger distances than at short distances.

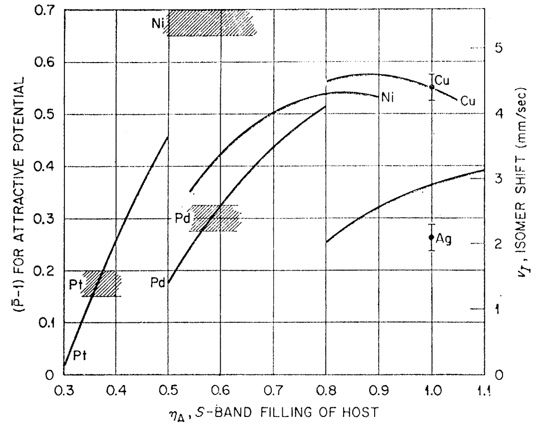

FIG. 6. Comparison between the calculated isomer shift $v_I = g_A(\bar{P}-1)$ using an attractive impurity potential, Eq. (32) and Fig. 5, and the experimental isomer shift, Table I. The experimental values for v_I are represented by points or crosshatched areas. The calculated v_I are given by the solid curves where $g_A = 8.0$ mm/sec has been chosen to give agreement between theory and experiment for Cu as host. Closer over-all agreement is found here than for a repulsive potential, see Fig. 7.

where w_F was defined in Eq. (30a) and

$$v_F = r_B(k_0^2 + k_{FA}^2)^{1/2}. \tag{38a}$$

The depth of this well is quite different in general from the depth of the square well in the Friedel-Blatt treatment, as their square well is used for all the partial waves.

IV. COMPARISON OF THEORY WITH EXPERIMENT

Figure 5 shows the calculated behavior of the charge polarization at the nucleus of the impurity atom, $\bar{P}(w_F)$ [Eq. (27)], as a function of the parameters $|k_0R|$ and w_F, which involve impurity size, s-band filling of the host metal and the well depth. For a given value for w_F, and compared with zero well depth, the charge polarization $\bar{P}$ decreases for a repulsive potential and increases for an attractive potential. For an attractive potential, when k_0R attains a value of $\frac{1}{2}\pi$, $\bar{P}$ reaches a maximum value. This corresponds to the appearance of a bound state. A maximum in $\bar{P}$ occurs because only contributions to $\rho_s(0)$ from the band states have been taken into account in the calculation. If bound states were included in the calculation $\bar{P}$ would not show a maximum, but rather would monotonically increase with the well depth. In our applications of the calculation of $\bar{P}$ we have thus far chosen to consider only those cases where the potential is too weak to hold a bound state.

We may now use the curves of Fig. 5 to understand in a qualitative way how the sign of the isomer shift of the resonance gamma ray for a dilute solution of ^{197}Au in the noble metals Ag or Cu has the same sign as for the cases where the host is one of the transition metals Ni, Pd, or Pt. If, as Mott[8] suggests, gold presents an attractive potential for the conduction band electrons in silver, then with w_F closely equal to 1.92, $\bar{P}$ will be greater than one. In the case of a transition metal host, η_A is expected to be less than 1. However, if the potential is sufficiently attractive then $\bar{P}$ may be greater than one here also. Furthermore if $r_B/r_A > 1$, then the decrease in w_F as η_A decreases will be partially compensated [see Eq. (30b)]. Thus one has a mechanism whereby the isomer shifts may be of the same sign, even though the band fillings may differ substantially for the several host metals.

As shown in Eq. (32), the isomer shift v_I is proportional to $(\bar{P}-1)$. This $(\bar{P}-1)$ is estimated from $\Delta\rho/c$ by the calculation outlined in Sec. III, where, in the calculation, there are two free parameters, the s-band filling in the host metal η_A, and the choice between the two possible solutions of Eqs. (35), (36), and (38) from which the impurity potential is obtained.

Because the experimental isomer shifts are all of the same sign and η_A is always less than or equal to η_B, one must have the same kind of potential, attractive or repulsive, associated with the s-partial waves for all of the alloys. In Fig. 6 the calculated $(\bar{P}-1)$ is presented for Au alloyed in Cu, Ag, Pd, Pt, and Ni as a function of s-band filling for the case where the impurity potential is attractive and in Fig. 7 for the case where this potential is repulsive. The proportionality constant G of Eq. (32), which relates v_I and $\bar{P}-1$, is obtained by normalizing the theoretical value of $\bar{P}-1$ at $\eta_A = 1$ for Au in Cu, to the experimental value $v_I = 4.4 \pm 0.2$ mm/sec.

This must be done separately for the attractive well solution, yielding a constant $G_A = 8.0$ mm/sec, and for the repulsive barrier, giving a constant $G_R = -31$ mm/sec. The quantities $G_A(\bar{P}-1)$ are given as functions of η_A in Fig. 6, and the quantities $G_R(\bar{P}-1)$ are

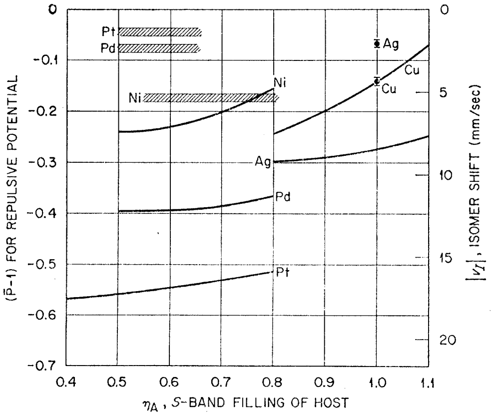

FIG. 7. Comparison between isomer shifts $v_I = g_R(\bar{P}-1)$, Eq. (32) and Fig. 5, calculated using a repulsive s-wave impurity potential, and the experimental isomer shifts of Table I. The experimental values for v_I are represented by points or crosshatched areas. The calculated v_I are given by the solid curves where $g_R = -31.0$ mm/sec has been chosen to give agreement between theory and experiment for Cu as host. Little agreement is found, whereas in the case of an attractive potential a close over-all agreement is found. See Fig. 6.

given similarly in Fig. 7 [Eq. (32)]. For Cu and Ag, η_A is taken to be unity so the experimental isomer shifts are plotted as points at $\eta_A=1$ with the experimental errors indicated. For the three transition-metal alloys the value of η_A is less certain, so that the experimental isomer shifts are plotted as crosshatched bands with heights equal to the experimental errors.

An examination of Fig. 6 shows a good measure of agreement between theory and experiment for the attractive potential case. In detail, experiment and theory agree for Au in Pd with a Pd s-band filling in the range 0.56 to 0.60. This is in quite reasonable agreement with the usual interpretation of the results of magnetic measurements on Pd. For the case of Pt as host, the s-band filling at which experiment and calculation agree, Fig. 6, is in the range 0.35 to 0.38. There have been several previous papers on the subject of the s-band filling in Pt. Some years ago, Wohlfarth[27] gave an interpretation of measurements of the magnetic susceptibility and of the specific heat of pure Pt in which it was suggested that the number of holes in the d band was in the vicinity of 0.2–0.3. The number of electrons in the s band would then be expected to lie in a similar range. A recent treatment of the Knight shift in Pt by Clogston *et al.*[28] also indicates an s band filling in this range. Thus there is reasonable agreement between these results for the s-band filling in Pt and the result obtained here. A much higher value of 0.58 for this s-band filling has been suggested by Budworth, Hoare, and Preston[29] from a rigid-band-model interpretation of their specific-heat measurements on platinum-gold alloys. Perhaps estimates of the band filling of pure Pt may be derived more easily from investigations of the pure or nearly pure metal as in the work of Wohlfarth,[27] Clogston *et al.*,[28] or from the results reported here, than from a rigid-band-model interpretation of the properties of concentrated alloys.

For the case of Au in Ag, Fig. 6, our experimental isomer shift lies about 30% below the theoretical curve. For the case of Au in Ni at an $\eta_A=0.6$, the experimental result lies about 60% higher than the theoretical curve. The agreement between theory and experiment for the case of Au in Ag could be made to appear better by changing the normalization constant to a somewhat lower value near $G_A=7.0$ mm/sec. The experimental results for both Au in Ag and Au in Cu would then lie almost within their experimental error of the theoretical curves and the results for the s-band filling in Pd and Pt would be very little changed. On the other hand the disagreement between theory and experiment for Au in Ni would be somewhat worse. In our calculation of the isomer shift from the electrical resistance, ferromagnetism of the host was not taken into account in any way. We find a reasonable agreement between theory and experiment for the paramagnetic or nonmagnetic cases but not where ferromagnetism occurs. As was observed earlier, $\Delta\rho/c$ for Au in Ni is strongly temperature-dependent. While this temperature dependence must be due mainly to magnetic scattering, it is not absolutely clear that $\Delta\rho/c$ at $T=0$°K gives a useful measurement of the transport cross section associated with the Au impurity in the context of our model.

Figure 3 gives $\Delta\rho/c$ for Au in Fe. We have used this measured $\Delta\rho/c$ at 4.2°K in a calculation of the above type to estimate the isomer shift. We do not present this calculation here, however, since the relatively very large $\Delta\rho/c=3.1\mu\Omega$ cm/at.% implies that a bound state may exist on the Au for Au in Fe. For the present we prefer not to extend the model of Sec. III to include bound states.

Turning to Fig. 7, we may now investigate the comparison between experiment and the theoretical model for the case of a repulsive potential. With theory and experiment again normalized for Au in Cu we find $G_R=-31$ mm/sec. Here, however, for Au in Ag, Pd, and Pt the theoretical values for $|v_I|$ are all greater than for Au in Cu while the experimental values are all less. There is no agreement for these cases between theory and experiment for any value of the s-band filling η_A. In the case Au in Ni, theory and experiment still do not agree at $\eta_A=0.6$ although the disagreement in this case is less servere than for the attractive potential Fig. 6. Considering all of these cases, the use of a repulsive well in the above calculation is not consistent with experimental results.

The results presented in Fig. 6 thus indicate that in Au alloys or compounds where v_I is greater than zero, the electron probability density near the gold nucleus is greater than that density in pure gold, $(\rho_B'(0)-\rho_B(0))>0$. This result is in agreement with the conclusion of Mott[8] that gold when alloyed in silver should present an attractive potential to valence-band electrons. From a study of the correlation between the isomer shift of gold in a variety of alloys with the electronegativity difference between gold and the host metal, Shirley *et al.*[11] have also concluded that $v_I>0$ corresponds to $(\rho_B'(0)-\rho_B(0))>0$. We note from Eq. (1), in agreement with Shirley *et al.*, that with $(\rho_B'(0)-\rho_B(0))>0$ one has $(\langle r^{2\sigma}\rangle_e-\langle r^{2\sigma}\rangle_g)>0$. This result is in agreement as to sign with the description of ^{197}Au given by Zeldes[30] using the shell model.

It is important to note that we have not given here a calculation of the charge distribution over the whole gold atom but only of $\rho_B(0)$. The methods of Sec. III could be extended to do this, but we defer this calculation until further isomer shift measurements associated with both the host as well as the impurity atom are available.

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In the use of the theoretical model given above to describe the isomer shift, the range of the pseudopotential was taken to be the radius of a gold atom. Strictly, this assumption is not required in the theoretical model. We have thus repeated the calculation for an R of $0.25r_B$, $0.50r_B$, $0.75r_B$, and $1.25r_B$. The best correlation between isomer shift and residual resistance was found for the case presented in detail, namely $R=r_B$.

All of the available information, as discussed above, is in agreement with the conclusion that $v_I>0$ corresponds to $(\rho_B'(0)-\rho_B(0))>0$. The use of our theoretical model gives a direct quantitative relation between v_I and the electronic charge density at the nucleus through the constant G_A. For example, taking $G_A=8.0$ mm/sec we note from Eq. (32) that the measured value[13] $v_I=7$ mm/sec in the alloy AuAl_2 would correspond to $\rho_{\mathrm{AuAl}_2}(0)/\rho_{\mathrm{Au}}(0)=1.88$. Thus a reliable value for G_A combined with measurements of v_I would be useful in obtaining information about gold wave functions in alloys and compounds. The calculation gives good agreement with experiment but this agreement will certainly be model dependent in some degree. Thus, before making extensive applications of isomer shift measurements to obtain information about wave functions for gold it is important to further investigate the value for the constant G_A. One way to do this would be the measurement of v_I as a function of pressure for pure Au. If one assumes that $\rho_{\mathrm{Au}}(0)$ due to the conduction band is inversely proportional to the atomic volume, using the compressibility of Au as 5.8×10^{-7} cm^2/kg and $G_A=8.0$ mm/sec one obtains $v_I=0.005p$ mm/sec, where the pressure p is in kilobars. A measurement of this type may be feasible and would be helpful in gaining a better understanding about size changes of the gold nucleus and about the wave functions of gold in alloys and compounds. It also appears possible to improve the calculation of the charge polarization factor $\bar{P}$, in particular through a better treatment of the impurity potential.

Note added in proof. The residual electrical resistance values we have obtained (Fig. 3) are in agreement with values in the literature for Au in Cu, Ag, Pd, and Pt, but we have found no previous measurements for $\Delta\rho/c$ for Au in Ni. Recently, we have made additional resistance measurements on two commercially prepared samples containing 1/2 and 1% Au in Ni. These new values agree with each other, but lie considerably lower than our previous values of $\Delta\rho/c$ for Au in Ni (Fig. 3), which were obtained from measurements on three NiAu samples. In view of this, the results of Fig. 3 for $\Delta\rho/c$ for Au in Ni may not be correct, and the comparison of the theoretical isomer shift for Au in Ni with the measured value must await further resistivity measurements.

It has been observed in many laboratories that the residual resistivity of a given impurity may depend appreciably upon other incidental impurities present.

APPENDIX: THE CHARGE TO BE SCREENED

When the host and impurity atoms have different sizes, the alloy lattice will be distorted. The Friedel[6] sum rule involves the change, produced by introducing one impurity atom, in the total charge within a sphere about the impurity. The sphere, of volume V, must be large enough that the conduction-electron wave functions take their asymptotic forms. If one considers only the scattering from the one impurity atom, and regards the crystal as being of infinite extent, then one may choose V to be as large as one likes. If there are other scattering processes in the crystal, however, such as phonon scattering or scattering from other impurity atoms, then the phase shifts entering into the Friedel sum rule will cease to describe the wave function after the electron has traveled a distance of the order of a mean free path from the impurity atom in question.

Seitz[31] has established that a center of dilatation of strength s, that is, for which a small sphere about the center of dilatation is increased in volume by $4\pi s$, produces a change in the volume of an elastic solid of finite extent by an amount $\Delta\Omega=\gamma\ 4\pi s$. Here γ is defined in terms of Poisson's ratio σ by $\gamma=3(1-\sigma)/(1+\sigma)$ and is about 1.5 for most metals. That the solid as a whole expands more than the region in the vicinity of a center of dilatation is associated with maintaining a stress-free surface.[32] A rough calculation[33] of the elastic field about a center of dilatation indicates that the change in volume of a sphere of radius of the order of a mean free path is very nearly $4\pi s$. The additional expansion $(\gamma-1)4\pi s$ occurs predominantly at much greater distances from the center of dilatation. Consequently the volume of host material which is pushed out of a "Friedel sphere" of radius of the order of a mean free path or less is $\Delta\Omega/\gamma$, where $\Delta\Omega$ is the volume change per impurity atom. If $f=N_{\mathrm{imp}}/N$ is the atomic fraction of impurities in an alloy and the change in lattice parameter is $\Delta a=(\delta a)f+0(f^2)$, then the volume of material which passes through a Friedel sphere, per impurity atom, is

$$\Delta V=-\frac{1}{\gamma}\frac{(a+\Delta a)^3-a^3}{N_{\mathrm{imp}}}=-\frac{3}{\gamma}\frac{\Omega}{N_{\mathrm{imp}}}f\frac{\delta a}{a}=-\frac{3}{\gamma}v_A\frac{\delta a}{a}. \tag{A1}$$

The charge to be screened per impurity atom is therefore

$$Z=(\eta_B-\eta_A)-(3/\gamma)(\delta a/a)\eta_A. \tag{A2}$$

This derivation is for the case of only one impurity atom in the crystal. It makes use of experimental information on volume changes at finite concentration only to obtain $\delta a/a$, for which the expansion of the lattice resulting from one impurity atom can be inferred. The argument does not require the assumption that elasticity theory gives the correct volume of the impurity cell.

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