of Eqs. (A8) and separated into constant and time-dependent parts, the correlation function can be written

$$G(\tau) = \langle \mu_p \rangle^2 + (\langle \mu_p^2 \rangle - \langle \mu_p \rangle^2) e^{-\tau/\rho} . \qquad \text{(A9)}$$

The brackets $\langle \, \rangle$ in Eq. (A9) signify the statistical mechanical expectation value. The relationship $1/\rho = W\uparrow + W\downarrow = W(e^{-x}+1)$ was used in obtaining (A9). It is evident from (A9) that the correlation time τ_c is equal to the spin-lattice relaxation time ρ. The spectral density is defined as

$$J_z(\omega) = \int_{-\infty}^{\infty} d\tau \, e^{i\omega\tau} \, G(\tau).$$

Thus

$$J_z(\omega) = \langle \mu_p \rangle^2 \, 2\pi\delta(\omega) + \frac{(\langle \mu_p^2 \rangle - \langle \mu_p \rangle^2) 2\tau_c}{1+\omega^2\tau_c^2} . \qquad \text{(A10)}$$

The methods used here to find $G(\tau)$ and $J_z(\omega)$ for spin-$\frac{1}{2}$ particles can be applied to any spin. However, the solutions for higher spins become more complicated as more equations are involved [e.g., Eq. (A3) would have $2S+1$ equations].

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Charge Screening of Impurities in Gold Observed by the Mössbauer Isomer Shift

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The isomer shift of Au^{197} in Au-Hg alloys containing up to 12% Hg has been measured. The change produced by the Hg is extremely small, five times smaller than that produced by any solute studied previously. This result is compared with those in other gold alloys and compounds. A microscopic theoretical calculation based on a partial-wave model is successful in explaining this anomaly.

I. INTRODUCTION

The isotope Au^{197} has been extensively used in Mössbauer-effect research in a wide range of systems. The two areas of research that have been investigated most intensively are the magnetic hfs of the gold nucleus produced by the hyperfine field (coming primarily from a contact interaction resulting from conduction-electron polarization) occurring in compounds of gold with magnetic atoms[1-3] and gold dissolved in magnetic metals,[4-6] and the "isomer shift," which determines the total electronic density at the gold nucleus.

Gold has been a widely used material for isomer-shift studies for two reasons: First, there is a large body of information on gold chemistry and metallurgy, so that there are large families of well-established materials which can be studied. Second, the strong Mössbauer absorption and large range of observed isomer shifts (about five times the experimental linewidth) make it relatively easy to make meaningful measurements on all of these gold-containing systems.

A detailed analysis of the isomer shift in insulating gold compounds has recently been given.[7] The extensive work done previously in metallic systems can perhaps best be characterized in terms of increasing sophistication as both experimental and theoretical techniques developed. Almost ten years ago, an extensive study was performed on the isomer shift of gold dissolved as a dilute impurity in a wide range of metallic hosts.[8] The conclusion of that work was that a correlation could be obtained between isomer shift and electronegativity of the host, suggesting that the increased isomer shift (corresponding to increased s-electron density at the gold nucleus) resulted from the less-electronegative hosts giving up electrons to the gold ion.

Since that time, a number of papers on the isomer shifts of gold in a wide range of transition-metal alloys (both ordered[1,2] and disordered[2,5]), and of gold with other noble metals,[9] have been published. The theoretical interpretation has ranged from qualitative discussion based on the rigid-band model[5] to a detailed analysis[10] of the electronic band structure of the alloy, invoking other measured parameters of the system. Chekin[11] had some success in explaining the isomer shift of gold dissolved in other metals in terms of the Goodings-Mozer model.[12]

All of the work on dilute alloys referred to above has been done on systems in which the gold was a dilute impurity in the host. As far as we know, this work is the first measurement and analysis in which small amounts of impurities have been added to gold, and their effect on the gold isomer shift determined. This difference is extremely important in the theoretical analysis of the results, since the isomer shift measured at a solute atom is a combination of two effects: the effect of the impurity on the host electronic wave functions (this is usually the parameter which is of interest), and the (unknown) effective potential at the "test" ion, which determines the amplitude of the conduction-electron wave function at the solute nucleus. The extra degrees of freedom allowed by the undetermined effective potential restrict the information that can be obtained from the theoretical analysis. In doing work on a system in which the gold is the *host*, we can measure directly the *change* in host wave functions resulting from adding impurity atoms without making detailed assumptions about the effective potential at the gold ion. This reasoning was the major impetus for both the experimental and theoretical work described below.

II. EXPERIMENTAL TECHNIQUES AND DATA ANALYSIS

Gold is a widely used Mössbauer isotope, and the details of experimental arrangements have been published.[2,5] In our experiments, the source was Au^{197}:Pt, produced by the β decay of 27-h Pt^{197}. The radioactive platinum was produced by the neutron irradiation of Pt foils enriched to 54% in Pt^{196}. The foils contained 5 mCi of Pt^{197} when freshly irradiated, and were used without annealing. The 77.345-keV γ rays were detected by a germanium solid-state detector, and the detector output was put through a standard nuclear counting system, with rates of ~ 20 kHz obtained with a fresh source.

Preparation of the Au-Hg alloys is much more difficult than one would expect, and was done essentially by the technique of Rayson and Calvert.[13] Appropriate amounts of gold and mercury were sealed in evacuated thick-walled quartz tubes. The samples were then heated for one week at 350 °C and one week at 550 °C to allow the mercury to be at least partially absorbed by the gold without creating unduly high pressure. Following this treatment, the samples (still sealed in their tubes) were melted. To ensure uniformity, the samples were given a final annealing in their tubes for 3 days at 550 °C. The lumps created in the alloying process were rolled to foils of about 150-μm thickness to form the absorbers. Since all our alloys were below the room-temperature solid solubility limit of mercury in gold, they were not annealed after rolling. After the Mössbauer experiments were done, the mercury content was determined both by wet chemistry and distillation; both analyses were in agreement.

The Mössbauer spectrometer used was of the constant-acceleration type, and has been described in detail in the literature.[14] Data were accumulated in a multichannel analyzer in the "time (multiscaling) mode." Both the source and absorber were maintained at about 21 K during the measurement to obtain a large recoil-free fraction. The drive motion was brought into the Dewar through a bellows using a glass pushrod; the source was cooled through a flexible reed. Some of the Mössbauer spectra obtained are shown in Fig. 1. The isomer-shift change produced by the Hg alloying is seen to be extremely small; the entire range of shifts measured here is only 1% of the experimental linewidth. Least-squares fitting of a single Lorentzian line to the data gave the isomer shifts shown in Fig. 2 for the various samples, and linewidths of about 2.7 mm/sec for all of the samples including the 150-μ gold foil used as a standard. This broadening over the natural linewidth of 2 mm/sec can be fully accounted for by saturation (thickness) effects.[5]

Because the isomer-shift changes are so small, there are three corrections normally ignored which we consider here: First, the interaction of an anisotropic recoil-free fraction with unresolved hyperfine structure (generally known as the Goldanskii-Karyagin effect)[15] can lead to shifts of a small fraction of a linewidth. This should be negligible in our case, both because the (fcc) lattice should have no anisotropy and the sharp lines obtained show that unresolved hf interactions are very weak.

The second-order Doppler shift[16] due to the zero-point motion is dependent on the effective Debye temperature,[17] which is altered by adding Hg to the lattice. If the addition of 10-at.% Hg raises the Au effective Debye temperature from 180 to 200 K, the resulting change in second-order Doppler shift (evaluated at $T = 0$ K) is -0.0015 mm/sec, which can be neglected.

The dilatation of the lattice due to the Hg, however, is a significant effect. It has been shown[18] that changing the lattice constant of gold (by pressure) changes the isomer shift by $-0.2\ \mathrm{mm\,sec^{-1}}$ for a 1% increase in the lattice constant, and this should be considered since the addition of Hg changes the lattice constant by $\delta a/a = 0.062\%$ per at. % concentration of impurity. This at first appears to be an enormous effect compared to the shift shown in Fig. 2, but is greatly reduced by the following considerations: Since the isomer shift is observed at the gold nuclei, we must consider only the dilatation suffered by the gold atoms. It is shown by Eshelby[19] that even though the strain field around an impurity in an infinite host is dilatation free, the introduction of a stress-free finite boundary gives rise to a strain which has a dilatation component. The change in volume of the matrix is the quantity called ΔV_I in Ref. 19 and is given by

$$\Delta V_I = \Delta V(\gamma_E - 1)/\gamma_E = 0.174\Delta V\ ,$$

where $\gamma_E = 3(1-\sigma)/(1+\sigma)$, and σ is Poisson's ratio, 0.42 for Au. The total volume change upon alloying is ΔV. Hence, $\delta a/a$ for the gold atoms is $0.174 \times \delta a/a$ lattice. The change in isomer shift due to this dilatation is

$$\delta I_S = -6.1\Delta V_I/V\ \mathrm{mm/sec}. \tag{1}$$

Thus, for $c = 10\%$ Hg, $(\delta I_S)_{\rm dil} = -0.022$ mm/sec, and this correction must be subtracted from the measured change of $+0.021$ mm/sec. Thus, the correction for the dilatation of the gold lattice roughly doubles the size of the effect observed, and the adjusted value is shown in Fig. 3.

III. THEORY

Before considering the detailed analysis of the data presented above, it is useful to discuss some of the more general theoretical background. The isomer shift of gold as an impurity in various metals has been found to be larger than that of gold metal.[8] This has usually been interpreted by saying that gold is the most electronegative of all metallic elements and hence tends to attract electrons away from other atoms. This is entirely plausible as there is no reason why in an alloy the different types of atoms should be electrically neutral; in fact, the opposite may be expected, depending, for instance, on the ionization energies of the constituents.[20] Screening considerations are not inconsistent with this atomic charge transfer as long as it remains reasonably localized. In other words, a short-range transfer of charge between different kinds of atoms is consistent with long-range screening, a fact which has been known for a long time.[21] The results of the assumption of complete charge transfer are easy to calculate in the free-electron model: Since Au has a 6s configuration and Hg a 6s^2, each replacement of an Au atom by an Hg atom adds one 6s electron. If this electron is assumed to go entirely into the conduction band with the same character as the pure-gold electronic states, a change of $0.08\ \mathrm{mm\,sec^{-1}/at.\%}$ Hg results[22]; this is roughly 20 times larger than the observed value (see Fig. 2). This complete failure of the free-electron model to explain the observed result is not surprising. The reason is that of all divalent metals, Hg is the one whose ion-core size and charge density are closest to that of Au, hence the difference in their respective ionic potentials is closest to that of a unit charge. In this case, screening requires the extra electron to remain mostly localized on the Hg atom, as other recent experimental results suggest.[23]

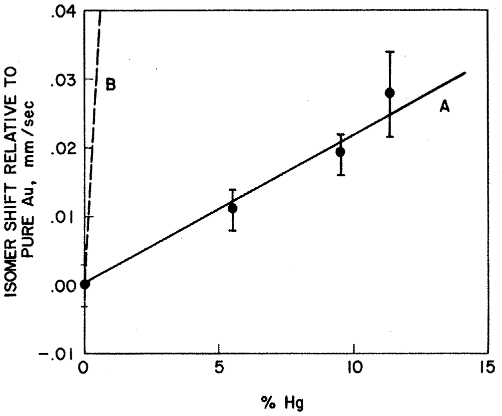

FIG. 2. Isomer shift of Au-Hg alloys as a function of Hg concentration. The line *A* is fitted to the data points shown. The line *B* has the slope that would be expected if the free-electron model were correct.

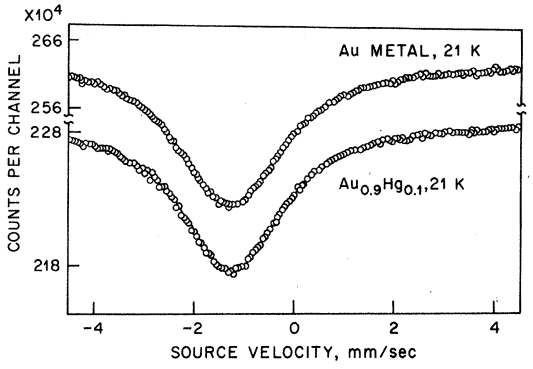

FIG. 1. Spectra of the pure gold and 10% Hg samples. The Lorentzian least-squares-fit line is obscured by the points.

We have analyzed the results in terms of scattering phase shifts, using the Friedel sum rule and the measured residual resistivity as constraints on the phase shifts. This approach is exactly the one developed by Roberts *et al.*[10] for the analysis of the isomer shifts of gold as an impurity in other

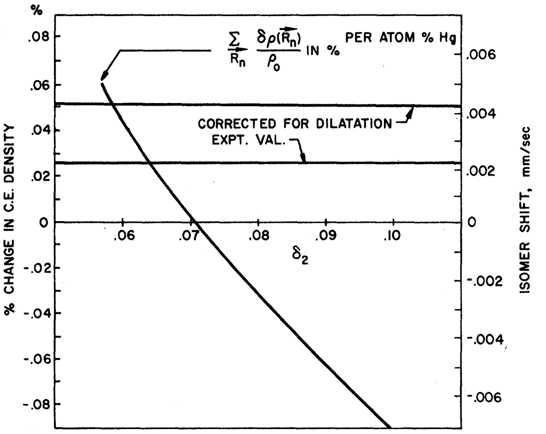

FIG. 3. Plot of Eq. (9), with δ_2 as a parameter. The termination of the curve near $\delta_2 = 0.06$ is the end of the range of real solution for Eqs. (3) and (4). The experimental value of isomer shift is also shown, with and without the dilatation correction [Eq. (1)].

metals. There is a difference in the application of the technique, though, since the fact that we are looking at the *host* isomer shift allows us to eliminate the extra uncertainty of the "well parameters" in the earlier work. This allows us to consider *s*, *p*, and *d* phase shifts, which not only provide a more realistic analysis than that used for the gold-impurity case, but are absolutely necessary in our case to provide real solutions for the phase shifts (see Sec. IV).

We find that the observed change in the isomer shift is consistent with calculations on this model provided the *d* phase shift is of the order of 0.06. In the analysis we have used the asymptotic expressions for the displaced charge in a region where this approximation is of questionable validity, namely, at the nearest neighbors. In spite of this limitation, the calculation is successful in accounting for the experimental results. We intend to further test it by making measurements with other divalent impurities and by refining the analysis if the need arises.

IV. ANALYSIS

We shall calculate the change δI_S of the isomer shift of the host that is due to the perturbation of the conduction band by the mercury impurities. The calculation has three parts: The scattering phase shifts due to the Hg impurity atoms must be found; the change in charge density due to the scatterer must be found as a function of distance; and the total charge density must be determined by summing over all the nearby scattering centers.

As is well known,[24,25] the modifications of the Bloch state by the scattering of the impurities give rise to inhomogeneities in the charge distribution, the so-called "Friedel oscillations." In a free-electron approximation, the local relative deviation of the charge density at a distance r from the impurity is given by the expression

$$\frac{\delta\rho(\vec{r})}{\rho_0} = -\frac{3}{2}\,\frac{1}{(k_F r)^3} \sum_l (-1)^l (2l+1) \sin\delta_l \cos(2k_F r + \delta_l) , \tag{2}$$

where k_F is the Fermi wave vector, $\rho_0 = k_F^3/3\pi^2$ is the charge density of the electron gas, and the δ_l are the phase shifts of partial wave l at the Fermi level. Knowledge of the δ_l is then sufficient for the determination of the charge density at all the lattice points and hence for the determination of the mean change of the isomer shift δI_S.

The fact that the conduction-band states are Bloch waves instead of plane waves has been taken into account by Kohn and Vosko[24] {see their Eq. (2.17); note that $u_{\vec{k}}(0)$ is real with their phase convention that $[u_{\vec{k}}(0)]^2 = |u_{\vec{k}}(0)|^2$}. If we make the crude approximation that the charge density at the nucleus $|u_{\vec{k}}(0)|^2$ is independent of $\vec{k}$, then the right-hand side of Eq. (2), evaluated at lattice sites $\vec{R}_n$ will give the relative charge-density change in the real alloy since the $|u_{\vec{k}}(0)|^2$ will cancel out in the ratio. This approximation will overestimate $\delta\rho/\rho_0$ for given values of δ_l, perhaps by a factor of 2,[26] as $|u_{\vec{k}}(0)|^2$ is expected to be largest at the bottom of the band where the s character is largest.

To calculate $\delta\rho/\rho_0$, we need the phase shifts. We will not attempt to calculate them from first principles but instead will make use of the Friedel sum rule and the known residual resistivity[25] to determine them from experiment. (We are not aware of any other existing measurements on AuHg that would give more relations between the phase shifts.) Our two conditions are

$$\textstyle\sum_l (2l+1)\,\delta_l^{(0)} = \frac{1}{2}\pi , \tag{3}$$

$$\Delta R = (0.417/r_s)(\sigma_0 + \Delta\sigma + \sigma_1)\ \mu\Omega\,\mathrm{cm/at.\,\%} . \tag{4}$$

Equations (3) and (4) are Béal-Monod and Kohn's[27] result which includes the contributions of the lattice strain to the resistivity. (σ_0 is the cross section of the impurity alone, σ_1 that due to the lattice strain alone, and $\Delta\sigma$ that due to the interference of the scattering amplitudes.) In our case, σ_1 is negligible but $\Delta\sigma$ is not. The expressions for σ_0 and $\Delta\sigma$ are

$$\sigma_0 = (4\pi/k_F^2) \textstyle\sum_l (l+1) \sin^2(\delta_l^{(0)} - \delta_{l+1}^{(0)}) , \tag{5}$$

$$\Delta\sigma = (4\pi/k_F^2) \textstyle\sum_l (l+1)(\delta_l^{(1)} - \delta_{l+1}^{(1)}) \sin 2(\delta_l^{(0)} - \delta_{l+1}^{(1)}) . \tag{6}$$

$\delta_l^{(0)}$ and $\delta_l^{(1)}$ are, respectively, the phase shifts due to the impurity atom and the displaced hosts atoms. The quantities k_F^2 and r_s in Eq. (4) are to be expressed in a.u.; their values for gold are $k_F^2 = 0.41$ and $r_s = 3.03$. The value of the residual resistivity according to Linde[25] is 0.44 $\mu\Omega$ cm/at.%. The values of $\delta_l^{(1)}$ depend on the lattice constant of the host (through the dielectric constant), on $\delta a/a$, the fractional change in the lattice constant per unit impurity concentration, and on the quantity $\gamma_E = 3(1-\sigma)/(1+\sigma)$ defined in terms of Poisson's ratio σ.

We have made use of the values of $\delta_l^{(1)}$ calculated in Ref. 27 [see their Eq. (4.27)] for Cu to approximate the values of $\delta_l^{(1)}$ for Au. We have not recalculated the θ dependence of the scattering amplitude $f_1(\theta)$ [see Ref. 27, Eq. (4.18)] that arises from the fact that the lattice constant of Au is about 10% larger than that of Cu. This correction is small. We have, however, multiplied $f_1(\theta)$ by the ratio $(\gamma_E)_{\mathrm{Cu}}/(\gamma_E)_{\mathrm{Au}}$ which is about 1.2.

Equations (3) and (5) now contain only the unknowns $\delta_l^{(0)}$. Since we have two conditions, the simplest thing to assume is that only two phase shifts (s and p) are important. This has often been done in the past as a means to extract information from the residual resistivity. However, if we try to determine $\delta_0^{(0)}$ and $\delta_1^{(0)}$ using the measured ΔR, we find that there are no real solutions. (For divalent impurities, ΔR would have to be larger than 1.2 $\mu\Omega$cm for this to be possible; see Ref. 24, p. 915.) The impossibility of accounting for $\Delta\rho$ in terms of $\delta_0^{(0)}$ and $\delta_1^{(0)}$ alone is understandable and even satisfying: Because of hybridization, the d shell of a noble metal is not quite full. However, on the divalent impurity the d shell is much deeper and must be essentially filled. Small, but nevertheless important [because of the factor $(2l+1)$ multiplying $\delta_l^{(0)}$ in the Friedel sum rule], $\delta_2^{(0)}$ is thus necessary to fill the d holes on the impurity. It is estimated[28] that in Cu there are about 0.3 d holes. In Au, because the d band is closer to the Fermi level, this number is probably larger. It is thus not possible to ignore the d phase shift.

We have assumed that only the first three phase shifts are nonzero and have determined $\delta_0^{(0)}$ and $\delta_1^{(0)}$ for a range of $\delta_2^{(0)}$ values, starting from the smallest one for which a solution to Eqs. (3) and (4) exist (for $\Delta R = 0.44$ $\mu\Omega$cm/at.%, this is $\delta_2^{(0)} = 0.057$), up to $\delta_2^{(0)} = 0.10$. The corresponding values of $\delta_0^{(0)}$ and $\delta_1^{(0)}$ are given in Table I.

The fractional change in isomer shift predicted by the asymptotic expression (2) for an atomic concentration c of Hg is

$$\frac{\delta I_S}{I_{S0}} = c \sum_{\vec{R}_n} \frac{\delta\rho(R_n)}{\rho_0} , \tag{7}$$

where I_{S0} is the isomer shift resulting from the conduction electrons in pure gold. Defining the sums

$$S_c = \sum_{\vec{R}_n} \frac{\cos 2k_F R_n}{(k_F R_n)^3} \simeq 0.265 , \tag{8}$$

$$S_s = \sum_{\vec{R}_n} \frac{\sin 2k_F R_n}{(k_F R_n)^3} \simeq 0.122 ,$$

we have

$$\sum_{\vec{R}_n} \frac{\delta\rho(R_n)}{\rho_0} = -\tfrac{3}{2} \sum_l (-1)^l (2l+1) \times (S_c \sin\delta_l \cos\delta_l - S_s \sin^2\delta_l) . \tag{9}$$

Equation (9) is plotted on Fig. 3 for the values $\delta_l^{(0)}$ given in Table I.

There is an ambiguity at this point about whether one should use $\delta_l^{(0)}$ or $\delta_l^{(0)} + \delta_l^{(1)}$ in computing the isomer shift. Clearly at the first-neighbor sites, one should use something very close to $\delta_l^{(0)}$, while further out one should tend toward $\delta_l^{(s)} = \delta_l^{(0)} + \delta_l^{(1)}$. Fortunately, the difference in the values of Eq. (9) calculated with $\delta_l^{(0)}$ and with $\delta_l^{(0)} + \delta_l^{(1)}$ is small and corresponds to a slight shift of the curve downward. We have entered in Table I the values of Eq. (9) calculated with $\delta_l^{(0)}$. To compare $\delta I_S/I_{S0}$ with experimental results, we must assume a value for I_{S0}.[22] Again using $I_{S0} = 8$ mm/sec, the experimental value of $\delta I_S/I_{S0}$ is $0.054c$. From Fig. 3 we see that this corresponds to a $\delta_2^{(0)}$ about 0.06.

In order to assess the validity of the "agreement" between experimental and calculated values, we now list the approximations that went into the calculation:

(i) The use of the asymptotic expression (2) is not justified since most of the isomer shift occurs at the near neighbors.

(ii) The assumed constancy of $|u_{\vec{k}}(0)|^2$ as a function of $\vec{k}$ overestimates the calculated $\delta\rho/\rho_0$.

(iii) Phase shifts for $l = 3$ and higher have been neglected. Even though $\delta_3^{(0)}$ is expected to be quite small, it affects our results in two ways. First, it will contribute a positive term to the sum, Eq.

TABLE I. Values of $\delta_0^{(0)}$ and $\delta_1^{(0)}$ calculated[a] from Eqs. (3) and (4) for a set of values of $\delta_2^{(0)}$.

$\delta_0^{(0)}$	$\delta_1^{(0)}$	$\delta_2^{(0)}$
0.432	0.280	0.06
0.453	0.256	0.07
0.458	0.237	0.08
0.456	0.222	0.09

[a] This set of values of δ_0, δ_1, δ_2 is not the only solution of Eqs. (3) and (4): The residual resistivity of 0.44 $\mu\Omega$cm is sufficiently small that we find that all three δ's must have the same sign. Since the perturbing potential is attractive, we have taken them positive. However, for a given value of δ_2, there are usually two sets of values of δ_0 and δ_1 that satisfy (3) and (4). For one of these, $\delta_0 > \delta_1$, and for the other, $\delta_0 < \delta_1$. We have chosen the set $\delta_0 > \delta_1$ because it seems unreasonable that the Hg impurity would present a potential that is more attractive to the p wave than it is to the s wave.

(9). This term will be small compared to the individual l terms of Eq. (9); however, the net value of Eq. (9) results from a near cancellation of a positive term (from the p phase shift) against the s and d terms, which are negative. Thus, a small positive term from an f phase shift and a decreased negative term from the d phase shift, which now depends on the difference of the d and f phase shifts, will significantly increase the value of $\delta I_S/I_{S0}$. Second, inclusion of $l=3$ modifies the other phase shifts. However, we do not have experimental information to determine them.

(iv) Finally, in computing $\delta\rho(\vec{R}_n)/\rho_0$, we have used the values of $\vec{R}_n$ appropriate to the unstrained lattice. We have verified that for our range of phase shifts, this does not introduce a significant error.

(v) We have neglected the possibility that the effects we observe in the 10% concentration range may be different from those in the dilute (i.e., isolated impurity) case for which the theory is valid. This is supported by the fact that gold alloys normally show a linear relation between isomer shift and composition over the entire range.[10]

In summary, we have attempted to correlate the measured small change in isomer shift due to Hg impurities, with the phase shifts of the conduction band. Although our calculation cannot claim to be exact, we feel that it suggests that a more accurate calculation may further increase our understanding of this complicated subject.

V. DISCUSSION AND CONCLUSIONS

It might at first appear that the agreement obtained between the theory and the experimental result is not meaningful because of the availability of a "free" (i.e., undetermined) parameter which allows the calculated δI_S to vary over a range of values. In fact, there are a number of simple tests which can be applied which suggest that the analysis developed here does indeed have physical significance and is not simply a mathematical construct. The first pertinent observation is that the maximum δI_S that can be calculated from the theory is 0.005 mm sec^{-1} at.%Hg. This fixed limit is imposed by the measured residual resistivity, in combination with the requirement that the phase shifts be real. If the measured value were substantially higher, it would be impossible to explain by the model used here.

The calculation also succeeds in explaining a highly anomalous result: the isomer-shift change produced by alloying mercury is five times smaller than that produced by adding silver to gold, and the many other elements which have been studied as alloying additions all produce still larger isomer-shift changes. The success of our analysis in reproducing the anomalously small effect of mercury could not be reproduced by phenomenological models based on ionic size or electronegativity.

In addition, the relatively small size of the d phase shift and the over-all result which suggests that the extra electron remains well localized on the impurity, conform to our preconceptions of the behavior of such a dilute alloy.

The use of the Mössbauer isomer shift for determining the effects of moderately dilute impurities on host conduction-electron wave functions appears to be a useful technique. The initial success of the theoretical description used above justifies further study, and this is now being carried out in the Au-Cd and Au-Zn systems.

ACKNOWLEDGMENT

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Electric Field Effect in Paramagnetic Resonance for Mn^{2+} in $SrWO_4$

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The electric field shifts in the paramagnetic resonance (EPR) for Mn^{2+} in $SrWO_4$ have been measured to be 104 and 225 for $R_\perp$ and $R_\parallel$, respectively, in units of Hz per V/cm. Comparison is made with the corresponding results obtained earlier for Mn^{2+} in $CaWO_4$. The experimental evidence indicates that the magnitude of the shifts depends on the ease with which the Mn^{2+} ion is displaced by the applied electric field, i.e., on the looseness of the ion in its substitutional site. In an earlier study involving the Yb^3 ion in the same host lattices, it was found that "ionic-motion" effects of this kind could be explained in terms of new even crystal field components seen by the displaced ion. In the present case, however, the observed magnitudes were too large to be attributed to the motion-induced crystal field components. The polarization of the Mn^{2+} ion induced by the applied field appears to be the primary mechanism giving rise to the electric field EPR shifts; the ease of ionic displacement of the impurity ion entering into the result insofar as it enhances the magnitude of the electric field is actually seen at the Mn^{2+} site. This result is especially surprising in view of the fact that in the previous Yb^{3+} study, we found that polarization effects of the larger and better-fitting Yb ion were, by and large, negligibly small. It is suggested here that the classification of electric field effects as ionic or electronic is liable to be misleading and that it is more appropriate to distinguish electric shifts which involve odd-even–state interactions from those which do not. In either case, motion of the ions will play an important role.

I. INTRODUCTION

In a recent study[1] of the electric field *g* shifts for Yb^{3+} in the series of scheelite lattices $CaWO_4$, $SrWO_4$, and $BaWO_4$, we found evidence that the shifts were due primarily to an electric-field-induced motion of the Yb^{3+} ion in their substitutional sites. This movement was larger than the movement of the cations in the normal scheelite lattice and was strongly dependent on the ratio between the size of Yb^{3+} and the size of the ions (Ca^{2+}, Sr^{2+}, and Ba^{2+}) replaced by it. This increased motion of the substituent ion was due in part to the extra positive charge of Yb^{3+}. The principal reason lay, however, in the considerable reduction in the short-range repulsive forces which occurs when a smaller loose-fitting ion is substituted for a larger ion in a crystal lattice.

These results have prompted us to reconsider the interpretation of an earlier set of experiments[2] in which the paramagnetic electric shifts of Mn^{2+} in $CaWO_4$ were measured. We have also made new measurements on the electric shifts of Mn^{2+} in $SrWO_4$ in order to find out whether the same pattern of behavior would be followed in this case as in the parallel case of Yb^{3+}. Unfortunately we were not able to extend the comparison to the case of Mn^{2+} as a substituent for Ba^{2+} because of the dominant tendency for Mn to form $(MnO_4)^{2+}$, $(MnO_4)^{3+}$ ions in the $BaWO_4$ lattice. This would otherwise have constituted an interesting case since calculations suggest that the Mn^{2+} ion should become unstable and switch to off-center positions[3] here.

The spectroscopic interpretations of the paramagnetic electric shift for Mn^{2+} (an *S*-state ion) and for Yb^{3+} (a Kramers-doublet ground state) are different in detail, but the results confirm our earlier conclusion that the magnitudes are essentially proportional to the elastic restoring forces which act on the ions in the different lattices. However, we