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ABSTRACT

Isomeric chemical shifts were observed in the Mössbauer spectra of Au^{197} atoms in dilute solutions in nineteen metals and semiconductors at 4.2°K . The shifts were interpreted as arising from transfer of (conduction) electrons in the 6s shell of gold, probably toward the gold atom, in the alloys. A correlation was found between the shifts and the host electronegativities. The relationship between the 6s electron of gold and the nickel d bands in gold-nickel alloys is discussed. It is shown that the ground and first excited nuclear states of Au^{197} have radial charge moments sufficiently different (the excited state is probably "larger") to require collective nuclear excitation. The isomeric shift in Al_2Au does not directly confirm the electroneutrality hypothesis for intermetallic compounds.

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I. INTRODUCTION

The chemical properties of binary alloys and intermetallic compounds constitute one of the most empirical areas of modern physical chemistry. The great majority of studies which have been reported deal with criteria for existence of solid solutions on the theoretical side or with phase diagrams on the experimental side. Although some theoretical work has appeared discussing the nature of intermetallic bonds or the configurations of conduction electrons in alloys, there are very few experimental data available bearing on these subtler problems. The reason for this situation seems to be the inapplicability to alloys of most of the spectroscopic techniques which have elucidated the bonding structures of ions and molecules.

On an atomic scale the most basic type of information about a single-phase binary solid is the spatial disposition of its constituent atoms. For a stoichiometric intermetallic compound this is simply the crystal structure, and one may draw inferences about intermetallic bonding from such parameters as internuclear distances and coordination numbers. Such information is usually obtained by x-ray diffraction techniques, which are often not applicable to very dilute alloys. Even in favorable cases the atomic positions

alone cannot fully characterize the states of bonding electrons in systems for which so little theoretical guidance is available. Thus independent measurements of other parameters are vitally needed to stimulate any real progress in this area.

Nuclear resonance experiments, which may yield the electric monopole, magnetic dipole, and electric quadrupole moments of an atom's electron distribution (evaluated at the nucleus) are in principle capable of extending considerably our understanding of the metallic bond. The two types of nuclear resonance, magnetic (NMR) and recoil-free (Mössbauer), are somewhat complementary, with neither having a very wide range of applicability as yet. Recoil-free resonance gives a direct measure (within a sometimes uncertain scale factor) of the difference between the electron densities at the nuclei of sources and absorbers via the isomeric chemical shift, while a less direct determination of this (monopole) moment of electron density is given by NMR via the Knight shift, which is really a magnetic effect.

In this paper we report a systematic survey, using Mössbauer resonance, of the isomeric chemical shifts experienced by Au¹⁹⁷ atoms in very dilute solution in several metallic hosts. With some interpretation the increase in electron density on the Au solute atoms may be calculated in each case. The magnitude and direction of electron transfer is correlated with the electronegativity of the host metal.

II. EXPERIMENTAL

A. Apparatus

Two spectrometers, described briefly elsewhere,^{1,2} were used in this work. They were intercalibrated and several shifts were measured in each instrument. Calibration against an Fe⁵⁷-in-iron spectrum³ gave a velocity scale with an absolute accuracy of 2%. The sources and absorbers were always within one degree of the helium boiling point, 4.2°K.

B. Samples

The γ -ray source was the 77-keV isomeric state of Au¹⁹⁷ ($t_{1/2} = 1.9$ nsec), populated in the decay of Pt¹⁹⁷ ($t_{1/2} = 18$ hours), which was produced by thermal neutron irradiation of isotopically enriched Pt¹⁹⁶. Preparation of an alloy source consisted of dissolving the irradiated platinum in the (molten) host metal in an argon atmosphere. After the melt had been held at a temperature well above the melting point for at least an hour to allow for complete mixing to take place, it was quenched to room temperature within 20 seconds. The sources were thus solid solutions of from 0.2 to 1.0 atomic percent platinum in the host metal. The atomic percentage of gold produced by decay was always less than 10^{-5} ; as gold alloys the sources were very dilute. We estimate that the small amount of platinum present did not alter the shifts more than 1% from the values in the pure host metals. This is well within experimental error. The few data available indicate that isomeric chemical shifts vary linearly with composition in single-phase alloys.⁴ Thus we shall take the data reported herein as representing shifts for gold in the pure host elements. Of course, when alloys are prepared in this manner some assurance is necessary that the platinum has actually dissolved. Such assurance was provided in all cases except one by the absence of resonant absorption at the platinum position.⁵

An absorber of 0.005 inch gold foil was used in the dilute alloy experiments. One experiment was done with an absorber of Al_2Au and a source of metallic platinum.

C. Results

A single absorption region was observed in each of the nineteen hosts investigated. The absorption magnitudes varied from 2 to 11% and the apparent linewidths from 0.26 cm/sec to 0.46 cm/sec on the doppler velocity scale. The theoretical minimum apparent linewidth for a 0.005 inch gold absorber is 0.24 cm/sec and about 40% of the resonant radiation is absorbed. Approximately (60-90)% of the incident radiation in the energy range selected was actually associated with the 77-keV γ -ray.

These survey experiments were designed to yield the isomeric chemical shifts in a large enough number of hosts to reveal any trends. It was not practical at the same time to make sufficiently detailed studies of line shapes to justify derivation of unresolved quadrupole splitting or of recoil-free fractions from the data. The isomeric chemical shifts and percent absorption are given in Table 1. The possible presence of quadrupole splitting is of no consequence in this investigation because such (unresolved) splitting would merely widen the absorption area without changing its mean energy and thus the apparent chemical shift. This result would be more complicated for nuclei with higher spins. For Au^{197} the spins are 3/2 for the ground state and 1/2 for the excited state, and quadrupole splitting thus produces two lines with the same intensity equally spaced from the nominal transition energy.

III. THE SPIN HAMILTONIAN

Recoil-free resonance spectra can be discussed most concisely within the framework of a nuclear spin Hamiltonian. We describe below a procedure for relating the Hamiltonian to the positions of resonance lines.

In the complete absence of hyperfine splitting, and for source and absorber nuclei in identical environments, the resonant γ -ray energy will be (within the recoil energy of a crystallite) just equal to the nominal nuclear transition energy for a bare nucleus in field-free space, $E_1 - E_0$. If the source (absorber) is replaced by one in which hyperfine splittings are present, a complex emission (absorption) spectrum will replace the single line. The absorption pattern will now be that of a complex spectrum scanned with a single line, and will, of course, resemble the complex spectrum.

The effects which produce this complex spectrum are magnetic dipole and electric quadrupole hyperfine structure interactions. Electric monopole interactions, which differ between source and absorber, plus gravitational and temperature shifts contribute terms to the Hamiltonian that shift the whole absorption pattern in energy. The nominal energy and splitting of the nuclear states may be described by appropriate tensors which reduce, in the common case of axial symmetry and vanishing off-diagonal terms, to the form

$$H_0 = E_0' + AM + P [M^2 - I(I+1)/3], \quad 1(a)$$

$$H_1 = E_1' + A'M' + P' [M'^2 - I'(I'+1)/3]. \quad 1(b)$$

The emission spectrum is obtained by substituting all possible values of the magnetic quantum number M and M' into Equations (1) and subtracting, from the resultant energies in Eq. (1b), those in Eq. (1a) which are connected by the transition selection rules. If, for example, the transition is dipolar, there will be components corresponding to the possibilities $\Delta M = 0, \pm 1$. For the $\Delta M = 0$ component, for example, lines will appear at energies

$$E'_1 - E'_0 = (A' - A)M + (P' - P)M^2 + [PI(I+1) - P'I'(I'+1)]/3. \quad (2)$$

Similar equations apply to the other components. Relative intensities are given by the squares of appropriate Clebsch-Gordan coefficients. This approach is easily extended to higher multipolarity transitions.

Specializing now to the isomeric chemical shifts in Au^{197} , we consider only the monopole term which in the usual approximations gives a shift for the excited state of the source⁶

$$E'_1 - E_1 = - (2\pi/5) Ze^2 R^2 \langle X^{2\rho} \rangle_1 \sum_S \psi(0)^2. \quad (3)$$

Here $\langle X^{2\rho} \rangle$ is the 2ρ -th reduced radial charge moment of the excited state, ρ is the relativistic parameter $(1 - a^2 Z^2)^{1/2}$, where a is the fine-structure constant and Z the atomic number, R is the nominal nuclear radius, and the sum is taken over the electron density at the nucleus in the source. We may subtract from Eq. (3) a similar expression for the shift in the ground state of the source to obtain the shift in energy of the emitted resonant γ -ray relative to the nuclear transition energy,

$$(E'_1 - E'_0)_{\text{S}} = (E_1 - E_0) + (2\pi/5)Ze^2 R^2 [\langle X^{2\rho} \rangle_0 - \langle X^{2\rho} \rangle_1] \sum_S \psi(0)^2. \quad (4)$$

A similar equation may be written for the absorber. Resonant absorption occurs when the absorber energy is augmented by a doppler velocity corresponding to the difference between the shifted energy of the source (Eq. 4) and that of the absorber. If we take this velocity as positive for the absorber moving toward the source, the resonant velocity is

$$v = \frac{2\pi c Z e^2}{5(E_1 - E_0)} R^2 [\langle X^{2\rho} \rangle_0 - \langle X^{2\rho} \rangle_1] \left[\sum_s \Psi(0)^2 - \sum_a \Psi(0)^2 \right]. \quad (5)$$

It is this velocity which is directly measured. The first term in square brackets depends only on nuclear, and the second term only on electronic properties. Neither is at present calculable from first principles; often, as in this case, neither can be accurately calculated from other data. In the next two sections we shall attempt to extract these two terms from their measured product.

IV. THE DIRECTION OF ELECTRON TRANSFER

A most fundamental question to settle in isomeric chemical shift studies is the sign relationship, for a given nucleus, between the direction of electron transfer and the observed shift. Nuclear theory is usually not reliable enough to allow calculation of the nuclear factor in Eq. (5) and thus to provide an unassailable answer. For the recoil-free isotopes of some atoms the problem is simply solved because enough is understood about the chemical properties of the elements to calculate reliably the differences between the electron densities at the nucleus in different chemical environments. This is true, for example, for Fe^{57} , because iron has definite, well-understood charge states.

For Au^{197} the problem is much more difficult. Gold does not form strongly ionic bonds, even with fluorine. We cannot turn to hybridization arguments with any confidence, because the simple hybrid pictures which work so well in the first row of the periodic table are not so readily applicable to gold, with its 79 somewhat relativistic electrons. We discuss below the available evidence on the direction of electron transfer in the gold alloys. Two moderately strong, but not completely convincing, arguments indicate that electrons are transferred toward the gold atom in these alloys.

A. The Nuclear Model

Recently Braunstein and de-Shalit⁷ have interpreted the nuclear energy levels of Au^{197} in terms of a "core-excitation" model. The ground state is considered to consist of a paired-nucleon core with positive parity and zero spin, plus a single unpaired $d_{3/2}$ proton. In the 77-keV excited state, the core is excited to a spin-and-parity 2^+ configuration, which

couples to the odd proton to form the observed spin-and-parity $1/2^+$ state. The model explains the observed structure of Au^{197} very convincingly; we shall use it in our interpretation.

The phenomenological calculations on the core excitation model do not provide a detailed picture of the 2^+ core state; thus it is not possible to calculate the nuclear factor in Eq. (5) directly. It is quite probable, however, that the excited core, with its higher spin and greater excitation energy, is larger than the ground-state core, and thus has a larger $2p^{\text{th}}$ radial charge moment. This would yield a negative nuclear factor and comparison with the observed negative shifts in Table 1 implies that the electronic charge density at the gold nuclei in any alloy source is greater than in the gold absorber. Thus from this argument we would infer that electrons are transferred toward gold atoms in these alloys.

B. Electronegativity Arguments

In Section V we discuss the electronegativity-isomeric shift correlation. For purposes of deciding the direction of electron transfer we note that the shifts are correlated with the electronegativity differences between gold and the hosts. The largest shifts occur for the least electronegative hosts, all of which are less electronegative than gold. The natural conclusion from these data is that electrons are transferred toward gold in the alloys.

C. The Nickel d-Bands

The above arguments are qualitative, and there is available at present no satisfactory way to put them on a quantitative basis. The agreement

in sign of electron transfer deduced from these two independent arguments tends to establish confidence in this sign. In the complete absence of any evidence to the contrary it seems probable that gold gains electron density at the nucleus in the alloys. The question is still open, however; a final decision must await more conclusive evidence.

It is somewhat disquieting that the direction of change of electron density at the gold nucleus in Au-Ni alloys is opposite to the accepted direction of electron transfer in Cu-Ni alloys, inasmuch as gold and copper are both in Group 1-B. In Cu-Ni alloys the magnetic behavior is very nicely explained in terms of the Cu 4s electrons filling the Ni d-bands. Roberts and Thomson⁴ have measured the isomeric shift in gold-nickel alloys, and they found a linear variation with composition throughout the composition range, rather than the expected break (by analogy with the Cu-Ni system) at ~60% gold. Thus there seems to be no direct evidence that the isomeric shifts can be accounted for by gold 6s electrons "filling in the d-bands" of nickel.

It still might seem possible that gold 6s electrons could go into nickel d-bands in very dilute solutions, but that the band structure would be disrupted at higher gold concentrations by the presence of the gold atoms, which are quite different from copper atoms. Thus the analogy between Au-Ni and Cu-Ni alloys would not be valid. An experimental test which would preserve the analogy would involve measuring the isomeric chemical shifts for gold atoms in very dilute solutions in Cu-Ni alloys as a function of the Cu-Ni composition. If gold 6s electrons were filling the nickel d-bands the shift should vary monotonically with Cu-Ni composition from pure nickel to about 60% copper (where the d-bands are filled), then remain nearly constant to the pure copper composition. Thus the amount of isomeric shift which

could be attributed to d-band filling, if this were the only important mechanism, would be the difference between the shift in some Cu-Ni alloy which is more than 60% Cu and the shift in pure nickel. We have measured the shifts in pure Cu and pure Ni (Table 1). They are the same within experimental error. We conclude that there is no evidence for gold 6s electrons filling nickel d-bands.

V. A SEMIQUANTITATIVE INTERPRETATION

It would be interesting to derive quantitative values for the changes in electron density on the gold nuclei accompanying the isomeric shifts. Unfortunately it is not possible to separate completely the electronic and nuclear factors in Eq. (5), as would be required. By invoking some rather general arguments we can, however, make a qualitative interpretation of the shifts and set reasonable limits on the electron density changes as well as on the nuclear factor. We treat these separately.

A. The Electronegativity Correlation

In Fig. 1 the isomeric chemical shifts are plotted against host metal electronegativity.⁸ Despite the considerable scatter there is a very strong correlation between the two parameters. This is somewhat surprising in view of the approximate nature of the electronegativity concept and of the number of seemingly important variables which are completely ignored in such a comparison. It is, however, probably more reasonable to expect a correlation in dilute metallic solutions than in molecules, where angular variables and hybridization are relatively more important.

The chemical picture which may be derived from this correlation is straightforward. The less electronegative host elements tend to give up electrons to the gold impurity atom roughly in proportion to their electronegativity differences from gold. The gold atom does not experience discrete oxidation states; rather the electron transfer varies continuously with electronegativity difference with irregularities arising from zone structure, atomic size, and other factors. Eventually the 6s shell must be filled, and

the Pauli principle operates to prevent further electron transfer. Thus, saturation should occur for large electronegativity differences.

An electronegativity range of only about 1.4 units is available using metallic elements as hosts. Still there is some evidence for the onset of saturation. To illustrate this we have plotted in Fig. 2 the averages of the five sets of data points in Table 1 which differ by 0.1 unit or less of electronegativity. Remembering that the correlation which these average points show is fortuitously smooth, we have drawn curves through them and extrapolated to limits which would probably be realized if the 6s electron shell could be filled. Setting wide limits of error commensurate with the uncertainties involved,⁹ we believe that saturation would occur at a shift between 1.0 and 2.0 cm/sec, which is thus the shift that we associate with the transfer of one 6s electron. Thus in the least electronegative hosts such as lithium and calcium we may infer that a gold atom gains nuclear electron density equivalent to 0.4-0.8 6s electrons.

B. The Nuclear Factor

Having established within a factor of two the shift associated with the transfer of one 6s electron, we may estimate the electronic factor in Eq. (5) and compute the nuclear factor. The density of a 6s electron in the nucleus of a free gold atom is given by the equation¹⁰

$$\psi(0)^2 = \frac{Z_i Z_a^2}{\pi a_0^3 n_a^3} \left(1 - \frac{d\sigma}{dn}\right) \quad (6)$$

where Z_i , Z_a , a_0 , n_a and $(1 - \frac{d\sigma}{dn})$ are, respectively, the effective nuclear charge inside and outside the atomic core, the Bohr radius, the effective principle

quantum number, and the Fermi-Segrè factor. For atomic gold we find, using $Z_1 = 79$, $Z_a = 1$, $n_a = 1.21$,¹¹ and $(1 - \frac{d\sigma}{dn}) = 1.424$,¹² a value $\psi(0)^2 = 1.4 \times 10^{26} \text{ cm}^{-3}$ for one 6s electron.¹³ Using this value for the electronic term and the extrapolated velocity shift of $1.0 \rightarrow 2.0 \text{ cm/sec}$ obtained in the previous section we find on comparison with Eq. (5).

$$\Delta \langle X^{2p} \rangle = 0.0039 \pm 0.0013. \quad (7)$$

We have used a nominal radius of 7.0 fermis in this calculation.

This large nuclear factor is possible for a single particle transition only by making the most extreme assumption within the nuclear shell model. If the excited and ground states differed by a proton transition from a $3s_{1/2}$ state to a $1h_{11/2}$ state and the nuclear potential was a square well, the radial moments are just enough different to satisfy Eq. (7).¹⁴ Since such assumptions are not compatible with the isomeric states in question we conclude that the nuclear factor is too large to be accounted for by single-particle excitation and must therefore arise from a collective effect. This factor thus provides support for the core-excitation model.

Some information about the excited core may be derived from the nuclear factor. The details of the core excitation are not known. In order to get a qualitative idea of the amount of collective behavior accompanying this process, we may estimate the magnitude of prolate ellipsoidal nuclear deformation which would produce the same isomeric chemical shifts. Barrett and Shirley¹⁵ have shown, following Wilets, et al.¹⁶ and Lardinois¹⁷, that the shift accompanying a change in deformation $\Delta\alpha^2$ between two isomeric states is given by

$$\Delta E = \frac{2\pi}{5} Ze^2 \frac{3}{2\rho+1} R^2 \Delta \left[\sum \psi(0)^2 \right] \Delta \left\{ \alpha^2 \left[1 + \frac{2}{21} (2\rho+3)\alpha + \dots \right] \right\} \quad (8)$$

Here it is assumed that the equation for the nuclear surface is

$$R(\theta) = R \left[1 + \alpha P_2(\cos \theta) \right], \quad (9)$$

where P_2 is a Legendre polynomial and θ is the polar angle from the symmetry axis. Applying Eq. (8) to the measured shifts we find $0.0023 < \Delta \alpha^2 < 0.0046$, with $\alpha_1 > \alpha_0$. Thus core excitation has an effect on the isomeric chemical shift equivalent to a substantial change in nuclear deformation.

VI. THE ELECTRONEUTRALITY PRINCIPLE

Pauling has suggested that electron transfer in intermetallic compounds is governed by the principle of "electroneutrality", i.e., that there is a tendency for no net charge transfer to occur.^{18,19} Thus in the purple alloy Al_2Au , which Pauling has discussed, about 1.2 electrons per gold atom should be transferred from each gold atom to the aluminum atoms. The resulting positive charge on the gold atoms would be neutralized by the partial ionic character of the Al-Au bonds.

The Mössbauer effect affords an experimental test of this hypothesis, at least insofar as it applies to s electrons. We have observed that gold isomer shift in Al_2Au , using a platinum source and an Al_2Au absorber. The shift is -0.71 cm/sec relative to gold, very near the -0.76 shift for a dilute solution of Au in Al. This corresponds to a very substantial transfer of s electrons — between 0.35 and 0.7 6s electron equivalents — rather than none as would be expected if the electroneutrality principle were to hold for 6s electrons alone (or to hold without rehybridization). Perhaps electrons are transferred from the gold d shell to aluminum and other electrons are transferred from Al to the 6s shell of gold. If such a mechanism does not occur we must tentatively conclude that the large shift does not directly support the electroneutrality hypothesis.

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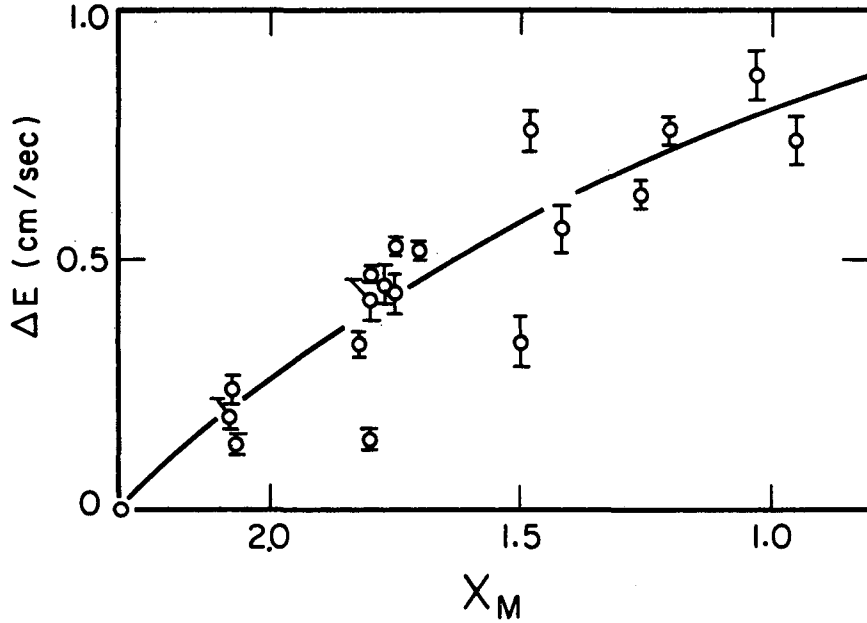
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Table 1. Isomeric Chemical Shifts, Relative to a Gold Absorber, in Dilute Gold Alloys. Errors in the Last Place are given Paranthetically.

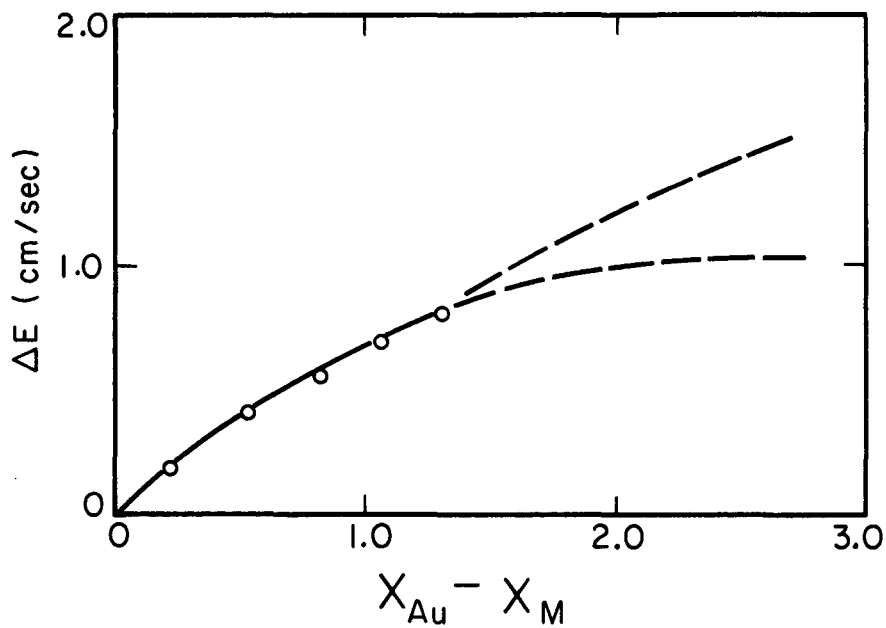
Host Element	$-\Delta E$ ($\frac{\text{cm}}{\text{sec}}$)	Percent Absorption (uncorrected)
Li	0.74(5)	2.5
Be	0.56(5)	11
Mg	0.63(3)	5.2
Al	0.76(4)	4.1
Si	0.33(3)	5.4
Ca	0.87(5)	2.0
Fe	0.54(2)	5.8 ^a
Co	0.53(2)	6.9 ^a
Ni	0.47(2)	4 ^a
Cu	0.42(4)	8.7
Zn	0.34(5)	5
Ge	0.45(4)	5.9
Y	0.76(3)	3.6
Pd	0.24(3)	5.7
Ag	0.13(2)	5.5
Sn	0.43(4)	5.7
Te	0.19(3)	4.2
Pt	0.12(1)	12
Au	(0)	1.4
Al ₂ Au	0.71(4)	8.6
Se	0.18(4)	6.7

^aDepth of each peak.



MU-28987

Fig. 1. Isomeric chemical shifts for gold atoms in nineteen hosts, vs. host electronegativity. The shifts are taken relative to a gold absorber. The transition energies are higher in the alloys than in gold. Two shifts in Table 1 are omitted: selenium, in which gold probably forms a chemical compound, and the intermetallic compound Al_2Au .



MU-28986

Fig. 2. Plot of average shifts for several electronegativity ranges against electronegativity difference between host and gold. Limits of extrapolated saturation value for shift are taken as 1.0 and 2.0 cm/sec.

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