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Solute Knight Shifts in Noble Metals

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Knight shifts are reported for Cu, Cd, Al, In, Sn, and Ga as dilute solutes in Au; Hg, In, and Al as dilute solutes in Ag; In as a dilute solute in Cu; and Sn as a dilute solute in Ag-Au alloys. These data are considered together with all other Knight-shift data on dilute solutes in the three noble metals. A valence effect is found which is opposite in sense for Cu and Ag on the one hand, and Au on the other. Cd resonance linewidths for Au-Cd alloys show appreciable broadening with increase in alloy content or test frequency. New values of hyperfine fields for the free atom are obtained, together with several choices of values for the paramagnetic spin susceptibility of the hosts. Implications of the rigid-band theory for lattice volume effects are examined. The problem of exchange enhancement of the spin susceptibility is reviewed. Values for Knight's parameter ξ, usually considered as a measure of the amount of s character in the metal, are tabulated and discussed. The valence trends found in the Knight shifts are also evident in the ξ values, and these cannot be attributed to a phase-shift analysis common to the three noble metals. Varying band character and local effects appear important to the results. The origin of the *solvent* Knight shifts in noble metal alloys is examined in terms of the rigid-band theory; the results emphasize several shortcomings in charge screening theory as currently applied to solvent shifts.

I. INTRODUCTION

THE study of various physical properties of dilute alloys provides insight into the electronic structure of the pure host metal as well as that of the alloy in question. Knight-shift studies have proven particularly fruitful in this. Extensive measurements of the variation in the Knight shifts of noble metal *solvent* atoms, as a function of alloying with various group B solutes, such as Cd, Al, Sn, or P, have been reported in the literature.[1–4] Valence effects (depending on the difference in group valence between the solvent and the solute) have been observed, and in a number of cases, a semiquantitative understanding of a body of data has been offered by charge phase-shift analysis. We show that the rigid-band model also yields[5] semiquantitative agreement with the solvent resonance valence effects. Charge screening is, of course, required from physical consideration, but the rigid-band results emphasize several serious shortcomings in screening theory as presently applied to solvent Knight shifts. Recently, *solute* atom Knight shifts have been studied in a number of dilute alloys of silver and copper[6] and it is of interest to extend our knowledge to the third noble metal, gold. With this end in mind, we will report the solute Knight shifts of dilute binary alloys of In in Cu; Hg, In, and Al in Ag; Cu, Cd, Al, Ga, In, and Sn in Au; and a ternary alloy system, Sn in Ag-Au. These values, together with those previously reported for other solutes in silver, copper, and gold,[7] will be inspected.

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[*] Also consultant, National Bureau of Standards.

[†] Supported by U. S. Atomic Energy Commission.

[1] T. J. Rowland, Phys. Rev. **125**, 459 (1962).

[2] R. L. Odle and C. P. Flynn, Phil. Mag. **13**, 699 (1966).

[3] L. E. Drain, Phil. Mag. **4**, 484 (1959).

[4] A. Narath, Phys. Rev. **163**, 232 (1967).

[5] A short account has been reported by R. E. Watson, L. H. Bennett, and A. J. Freeman, Phys. Rev. Letters **20**, 653 (1968). Contrary to the caption, the "theory" curves of the Letter's figure included estimates of the effect of lattice volume changes. The "theory" curves of the Letter differ somewhat from what will be reported here due to different estimates of the Pauli susceptibility from the specific heat data.

[6] T. J. Rowland and F. Borsa, Phys. Rev. **134**, A743 (1964).

[7] G. A. Matzkanin, D. O. Van Ostenburg, J. J. Spokas, and C. H. Sowers, Bull. Am. Phys. Soc. **12**, 911 (1967); G. A. Matzkanin, J. J. Spokas, H. G. Hoeve, and C. H. Sowers, *ibid.* **13**, 44 (1968).

Valence effects will be evident. While these are difficult to rationalize, their nature implies that there can exist no phase-shift analysis common to the three host metals which accounts for these solute effects.

A conventional description[8] of the Knight shift of a nontransition metal solute atom (such as those coming from subgroup IB to VB in the periodic table) in a nontransition metal such as Cu or Sn is

$$ {}^{\mathrm{A}}K_{\mathrm{B}} = {}^{\mathrm{A}}(\Delta H/H)_{\mathrm{B}} = (1/\beta) H_{\mathrm{eff}}{}^{(\mathrm{B})} \chi_p{}^{(\mathrm{A})} \xi \,, \tag{1} $$

where $H_{\mathrm{eff}}{}^{(\mathrm{B})}$ is the hyperfine field appropriate to a free solute (B) atom's valence electrons, $\chi_p{}^{(\mathrm{A})}$ is the Pauli spin susceptibility per atom of the solvent (A) metal, β is the Bohr magneton, and ξ is Knight's ratio accounting for the difference in hyperfine fields at the nucleus appropriate to a Fermi-surface conduction electron and to an atomic valence electron. In first approximation ξ might be defined in terms of solvent conduction electrons and solute valence electron character.[9] H_{eff} and ξ are usually entirely attributed to *s*-electron character and its associated Fermi contact interaction (perhaps scaled with additional core-polarization terms). There are, of course, other terms such as those arising from orbital or diamagnetic effects which are very important (or even dominant) in some transition metals and semimetals; these terms will be largely neglected. Equation (1) was proposed so as to display the essential physics of the Knight shift and it cannot reasonably be required to account for the complexities encountered in the alloy systems of interest here. Not surprisingly, the results of this paper are inadequately described with the above definitions of the terms. We will nevertheless follow common usage and use Eq. (1) as a *definition* of ξ, which is then found to depend on both solute and solvent.

Knight, in his review paper,[8] calculated the various factors separately for all metals on which Knight shifts had been measured. He obtained the ratios of measured shifts for dilute solutes to those appropriate to the solute pure metals, for a number of alloys, and compared these with calculated values of the ratios. He found fairly good agreement for many alloys, but a few showed appreciable discrepancies. Rowland and Borsa[6] extended Knight's comparison to other solutes in Cu and Ag. They did not find close agreement between theory and experiment and attributed this to such matters as the crudeness of the square-well model employed by Daniel[9] in the phase-shift analysis and the error of assuming that the effective susceptibility of a solute atom in dilute solution is not appreciably different from that for the solvent metal itself. The present results suggest that the situation is in some ways even more severe than Rowland and Borsa indicated. This is due to *qualitative* differences in the body of Au alloy results from those of the Ag and Cu alloys. To the extent that the results can be described by consideration of the group valence difference between solvent and solute, the Au gives results opposite in sense to Cu and Ag.

We will encounter a variety of factors which appear to complicate the alloy behavior. Four deserve mention here. First, while there are 10 electrons in the "*d*" band, and one in the "conduction" band in the noble metals, interband mixing causes variation in the amount of *d* and *s* character in the bands. While the Knight shift is directly associated with electrons at the Fermi surface, electrons below significantly influence it (especially via the hyperfine coupling). Hence the band character at and below the Fermi surface must be considered. Important to Knight shifts is the variation in character from Ag, which may be most *s*-like, to Au, which is most nearly a transition metal. We should note the obvious, but frequently abused, fact that a change in character of the bands below the Fermi surface does *not* imply a similar change at the Fermi surface. Secondly, one is interested in the character as well as the magnitude of the screening charge at and about a solute site. Thirdly, and related to this, the results suggest the presence of *local* effects involving the susceptibility as well as the hyperfine coupling. This is perhaps most important for the Au alloys. Finally, the Knight shift samples the hyperfine coupling of electrons at some segment of the Fermi surface weighted by the contribution of that segment of χ_p and then summed over the Fermi surface. Equation (1) assumes that this sampling can be replaced by the total susceptibility multiplied by the average hyperfine coupling constant. There is some suggestion that the weighting of the sampling varies observably from one noble metal to another. Lack of experimental and theoretical data makes it impossible to disentangle the relative roles of these and other factors.

Sections II and III review experimental details and experimental results and compare these with earlier results. In order to obtain ξ factors from the Knight shifts, it is essential to have a consistently chosen (and, if possible, accurate) set of values for the free atom *s*-valence electron hyperfine fields H_{eff} for the solutes. Such a set is offered in Sec. IV. The relationship of band theory to the alloy hyperfine coupling is considered in Sec. V. Estimates of the Pauli susceptibilities are complicated because the noble metals are diamagnetic. Several sets of values of χ_p are obtained in Sec. VI. The values of ξ are obtained and their significance discussed in Sec. VII. Solvent Knight shifts are discussed in terms of free-electron rigid-band and screening theory in Sec. VIII.

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[8] W. D. Knight, Solid State Phys. **2**, 93 (1956).

[9] Modifications of Eq. (1) to account for screening have been presented by E. Daniel, J. Phys. Chem. Solids **10**, 174 (1968), and (especially pertinent to transition metals) by A. M. Clogston, Phys. Rev. **125**, 439 (1962).

II. EXPERIMENTAL DETAILS

Sample preparation was similar to that given in earlier papers[10] except that the gold alloys, in addition to being ground to a 200 mesh, were mixed with petroleum jelly in order to minimize eddy current shielding within the sample. Analysis of the powders by x-ray diffraction was used to verify that the alloys were primary solid solutions. In the case of the Ag-Hg alloys, the diffraction rings were too diffuse to state with certainty that there was not any intermediate phase present. Thus we cannot be certain that the result we report for Hg in Ag is from the primary phase.

The spectrometer and measuring techniques were also similar to that described earlier[10] except that the field was swept repeatedly over a fixed range, and the trace of the resonance signal built up on a time averaging recorder. As an example, Fig. 1 shows the nuclear magnetic resonance absorption derivatives of ^{63}Cu in two dilute alloys in Au, as well as in Cu metal.

In determining the Knight shift, the field shift of the impurity in the alloy was measured with respect to that of the pure solute metals for copper, cadmium, mercury, aluminum, and tin. The values we report are defined with respect to an appropriate salt using the data in Rowland's review article.[11] For the solutes gallium and indium, the resonances in the salts $GaClO_3$ and $InClO_3$ were used directly as references.

Inasmuch as the spectrometer probes used in this investigation were made of aluminum, a unique method was employed for measuring the resonance of Ag-Al and Au-Al alloys. A record was obtained of the alloy on the time averaging recorder in the *add* mode to obtain a signal which arises both from the alloy and from the probe. Following this, a noble metal sample of similar impedance, but without aluminum, was placed in the detection system for an equivalent number of sweeps in the *subtract* mode to remove the signal which arises from the probe alone. A satisfactory resonance signal was thus obtained for the aluminum in the alloy.

III. EXPERIMENTAL DATA AND COMPARISON WITH EARLIER RESULTS

The data were averaged from a number of determinations. No change, within experimental error, was found in the Knight shift as a function of alloy concentration up to 5% solute (12% for Cd in Au). (The trend for Cd was to a decreased shift for the higher concentrations, but the experimental error was too large to be certain of the validity of this result). The Knight shifts reported are expected to be characteristic of infinite dilution. For the gold solvent, the solute Knight shifts (together with our estimates of uncertainties) found are Cu (0.164±0.008)%, Cd (0.514±0.008)%, Al (0.174 ±0.010)%, Ga (0.690±0.020)%, In (0.859±0.015)%, Sn (1.333±0.025)%; for the Ag solvent, Hg (1.730 ±0.025)%, In (0.720±0.020)%, Al (0.161±0.010)%; for the Cu alloy, In (0.577±0.020)%. The data for Au-Cu, Au-In, and Ag-Al agree, within the stated experimental errors, with those of Matzkanin *et al.*[7] The data for Au-Al and Ag-Al agree within experimental error with those of Knight.[8] The Knight shift of Au-Cu reported here differs significantly from that of Knight.[8] The data for Ag-In agrees with unpublished data of Rowland but differs significantly from the data of Matzkanin *et al.*[7]

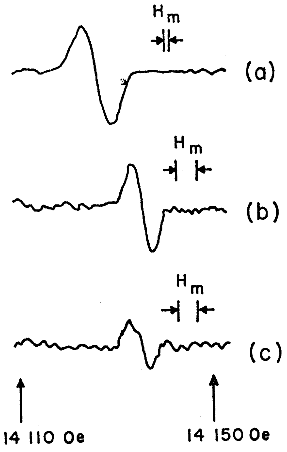

FIG. 1. Room-temperature NMR absorption derivatives of ^{63}Cu in (a) Cu (2 scans), (b) 97 at.% Au - 5 at.% Cu (132 scans), and (c) 95 at.% Au - 3 at.% Cu (150 scans). Each scan is in the direction of increasing field and takes 25 sec to scan about 42 G. A time constant of 0.8 sec was used. The field scanned is the same for each scan in all three plots, so that shifts may be read directly, except for time constant corrections.

Data are summarized in Table I for the Knight shift ($^{A}K_{B}$) of various dilute solutes in copper, silver, and

TABLE I. Knight shifts[a] ($^{A}K_{B}$) of various solutes in solid-phase dilute solutions in the noble metals Cu, Ag, and Au, and Knight shifts $^{B}K_{B}$ in solid and liquid "pure solutes."

	Solvent (A)			Isotropic Knight shift in solid solute $^{B}K_{B}$	Knight shift of molten solute metal $^{B}K_{B}$
Solute (B)	Cu	Ag	Au		
Cu	0.23	0.23[b]	0.16[c,e]	0.23	0.24[h]
Ag		0.52	0.39[g]	0.52	
Au			1.64[g]	1.64[g]	
Cd	0.52[b]	0.60[b,d]	0.51[c]	0.42	0.60[i]
Hg		1.73[c]		2.46	2.46
Al	0.11[b]	0.16[c,e]	0.17[c]	0.16	0.16[j]
Ga	0.32[b]	0.43[b]	0.69[c]		0.45
In	0.58[c]	0.72[c,f]	0.86[c,e]		0.79
Sn	0.62[b]	0.80[b]	1.33[c]	0.73	0.73[j]
P	0.19[b]				

[a] All Knight shifts expressed in % with estimated uncertainties less than ±0.02%. All Knight shifts are positive. Unlabelled values are from Rowland, Ref. 11.

[b] Rowland and Borsa, Ref. 6.

[c] Present investigation. The value for $^{Ag}K_{Hg}$ is uncertain. See text for details.

[d] Drain, Ref. 3.

[e] The values reported by Matzkanin, *et al.* (Ref. 7) for these alloys lie within ±0.02%.

[f] T. J. Rowland (private communication).

[g] Narath, Ref. 4.

[h] Extrapolated to room temperature from value given in R. C. Odle and C. P. Flynn, J. Phys. Chem. Solids **26**, 1685 (1965).

[i] E. F. W. Seymour and G. A. Styles, Phys. Letters **10**, 269 (1964).

[j] W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. (N. Y.) **8**, 173 (1959).

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[10] L. H. Bennett and R. J. Snodgrass, Phys. Rev. **134**, A1290 (1964); R. J. Snodgrass and L. H. Bennett, *ibid.* **132**, 1465 (1963).

[11] T. J. Rowland, Progr. Mater. Sci. **9**, 1 (1961).

gold as obtained in this and other investigations.[12] Also listed are the isotropic Knight shifts of the pure solute metals as solids and as molten liquids. The latter values have been corrected to room temperature, in order to account for the influence of the expansion of the metal between room temperature and its melting point on its Knight shift. This correction is significant only in the higher melting point metals.

It is of interest to compare the variation of Knight shifts ${}^{A}K_{B}$ for the various solutes in copper, silver, and gold. Normalizing the shift obtained for copper and gold with respect to the values obtained for silver yields the results plotted in Fig. 2. We have indicated the subgroups in the periodic table to which the various solutes belong. The Knight shifts for the silver alloys were employed for normalization inasmuch as the conduction bands and the Fermi surface of silver are believed to be the most free-electron-like of the three noble metals, making it the obvious reference host. Any such normalization, of course, affects the apparent trends to be seen in the results but we will see the gross features of Fig. 2 reappearing in the more detailed analyses of Sec. V. Results normalized with respect to the pure molten solute metals are nearly identical in character.

The Knight-shift ratios of Fig. 2 for the solvent copper are largest for the subgroup IB solutes and decrease as the subgroup number increases to IIB and, in turn, to IIIB; the ratio for the subgroup IVB Cu-Sn alloy lies among the IIIB values. The reverse trend is seen for the gold alloys, namely, the Knight-shift ratios are lowest for the group IB alloys, and increase monotonically with subgroup number; that for the IVB Au-Sn alloy is essentially the same as that for the IIIB Au-Ga alloy. It should also be noted that the IB elements, Cu and Ag, have their smallest Knight shifts in Au. In other words, in addition to a reversal in a distinct valence effect, there is a drop in the "zero line" as indicated by the Knight shifts of the zero valence difference solutes. The valence reversal and the drop will be seen again in Sec. V. Such behavior is not describable in terms of a phase-shift analysis common, in its essential features, to the three noble metals.

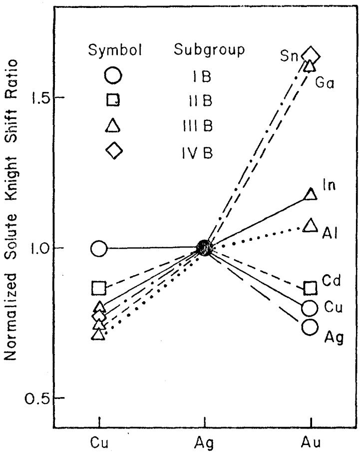

FIG. 2. Room-temperature Knight shifts ${}^{A}K_{B}$ for various dilute solutes in Cu and Au, normalized to the values in Ag.

The results of Fig. 2 may be compared with other variables appropriate to the alloys. For example, while valence effects are seen, there is no trend attributable to the periods to which the several IIIB solutes belong. There may be a period effect for solutes Cu, Ag, and Au.

One might expect repercussions from atomic size effects, i.e., the volume per atom. The atomic size is approximately the same for the pure solvents Ag and is 30% smaller for Cu. The Knight-shift ratios do not reflect such volume changes. One reason for this will be seen in Sec. V. Neither solute size nor the fractional change in lattice spacing on alloying the various solutes in Ag, Cu, and Au can be correlated with Fig. 2.

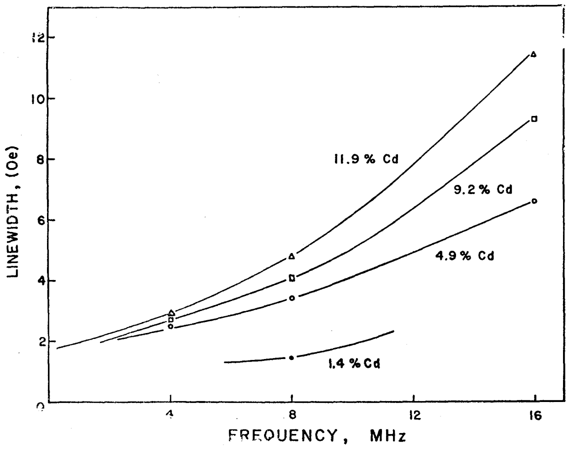

FIG. 3. Room-temperature linewidths of ^{113}Cd in Au as a function of alloy content and magnetic field.

Further discussion requires consideration of the solvent susceptibility and solute hyperfine constants, matters considered in the sections which follow, but first other experimental results should be mentioned.

Linewidth measurements were made on all alloys at 8 MHz. The ^{27}Al resonance was narrow in both Ag and Au (~2 Oe). The broadest was ^{115}In in Cu, Ag, and Au (~10 Oe at low concentrations, ~20 Oe at ~5% In). An important source of linewidth in the In case is undoubtedly quadrupole broadening.

An extensive investigation was made on the alloys of Cd (spin $I=\frac{1}{2}$) dissolved in Au. The ^{113}Cd linewidths, corrected for modulation broadening are plotted against alloy content and resonance frequency in Fig. 3. It is noted that there is a marked increase in linewidth with both frequency and with alloy content. Drain[3] provided measurements of ^{113}Cd linewidths in cadmium-silver alloys having 10% or more cadmium. He attributed the

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[12] The notation employed is that of Rowland and Borsa (Ref. 6).

increase in linewidths with Cd addition partly to an increase in Cd spin-spin interactions. His analysis indicated, at least for the 24% Cd alloy, that broadening was primarily due to the variation in Knight shift from site to site arising from nearest neighbors and slightly beyond. There is some indication that such broadening may also arise from an anisotropic Knight shift since, in the disordered alloy, the cadmium atom does not lie in a cubic environment. The increasing slopes of the linewidth-versus-field curve in Fig. 2 would tend to substantiate this latter premise. The Cd in Au linewidth result contrasts with the case of Sn in Ag, where the linewidth-field curve did not show[6] an increasing slope. Rowland and Borsa[6] interpreted the Ag-Sn result to indicate that the major source of broadening in that system is an inhomogeneous Knight shift. The anisotropic Knight shift was first proposed as an important source of broadening in alloys for Pb alloys.[10]

The different behavior of the Au versus the Ag and Cu alloy results raises the natural question of how this arises in Ag-Au alloys with varying concentration. Narath has reported[4] the Ag Knight shift in Ag-Au alloys and we have obtained the Sn shift for dilute (4 at.%) Sn in this alloy sequence. Ag and Sn lie on the extreme ends of the valence trends we have seen. The results appear in Fig. 4. Except for one datum point, the Ag results fall on a straight line while the Sn results show curvature. This curvature may have a metallurgical explanation, namely, Sn may tend to find itself in an Ag-rich environment inasmuch as it is more soluble in pure Ag than in pure Au. Unfortunately, this question reduces the usefulness of such data.

A proposal has been made by Henry[13] that the Knight shifts in noble metal alloys can be understood on the basis of charge transfer to the higher valence solute sites from the noble metal solvent. Measurements on Ag-Cd alloys[3] were given[13] as an example. The decrease in the Ag Knight shift as Cd is added is due, in this view, to a decrease of charge on the Ag. There would then be a corresponding increase of charge on the Cd (and, it was argued, a corresponding increase in the Cd Knight shift). Several physical arguments can be made against the details of this proposal, and it is not substantiated upon examination of the main body of solvent and solute Knight-shift data for the noble metal alloys. For example, the valence effect reversal revealed in this paper is incompatible with Henry's suggestion.

It is unfortunate that Henry[13] chose to compare the Knight shift of Cd as a solute in Ag with solid Cd, since Cd is one of the few metals in which there is a substantial change in Knight shift upon melting. (See Table I.) The liquid Cd, which might be expected to have a more free-electron-like electronic structure, has as large a Knight shift as when Cd is dissolved in any of the noble metals.

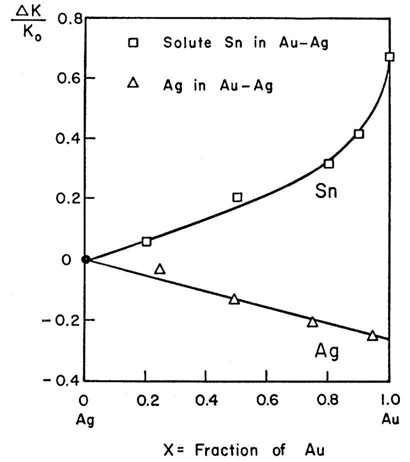

FIG. 4. Variation of the Ag Knight shift with Au-Ag ratio (from Narath, Ref. 4) and the Sn Knight shift for dilute added (≈4 at.%) Sn solute. ^{119}Sn resonance is at room temperature.

IV. HYPERFINE FIELDS

In order to make use of Eq. (1) it is necessary to obtain a value for the effective atomic hyperfine field $H_{\rm eff}$. This problem is often considered to be formally equivalent to obtaining the Fermi contact density appropriate to a valence s-electron wave function, i.e.,

$$H_{\rm eff}=(8\pi/3)\beta\psi^2(0)\,, \tag{2}$$

where $\psi(0)$ is the s electron's density at the nucleus. Methods of estimating $H_{\rm eff}$ have been discussed in great detail by Knight,[8] who emphasized the difficulties of a direct solution to this problem. We require (and will attempt to obtain) a consistently chosen set of $H_{\rm eff}$'s in order to study the variation in Knight shift from solute to solute.

In the case of the monovalent metals, the most accurate method of finding the effective hyperfine field is from the results of an atomic beam experiment. The numerical values for $H_{\rm eff}$ depend on the hyperfine coupling constant $a(s)$ obtained in an atomic beam experiment,[14] and on the nuclear magnetic moment.[15] Values for the $^2S(d^{10}s^1)$ atomic states of Cu, Ag, and Au from atomic beam experiments are listed in Table II. Calculations, to be described later in this section, yield s-valence contact terms of 1.6, 3.2, and 16 MOe for Cu, Ag, and Au, respectively. These are substantially smaller than the observed hyperfine fields (2.6, 5.0, 20.6) listed in Table II. It is believed that the discrepancy between these values for Cu and Ag and probably for Au, is almost entirely due to core polarization effects.

For the polyvalent atoms, neither Knight's method[8] of using measurements on *excited ionic* states and then

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[13] W. Henry, Proc. Phys. Soc. (London) **76**, 989 (1960). For a discussion of the Knight shift in solid and liquid pure metals, see J. M. Ziman, Advan. Phys. **16**, 421 (1967).

[14] For Cu, Y. Ting and H. Lew [Phys. Rev. **105**, 581 (1957)] obtain $a(s)=0.196$. For Ag and Au, G. Wessel and H. Lew [Phys. Rev. **92**, 641 (1953)] obtain $a(s)=0.0659$ and 0.1018, respectively.

[15] We use $\mu_I(^{63}\mathrm{Cu})=2.221$, $\mu_I(^{109}\mathrm{Ag})=0.1299$, and $\mu_I(^{197}\mathrm{Au})=0.1459$. The Au value is from Narath, Ref. 4.

Table II. Neutral-free-atom s-valence-electron hyperfine fields H_{eff}.

Group	Atom	H_{eff} (MOe)	Source
I	Cu	2.6	a
	Ag	5.0	a
	Au	20.6	a
II	Cd	7.0	b
	Hg	25.8	c
III	Al	1.9	d
	Ga	6.2	d
	In	10.1	b
IV	Sn	12.8	d
V	P	4.7	d

[a] Experimental.
[b] Hartree-Fock-Slater, scaled to Hartree-Fock and then scaled for core-polarization and relativistic effects.
[c] Hartree-Fock-Slater, scaled with respect to Au.
[d] Hartree-Fock, scaled for core-polarization and relativistic effects.

correcting for the degree of ionization, nor the choice[6] of Rowland and Borsa of using measurements on excited neutral atom states, appears to us to be very accurate. The difficulty in both cases is that the excited states are atomic configurations inappropriate to the metals. We chose instead, in the polyvalent case, to rely on calculations of s-valence contact terms. Each calculated value is scaled by the factor necessary to account for the core-polarization effects suggested by the behavior described above for the monovalent atoms. Our approach also has its shortcomings, but it has its advantages as well. First, the resulting ξ's display less scatter than is displayed using the excited configuration hyperfine constants. Secondly, the process sheds some insight into the origin of the hyperfine fields and this has implications when employing Eq. (1).

Conventional neutral atom Hartree-Fock wave functions have been used, when available, to obtain the valence s-electron contact hyperfine fields. For the several atoms for which Hartree-Fock wave functions do not yet exist, we have employed suitably scaled[16] Hartree-Fock-Slater wave-function values.[17] We should perhaps note that the Cu and Ag, but not the Au, predictions are based on Hartree-Fock functions. At this point the results are nonrelativistic and this is clearly inadequate, especially for Au and Hg among the elements listed in Table I. One might hope to employ the correction factors tabulated in Kopfermann.[18] Inspection of Mayer's relativistic atomic functions[19] for Hg indicates that these correction factors are in significant error for Hg and Au. Mayer's results have been employed to estimate the relativistic effects for these two. Kopfermann's factors have been employed for the other elements, where relativistic effects are less important. With perhaps the exception of Au (and Hg among the other elements), we believe that we have obtained relatively accurate values for the s-valence-electron contact interaction, and as we have mentioned above, the discrepancy between these and atomic beam experiment values is largely due to core-polarization effects induced by the unpaired s-valence electrons. A spin unrestricted or exchange polarized Hartree-Fock estimate[20] of the core polarization for Cu $3d^{10}4s^1$ yielded a 15% increase in H_{eff}. This agrees in sign and order of magnitude with the observed 50% increase. Better quantitative accuracy cannot be expected.[21] We should note that a positive core polarization (i.e., enhancement of the contact interactions) should occur here: the exchange field due to the unpaired valence s-spin density at the nucleus attracts core s electrons of like spin in towards the nucleus, thus increasing the hyperfine field. Since the valence s-electron character in the immediate vicinity of the nucleus is expected to dominate in determining the core-polarization hyperfine field, one might expect the latter to scale with the valence s-contact interaction itself. Inspection of the Cu and Ag results (and the Au as well, within the noise) suggests that this is so to a remarkable extent. The H_{eff} values shown in Table II are the calculated Hartree-Fock values scaled by the same factor (1.6) except for Au and Hg, for which a slightly smaller factor (1.3) was used.

Some suggestion of the dependence of H_{eff} on atomic configuration is given in Table III. The 50% increase in H_{eff} seen here is somewhat larger than the shift occurring on the interchange of s- and p-valence electron population. We will return to the Cu results shortly.

It is obvious that some uncertainty must be attached to the polyvalent atom values of Table II. Nevertheless, we believe these are better defined than H_{eff} values deduced from excited configuration optical or beam data with the attendant uncertainty in them, as suggested by Table III. We will employ Table II in what follows.

Whatever the uncertainties of Table II, the considerations leading to it indicate that we must redefine terms appearing in Eq. (1). H_{eff} is *not* simply the contact interaction of an s-valence electron as implied in Eq. (2) and it would be incorrect to replace it by the bare contact interaction. In turn, ξ is not just the change in wave-function character as measured by the contact

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[16] Hartree-Fock and Hartree-Fock-Slater theory yield significantly different valence s-electron contact densities, the latter being 20 to 40% larger. Observations of those cases where both types of wave fuuction exist have been used as a basis for scaling the Hartree-Fock-Slater predictions.

[17] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

[18] H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958).

[19] D. F. Mayers, Proc. Roy. Soc. (London) **241**, 93 (1957); and (unpublished).

[20] R. E. Watson and A. J. Freeman (unpublished).

[21] Exchange polarized calculations for $3d$, $4d$, and $4f$ ions have yielded quantitatively accurate predictions of experiment but this must be viewed as due to a lucky, and as yet not understood, cancellation of errors involving correlation, spin symmetry, and other effects. With the exception of atomic P, all such calculations, done to date, yield the correct sign and order of magnitude. [See R. E. Watson and A. J. Freeman, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967).]

TABLE III. Calculated effective hyperfine fields H_{eff} for a single s electron in the ground and an excited configuration of a neutral Cu atom (see text).

Configuration	H_{eff} (MOe) 4s density alone	Scaled
$3d^{10}4s$	1.6	2.6
$3d^{9}4s^{2}$	2.4	3.9

interaction. H_{eff} may be viewed as an effective contact interaction, providing that the core polarization can be approximated by a scale or anti-shielding factor, which multiplies actual contact interaction. This factor could be appropriate to either a single atom or a group of atoms. Such behavior suggests that it is not sufficient to let ξ simply remain a measure of the change in the s-contact term associated with Fermi-surface conduction electrons. For example, one source of a reduced contact term is the replacement of s- by non-s wave-function character whose components will contribute their own core polarization terms to the Knight shift. Such effects cannot be incorporated in the scale factor and must enter ξ. For all atoms of Table II, except Al and P, these terms are expected[22] to make negative contributions to the Knight shift. A reversal in sign of these terms may reflect itself in enhanced ξ's for Al. Some suggestion of this will be seen in the results, but the trend, if real, is well within the noise.

The dependence of H_{eff} on atomic configuration deserves further note. The configuration in a metal is, in general, not equivalent to its atomic counterpart. For example, the d bands in Cu metal are filled, but due to mixing of orbital character between bands, there are actually about 9.8 $3d$ and 1.2 conduction electrons per Cu site. This might suggest, by interpolation, that a H_{eff} of 2.9 MOe, appropriate to a $3d^{9.8}4s^{1.2}$ atom, should be used. Such effects should be, and traditionally are, incorporated into the ξ. It should be noted that they can be larger than is usually presumed and, given the traditional choice of H_{eff}, will often tend to raise the ξ value.

It is quite clear that the choice of H_{eff} involves a certain arbitrariness. Granted this, the best one can do is to make a consistent choice of such values and this we have attempted here.

V. IMPLICATIONS OF ALLOYING ON CONDUCTION-ELECTRON HYPERFINE FIELDS

Atomic volume changes affect Fermi-surface conduction-electron normalization and presumably, in turn, the Knight shift. As we have already noted, volume effects are not seen in the results of Table I and it is interesting to ask why.[23] Also, in a rigid-band model, the addition of polyvalent impurities to a metal such as Cu, Ag, or Au raises the number of electrons per atom, n_e (sometimes designated e/a). This in turn means different Bloch states now lie at the Fermi surface and they will, in general, contribute a different hyperfine interaction ξH_{eff} to the Knight shift. The existence of such behavior has, of course, been known but its quantitative importance has somehow been overlooked. The implications of this to an explanation of the classic solvent Knight shift results of Rowland[1] for Ag and Odle and Flynn[2] for liquid Cu are considered[5] in Sec. VIII.

A. Rigid-Band Model

For simplicity let us approximate the conduction bands of the host metals Cu and Ag by essentially free-electron bands. For our purposes this is fairly good for Ag and worse for Cu. We expect that the model minimizes the effects of greatest interest to us here.

For free-electron bands the Fermi wave vector is given by the familiar expression

$$k_F=(3\pi^2 n_e/V)^{1/3}, \tag{3}$$

where V is the atomic volume in the lattice. We now wish to evaluate the contact interaction for a Fermi surface Bloch orbital φ_{k_F}. The antisymmetry of the many-electron system requires that our plane wave be properly orthogonalized to the ion cores,[24] i.e., that we evaluate the contact density for an orthogonalized plane wave. This gives

$$\begin{aligned} P_F &\equiv \frac{8\pi\beta}{3}|\varphi_{k_F}(0)|^2 \\ &= \frac{8\pi\beta}{3V}\,\frac{[1-\sum_n S_{n,0}{}^{k_F}R_{n,0}(0)]^2}{\{1-(4\pi/V)\sum_{n,l}(2l+1)(S_{n,l}{}^{k_F})^2\}}, \end{aligned} \tag{4}$$

where

$$S_{n,l}{}^{k_F}\equiv\int_0^\infty j_l(k_F r)R_{nl}(r)r^2dr \tag{5}$$

is the radial overlap integral between the spherical Bessel function j_l and the atomic radial function R_{nl} of the n,l shell. The curly bracket term in Eq. (4) is the additional normalization arising from orthogonalization: the sum in it spans all closed shells of the ion core. There is some question of how to evaluate this normalization term for an alloy. We will evaluate it assuming a pure host metal, i.e., host-metal core terms will be inserted into it. The square bracket of Eq. (4) is the

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[22] This follows from the fact that p-electron core polarization reverses sign somewhere above but presumably close to P in the periodic table. This can be seen in R. L. Christensen's Ph.D. thesis [Princeton University, 1957 (unpublished)], where the hyperfine fields observed for the $^4S(p^3)$ atoms are plotted. (There was some uncertainty in the sign of the P term at the time he reported this but this has subsequently proven to be positive.)

[23] It should be noted that simple volume renormalization is seldom useful in understanding Knight-shift variations, e.g., see L. H. Bennett and R. J. Snodgrass, Ref. 10.

[24] Or that the ion cores be orthogonalized to the plane wave, in which case there would be core contributions to the Knight shift, yielding a final total result identical to Eq. (4).

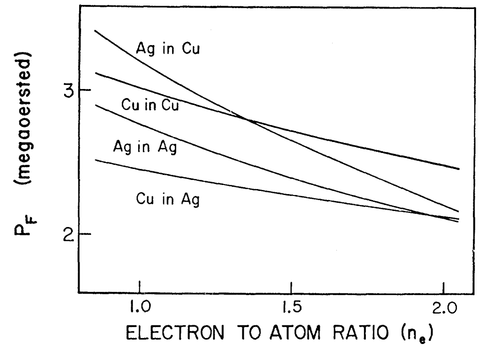

FIG. 5. Results of an OPW calculation of the variation of the conduction electron contact interaction versus hypothetical electron to atom ratio (n_e) for pure copper, pure silver, dilute silver in copper, and dilute copper in silver.

plane wave's contact density as modified by the interference with the s shells of the ion core. It, of course, should be evaluated for the ion core site at which the hyperfine field is to be inspected. Results for Cu and Ag contact terms in Cu and Ag hosts are plotted as a function of n_e in Fig. 5. We have not attempted to account for the additional core-polarization effects, so it is most appropriate to compare the curves with the Cu 4s and Ag 5s direct contact fields of 1.6 and 3.2 MOe, respectively.

The $1/V$ normalization term would suggest a 30% decrease in the hyperfine field on going from a Cu to a Ag host. Inspecting the results at $n_e = 1$, we see significantly smaller changes in the contact term at either a Cu or Ag site on changing host. This lessening of the volume effect is partially due to the additional normalization term but, more importantly, the volume change implies a change in k_F and, in turn, a change in contact density in the square bracket of Eq. (4). These results suggest that one should observe little volume effect in the Knight shifts.

The OPW contact term for Cu is larger than its atomic 4s counterpart. This is in part due to the fact that the valence s electrons undergo a significant compression on insertion into the metal. In fact, approximately 50% of an atomic s electron's charge lies outside the Wigner-Seitz sphere for Cu, Ag, or Au. The contact term depends in detail on the interference between individual terms in the square bracket of Eq. (4) (odd and even n-valued terms are of opposing sign.). The negative slopes of Fig. 5 are associated with a decrease in s character, as sampled at the nucleus, with increasing k_F (or n_e).

B. Lattice Volume and Conduction-Band Character

The Wigner-Seitz radii (r_{WS}), which reflect the lattice sizes, are listed in Table IV for these three metals. Also shown is the Pauling singly charged ionic radius, which is a conventional measure of the size of the ion core.

TABLE IV. Comparison of the Wigner-Seitz radii for the noble metals with conventional ionic radii and with atomic d extent of Hartree-Fock $d^{10}s$ atoms. All radii in atomic units.

	Cu	Ag	Au
Wigner-Seitz radius (r_{WS})	2.669	3.017	3.011
Pauling's ionic radius	1.82	2.39	2.59
Ratio (ionic radius to r_{WS})	68%	79%	86%
Radius at quarter maximum of d peak	2.3	2.8	3.1
Ratio ($\frac{1}{4}$ max. radius to r_{WS})	87%	94%	102%
Atomic d charge outside r_{WS}	1.5%	2.0%	2.9%

The ratio of the ionic radius to r_{WS} indicates[25] a loose-fitting core in Cu and a tighter-fitting core in Au, with intermediate behavior in Ag. Free-atom Hartree-Fock calculations suggest the same thing. The quarter maximum of the atomic ($d^{10}s$ configuration) d function lies within r_{WS} for Cu, but outside for Au, with Ag intermediate (see Table IV). This too suggests the likelihood of deformation within the Au core. There is almost twice the atomic d charge outside r_{WS} for Au than for Cu; the d bands are wider; the centripetal barrier lower.

Although we make no detailed calculations, it is thought that the unique position of Au as reflected in solute Knight shifts is related to these large ratios for Au. Raynor[26] attributed the lower solubilities of the B-group metals in Au to the lack of sufficient interionic space. He suggested that the solute atom deforms the Au core, enabling the outer Au core electrons to take on a conduction-electron character.

We would like to invert Raynor's reasoning and suggest that the small lattice constant for Au is simply a manifestation of depleted d and increased conduction (s) character in the occupied bands in the pure metal. This arises from interband mixing and affects the response of the metal to a charge impurity. As interband mixing reduces occupied d character, the ion core (which includes the d shell) contracts from its Au$^+$, d^{10} size, letting the metal conform to a different ionic radius. An increase in interband mixing also implies increased d character in the Fermi-surface conduction-electron states. In such a discussion one other fact must be noted; the optical constants of the three noble metals[27] suggest that the tops of the d bands lie at about the same energy ($\sim$2 eV) below the Fermi level (E_F) in Cu and Au but considerably lower ($\sim$4 eV) in Ag. This makes interband mixing energetically less favorable in Ag, making its conduction bands, in the vicinity of E_F, most free-electron-like. Whether viewed as a contributing cause or as a result, the lattice size considerations then suggest that interband mixing is greater in Au than in Cu.

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[25] Other conventional ionic radii, e.g., Goldschmidt or Zachariasen, would give somewhat different ratios, but the same general conclusion that the Au ion fits tightest in the metal.

[26] G. V. Raynor, Prog. Metal Phys. **1**, 1 (1949).

[27] For example, B. R. Cooper, H. Ehrenreich, and H. R. Philipp, Phys. Rev. **138**, A494 (1965); H. Ehrenreich and H. R. Philipp, *ibid.* **128**, 1622 (1962).

While grossly oversimplified, the above discussion has implications for the binding energies, band structures,[28] $H_{\rm eff}$ values, susceptibilities, and many other properties of these metals. We will limit consideration in this paper to $H_{\rm eff}$ here and to the susceptibility in later sections. Table III suggests that a reasonable choice of $H_{\rm eff}$ for Au may well be 10 or 20% larger than the $d^{10}s$ value. Lacking quantitative information of the metal configurations, we will incorporate such hyperfine field variation in the ξ's and retain the $H_{\rm eff}$ values appropriate to the simple atomic configurations. Having done so, the deduced ξ values will be observably affected by the interband mixing and this must be remembered when viewing the results.

Before leaving this section, two other matters deserve mention. First, Mössbauer studies[29] of dilute Fe in Au seem to show that the Fe induces long-range spin distributions reminiscent of Pd alloys.[30] This implies that the susceptibility is *not* simply that of a free-electron metal; d admixture and deviations from a simple free-electron Fermi surface can be important to this. While there are various Mössbauer results relevant to the problem at hand, they unfortunately cannot be unraveled. Secondly, Cohen and Heine, noting[31] the relative energies of atomic s and p valence electrons, observed that the p level is relatively higher in Au, compared with Ag or, in turn, Cu. From this they argue the presence of increasing p character in the Fermi surface states on going from Au to Cu. Such a tendency may be important for properties, such as optical absorption, which sample states above the Fermi level but we believe there are no observed effects from this at the Fermi level. Both the Knight-shift results for the pure noble metals and those for the solutes display trends in opposition to any such tendency for p admixture: d-electron effects seem more important.

In this subsection we have considered ways in which the noble-metal conduction bands deviate from purely free-electron character and some of the implications of these to the problems at hand. We attributed the most free-electron-like character to Ag, the least to Au. The experimental Fermi-surface cross sections, displayed in Fig. 6, clearly agree with this for Ag but raise some question of the relative behavior of Cu and Au.

VI. NOBLE-METAL SPIN SUSCEPTIBILITIES

Obtaining a reliable value for χ_p for use in Eq. (1) is not trivial. The difficulties have been discussed by Knight.[8] One can infer χ_p from measured specific heat γ's, from measured total susceptibilities, or from calculated densities of states (which we lack). As with the $H_{\rm eff}$ values, we are particularly interested in a consistent set of χ_p's. Each way of estimating χ_p suffers severe shortcomings. We will employ several alternative schemes in order to estimate the bounds on its value. Let us consider the total susceptibilities first.

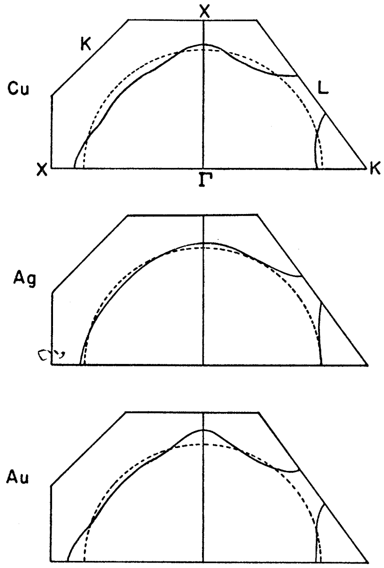

FIG. 6. Schematic cross sections of Fermi surfaces for Cu, Ag, and Au, after D. J. Roaf, Phil. Trans. Roy. Soc. London **A25**, 135 (1963). The dashed lines are the free-electron Fermi surface.

The susceptibilities of Cu, Ag, and Au are all negative, implying that the diamagnetism of the ion cores ($\chi_{\rm dia}{}^{\rm core}$) and of the conduction electrons ($\chi_{\rm dia}{}^{\rm core}$) overpowers the paramagnetism (χ_p) of the conduction electrons. Small errors in the calculation of the diamagnetic terms may produce large errors in any estimate of χ_p. Hartree-Fock values for Cu^+, Ag^+, Cd^{2+}, and Sn^{4+}, plus a value relying on a Au^+ Hartree-Fock-Slater function, appear in Table V. Unlike $H_{\rm eff}$, Hartree-Fock and Hartree-Fock-Slater[32] estimates of

TABLE V. Diamagnetic susceptibilities ($\chi_{\rm dia}{}^{\rm core}$) of some free ion cores. All values in -10^{-6} emu per mole.

Ion core	Hartree-Fock[a]	Hartree-Fock-Slater[b]	Traditionally employed value[c]	Experimental value from salts[d]
Cu^+	14.6	14.37	13	12–16
Ag^+	27.3	25.97	44	24–27
Au^+	37	36.17	65	40–45
Cd^{2+}	23.1	22.41	37	20–23
Sn^{4+}	17.9	17.61	28	13–16

[a] See text for details.
[b] C. M. Hurd and P. Coodin, Ref. 32.
[c] As tabulated in J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, England, 1932), p. 225.
[d] A. Paucault, Ann. Sci. Paris 84, 169 (1946).

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[28] A depletion in the d charge at an atomic site may stabilize d energies (with respect to the conduction bands) by better than a half eV on going from Ag to Au (this will be discussed by Ehrenreich, Hodges, and Watson elsewhere).

[29] R. Borg and T. A. Kitchens (unpublished).

[30] D. Shaltiel, J. H. Wernick, J. H. Williams, and M. Peter, Phys. Rev. **135**, A1346 (1964); J. W. Cable, E. O. Wollan, and W. C. Koehler, *ibid.* **138**, A755 (1965); G. G. Low and T. M. Holden, Proc. Phys. Soc. (London) **89**, 119 (1966); B. Giovannini, M. Peter, and J. R. Schrieffer, Phys. Rev. Letters **12**, 736 (1964).

[31] M. H. Cohen and V. Heine, Advan. Phys. **7**, 395 (1958).

[32] C. M. Hurd and P. Coodin, J. Phys. Chem. Solids **28**, 523 (1967).

$\chi_{\text{dia}}{}^{\text{core}}$ agree to several percent, the latter lying lower. Until recently, Hartree-Fock wave functions were not available for ions larger than Cu$^+$ and the traditionally employed values of $\chi_{\text{dia}}{}^{\text{core}}$ are listed in Table V, as are experimental values deduced from data for the ions in salts. The Hartree-Fock $\chi_{\text{dia}}{}^{\text{core}}$ agree quite well with the salt data whereas the traditional values do not. The traditional $\chi_{\text{dia}}{}^{\text{core}}$ lead to quite unreasonable values of χ_p and, in turn, of the ξ's.

The agreement between the experimental and Hartree-Fock $\chi_{\text{dia}}{}^{\text{core}}$ does *not* supply a measure of the accuracy of the latter. Unfortunately $\chi_{\text{dia}}{}^{\text{core}}$ should be quite sensitive to environment since it most heavily weights the outer reaches of the ion core. Approximately two thirds of the term comes from the outer d shells in Cu$^+$, Ag$^+$, and Au$^+$ (less so in Cd^{2+} and Sn^{4+}) and perturbations by the environment on these shells should affect $\chi_{\text{dia}}{}^{\text{core}}$. In the metals, a small, but significant percentage of the atomic d charge lies outside the Wigner-Seitz cell (see Table IV), the charge within the cell is violently perturbed and, as we have already noted, interband mixing leads to fewer than 10 electrons of d charge at an atomic site. A reduction in the number of d electrons causes an associated contraction of the ion core (particularly of the d shell), lowering $\chi_{\text{dia}}{}^{\text{core}}$ further. In our view, the uncertainties in $\chi_{\text{dia}}{}^{\text{core}}$, due to environmental and interband effects, are greater than the conduction-electron diamagnetism, which we will next consider. The estimate of $\chi_{\text{dia}}{}^{\text{core}}$ is worst for Au, which has the most diffuse d distribution relative to the size of its Wigner-Seitz cell. While the uncertainty is great for the above mentioned reasons, the theoretical results of Table V probably err to the high side.

Electron gas estimates of conduction-electron diamagnetism $\chi_{\text{dia}}{}^{\text{cond}}$ have concentrated on the alkali metals. Taking the results tabulated by Pines[33] and inserting the atomic volumes and effective masses[34] appropriate to the noble metals one can obtain bad estimates of -2.1, -5.1, and -3.2×10^{-6} emu per mole for $\chi_{\text{dia}}{}^{\text{cond}}$ for Cu, Ag, and Au, respectively. Given these, one can estimate χ_p with

$$\chi_p=\chi_{\text{expt}}-\chi_{\text{dia}}{}^{\text{core}}-\chi_{\text{dia}}{}^{\text{cond}}\,, \tag{6}$$

where χ_{expt} is the experimental susceptibility. The resultant values of χ_p are shown as row C in Table VI. Alternatively, one can invoke the free-electron approximation ($-\chi_{\text{dia}}{}^{\text{cond}}=\frac{1}{3}\chi_p$). Then

$$\chi_p=\tfrac{3}{2}[\chi_{\text{expt}}-\chi_{\text{dia}}{}^{\text{core}}]\,, \tag{7}$$

yielding the results, row B, in Table VI. It is reassuring that quantitatively compatible results are obtained for these two cases. It must be remembered, however, that the χ_p arise from strong cancellations of terms. Also note that a lower value of $|\chi_{\text{dia}}{}^{\text{core}}|$ implies a lower $|\chi_p|$. Au presumably has the strongest interband mixing, hence the greatest lowering of χ_p. Results (rows D and E) employing the traditional $\chi_{\text{dia}}{}^{\text{core}}$ show a strong variation in χ_p. This would have violent implications for the ξ factors but we believe these values of χ_p are wrong.

TABLE VI. Paramagnetic susceptibilities (χ_p) of metallic Cu, Ag, and Au as estimated by various means (see text). All values in 10^{-6} emu per mole.

	Cu	Ag	Au
A. From electronic specific heat[a]	9.5	8.5	10.3
B. $\frac{3}{2}(\chi_{\text{expt}}-\chi_{\text{dia}}{}^{\text{core}})$ Hartree-Fock core	13.7	11.7	13.5
C. $\chi_{\text{expt}}-\chi_{\text{dia}}{}^{\text{core}}-\chi_{\text{dia}}{}^{\text{cond}}$ Hartree-Fock core	11.2	12.9	12.2
D. $\frac{3}{2}(\chi_{\text{expt}}-\chi_{\text{dia}}{}^{\text{core}})$ Traditional core	11.3	36.8	55.5
E. $\chi_{\text{expt}}-\chi_{\text{dia}}{}^{\text{core}}-\chi_{\text{dia}}{}^{\text{cond}}$ Traditional core	9.6	29.6	40.2

[a] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, Inc., New York, 1963).

Also shown in Table VI (row A) are the χ_p values deduced from the specific heat γ's. These assume no electron-phonon or virtual magnon contributions to the γ's (which, if present, cause an overestimate of χ_p) and no electron-electron exchange enhancement of the χ_p's (which, if present, causes an underestimate of χ_p). The values show semiquantitative agreement with rows B and C involving our estimates of the $\chi_{\text{dia}}{}^{\text{core}}$.

Narath[4] has investigated the exchange enhancement of χ_p using the Korringa relation for Cu in Cu, Au in Au, and Ag in Ag-Au alloys. Since his results are of great relevance, for reasons in addition to the enhancement, let us consider them here. The traditional Korringa relationship between the Knight shift K, the spin-lattice relaxation time T_1, and the temperature T, is modified[35] in the presence of exchange enhancement to be

$$(\gamma_n/\gamma_e)^2(4\pi k_B/h)(K)^2T_1T=[K(\alpha)]^{-1}\,, \tag{8}$$

where $K(\alpha)$ (equal to 1 in the absence of exchange enhancement) is a function of α which measures the enhancement of the $q=0$ component of the generalized susceptibility. In other words,

$$\chi(0,0)\equiv\chi_0(0,0)/(1-\alpha)\,, \tag{9}$$

where χ_0 and χ are the unenhanced and enhanced susceptibilities, respectively. Moriya[35] has obtained $K(\alpha)$ in the free-electron approximation

$$K(\alpha)=2(1-\alpha)^2\int_0^1 dx\,x[1-\alpha G(x)]^{-2}\,, \tag{10}$$

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[33] D. Pines, Solid State Phys. **1**, 368 (1955).

[34] D. G. Howard, Phys. Rev. **140**, A1705 (1965); D. Beaglehole, Proc. Phys. Soc. (London) **87**, 461 (1966).

[35] T. Moriya, J. Phys. Soc. Japan **18**, 516 (1963).

where

$$G(x)=\tfrac{1}{2}\left[1+\frac{1-x^2}{2x}\ln\frac{(1+x)}{(1-x)}\right] \tag{11}$$

and $x=q/2k_F$. The G is the familiar normalized unenhanced susceptibility, $\chi_0(q,0)$ for $\omega=0$. Narath applied[36] Eqs. (7)–(10) to his results to obtain a nearly-free-electron estimate of α. This assumed that the deviations from the simple Korringa relation were entirely due to exchange enhancement. The choice of using this analysis was both logical and necessary since no better was (or is) available.

The values of α thus obtained for Ag remained almost independent of alloy concentration, including the Ag α in $\mathrm{Ag_{0.05}Au_{0.95}}$. These differed markedly from the Au in Au result. In other words, atomic or local character appeared to be manifested in the results. As Narath noted, this is incompatible with the free-electron assumption of the analysis, making the numerical estimates uncertain. The local behavior was, of course, already evident in his experimental determination of the $K(\alpha)$ and is undoubtedly a real effect. The presence of local effects is not surprising and we believe they also appear in the experimental results of this paper.

An unusual feature of Narath's analysis was the values of the exchange enhancement inferred[36] for the pure metals. A 30% enhancement was obtained for Au, 60% for Cu, and 90% for Ag. Comparison of either row B or C with row A in Table VI suggests weaker enhancements, with $\alpha(\mathrm{Ag})\gtrsim\alpha(\mathrm{Au})$. Since all evidence suggests that Ag is more free-electron-like than Au, this trend is the opposite of what is expected. An enhancement of a factor of 2 for Ag seems large when compared with results in most transition metals.[36] We believe that the presence of other contributions to the Korringa relation, Eq. (8), and the free-electron character of Eqs. (10) and (11), reduce their applicability to the noble metals. It is clear that analyses of the noble metals must take into account the deviation from free-electron behavior (see Sec. V B).

It is worth asking how one's estimate of the enhancement would change if we simply modified the susceptibility term $G(x)$ to crudely account for deviations from pure free-electron character. The principal effect would be for $G(x)$ to fall off more slowly (or even rise in some regions) as x goes from 0 to 1 and, given a $K(\alpha)$ value, this would lead to increased values for α. It appears that one would still be forced to conclude that Ag is the most severely enhanced of the three metals.[37] In this section we have explored several means of estimating the χ_p which we require to use Eq. (1). Rows A, B, and C, despite diverse origins, display crude quantitative consistency. Unfortunately they differ in details as to how the susceptibility varies from metal to metal and this will conceal some interesting features of the behavior of ξ inside the noise. In the process of considering evidence of the exchange enhancement on the χ_p derived from the specific heats, we noted that Narath's Korringa relation data suggested the importance of local effects. We believe that our results reflect similar behavior, at least for the Au alloys.

TABLE VII. Summary of ξ parameters for three choices (A,B,C) of χ_p (Table VI) in solvents Cu, Ag, and Au.

	Cu			Ag			Au		
Solute	A	B	C	A	B	C	A	B	C
Cu	0.52	0.36	0.44	0.58	0.42	0.38	0.33	0.25	0.28
Ag				0.68	0.50	0.45	0.42	0.32	0.35
Au							0.43	0.33	0.36
Cd	0.44	0.30	0.37	0.56	0.41	0.37	0.40	0.30	0.33
Hg				0.44	0.32	0.29			
Al	0.34	0.24	0.29	0.55	0.40	0.37	0.49	0.37	0.41
Ga	0.30	0.21	0.26	0.46	0.33	0.30	0.60	0.46	0.51
In	0.34	0.23	0.29	0.47	0.34	0.31	0.46	0.35	0.39
Sn	0.29	0.20	0.24	0.41	0.30	0.27	0.56	0.43	0.48
P	0.24	0.17	0.20						

VII. KNIGHT'S ξ FACTOR FOR SOLUTE SITES

Using the experimental values of the solute Knight shifts in Cu, Ag, and Au given in Table I (assuming them to be characteristic of infinite dilution), the free-atom s-valence electron hyperfine fields H_{eff} for the various solute atoms given in Table II, and the paramagnetic susceptibilities χ_p for the solvent metals given in Rows A, B, and C of Table VI, we obtain the three sets of Knight's ξ factors shown in Table VII. We have, of course, employed Eq. (1) as the definition of ξ. The ξ values obtained with choice C are plotted in Fig. 7. The lines joining the various solutes are for visual use only, and should not be used to interpolate intermediate (i.e., ternary) alloy data.

The ξ's display the valence effects already seen in Table I and Fig. 2, including the reversal on going from Cu and Ag to Au. For Cu and Ag as solvents, the ξ range from about 0.5 for the pure metals down to half this value for group IV or V solutes. Inspecting choices A, B, or C, we see that the spread in ξ's is smallest in Ag, the most free-electron-like of the solvents, and is somewhat larger in the less free-electron-like host Cu. Then, however, one encounters the reversal in ξ behavior when Au becomes the host, with $\xi\sim0.5$ for

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[36] *Note added in manuscript.* A. Narath (private communication) and T. Weaver and A. Narath (to be published) have pointed out two shortcomings in the analysis employed to obtain α values. First, Moriya's numerical values (Ref. 35) for $K(\alpha)$ are incorrect (in fact, they are too small). Correcting this leads to excessively large values of α for the noble and alkali metals. This suggests deficiencies in Eqs. (9)–(11) which Weaver and Narath ascribe to a breakdown of the δ-function contact interaction (employed for conduction electron-conduction electron exchange). Reasonable values for α must be obtained before specific-heat data can be accurately employed in estimates of χ_p.

[37] This is not entirely clear since, on one hand, a given change in $G(x)$ will most severely increase the enhancement factor for Ag but, on the other hand, $G(x)$ should change least for Ag, since Ag has the most spherical Fermi surface of the three metals.

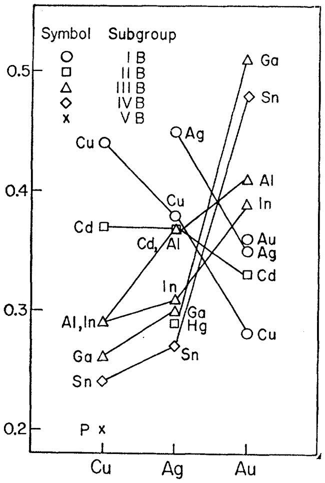

FIG. 7. Knight's ξ factor for all measured solutes for one choice (C) of χ_p, for Cu, Ag, and Au.

Sn and Ga falling to ~0.3 for Cu. This result was unexpected since we were used to regarding the three noble metals as having essentially common properties. Before considering these valence effects and the reversal further, let us first inspect the ξ's appropriate to the monovalent atoms, Cu, Ag, and Au in the three noble-metal hosts.

Considering cases A, B, and C collectively we see that, within the noise, the Cu ξ's appropriate to Cu and Ag hosts are roughly the same. The ξ's for both Cu and Ag drop when the atoms are inserted into the Au host. In other words, there is a drop in the zero line for ξ. Indeed, this was already seen in Fig. 2 for K. In Sec. VI it was suggested that the B and C values of χ_p were probably most seriously overestimated for Au (with its largest interband mixing). Correcting for any such error (in cases B and C) would scale down the ξ drop, but there are no grounds for suggesting that it would disappear. Apparently the zero-line behavior seen in Fig. 2 cannot be attributed entirely to variations in the bulk susceptibility from one host metal to the next. Discussed in terms of Eq. (1), this behavior depends, in part, on changes in ξH_{eff} with changing solvent. We should note that Eq. (4) predicts such changes. If P_F were evaluated for Cu or Ag in a Au host, with the Au volume (the same as for Ag) and the Au core terms in the curly bracket, a drop of the type seen in the ξ's would be expected. The drop would arise from increased core-plane-wave overlap renormalization. Such an estimate is worst for Au with its largest interband mixing and has not been made. It is not suggested that the drop is entirely due to P_F change.

Inspection of the pure metal ξ's appropriate to the various choices of χ_p suggests that $\xi(\text{Ag}) > \xi(\text{Cu}) > \xi(\text{Au})$. In other words, ξ tends to be largest for the most free-electron-like of the pure metals and smallest for the least. One can invoke a simple explanation for this. Deviations from free-electron character involve d- (and perhaps some p-) band admixture, reducing the s character in the Fermi-surface electron states implying, in turn, a reduction in ξ. While an argument of this type can have considerable validity (we will employ it when discussing valence effects) it is a dangerous oversimplification of the situation at hand. There arise questions of other effects, of interband mixing on the hyperfine coupling, of how ξ varies from element to element for pure conduction bands and, of course, of contributions to the Knight shift in addition to those implicit in Eq. (1). Let us consider two features of this briefly.

In addition to perturbing the character of the Fermi-level states, interband mixing changes both the effective atomic configuration at a lattice site and the placement of the Fermi level E_F in the conduction band. For d-interband mixing, Table III suggests a strong increase in hyperfine field, *opposing* the observed trend, as the number of d electrons is depleted. The associated (small) rise in E_F lowers the hyperfine field (comparison of Table III and Fig. 5 suggests this is a weaker effect). Neglecting all else, the observed trend in pure noble metal ξ's gives a measure of the minimum possible depletion of s character (from mixing and E_F shifts) in Fermi-level states relative to the depletion of d-electron count in the occupied bands. For example, using Table III, a shift from the $d^{10}s$ to a $d^{9.9}s^{1.1}$ configuration produces a 5% increase in ξ. To cancel this requires a 5% or greater depletion in Fermi-surface-state s character.

The ξ factor may vary from element to element in the absence of interband mixing. For example, the free-electron contact densities, plotted for pure Ag and pure Cu in Fig. 5, are nearly the same whereas their atomic H_{eff} values differ by a factor of 2. Defining an effective factor

$$\xi_{\text{eff}} = P_F / H_{\text{contact}}, \qquad (12)$$

H_{contact} being the atomic contact term alone (since P_F omits core polarization), one obtains ξ_{eff} values of 1.9 for Cu and 0.9 for Ag. The difference for the two elements is large, in opposition to the observed trend in ξ's and only partly due to lattice volume changes (see Sec. V).

Comparison of the noble-metal atom ξ's appropriate to a given host can be made independently of any knowledge of χ_p. For a given solvent we see that the heavier (and larger) the atom, the larger is its ξ. Such a trend is predicted by Fig. 5. In fact, comparing Cu and Ag solutes in a Ag host, the ratio of P_F's from the figure is in suspiciously good agreement with the ratio of the observed ξ's. The same trend would appear if Eq. (4) were evaluated with Au the solvent.

Quite different behavior is seen for the group-III elements as solutes, the one other group for which we have substantial data. Identical behavior cannot be expected since now there is a valence difference between solute and solvent. Two trends emerge from the scatter in the ξ's. First, of the three group-III solutes, Ga has the smallest ξ in Cu (less strongly so in Ag) and the largest in Au. This is reminiscent of the valence reversal already seen in Fig. 7, of which this may or may not be a part. The other, clearer trend is that the Al ξ's are as high or higher than those for Ga and In (except for Ga in Au). At first this is somewhat surprising and we do not think it is due to an inconsistent choice of H_{eff} for Al. We think it arises, at least in part, from the fact that the core-polarization terms, induced by non-s components of the Fermi-surface conduction-electron orbitals, are expected to be of the same sign as the s-component terms for Al, instead of opposing them as they do for the heavier atoms (see Sec. IV). This reduces the drop in ξ associated with a depletion in Fermi-surface s character, thus causing relatively inflated ξ values. More notable than these rather weak but smooth trends seen for Cu, Ag, and Au is the apparent haphazardness among the group-III solute ξ's. This disorder is outside of experimental error and will not be substantially reduced by refinements in the choice of any given H_{eff} or χ_p. The ξ for each of the group-III solutes increases from Cu, to Ag, to Au host for choice C of χ_p. More data are necessary to discover systematic trends, if any, in the polyvalent solutes.

We have seen that the ξ's are small when measured with respect to the ξ_{eff}'s obtained for free-electron conduction bands. This is important since it suggests that the ξ's arise from a cancellation of effects in turn implying that they are quantitatively sensitive to details of the cancellation. We saw ξ/ξ_{eff} ratios of $\frac{1}{4}$ for pure Cu and $\sim\frac{1}{2}$ for pure Ag, the two cases for which ξ_{eff} values were obtained. Interband mixing effects would tend to make the Cu ratio smaller but a change by a factor of 2 is large. Accounting for this may require replacing the conventional description of the Knight shift, as given in Eq. (1), by the more exact expression

$$K=\frac{1}{\beta}\sum_{\substack{\text{Fermi-}\\ \text{surface}\\ \text{segments}}}(\chi_p)_{\text{FSS}}(\xi H_{\text{eff}})_{\text{FSS}}\,. \tag{13}$$

In this expression, each contribution to the susceptibility from a Fermi-surface segment is multiplied by the hyperfine field appropriate to the Bloch orbitals making up the segment. In the conventional description the *total* susceptibility χ_p is multiplied by the *average* hyperfine field ξH_{eff}. This can lead to considerable error if there are radical variations in orbital character over the Fermi surface such as there may be with interband mixing. We have already noted that there is a suggestion for Au that the regions of the Fermi surface, which deviate most strongly from the free-electron sphere, are very important to the susceptibility.[29] This effect is, of course, incorporated into the ξ's appearing in Table VII. This factor and the small size of the ξ's must be noted when considering valence effects, the matter we return to now.

The decrease in ξ with increasing solute valency for Cu and Ag hosts is readily understood in terms of an oversimplified traditional argument. Conduction-electron charge builds up at an impurity site so as to screen the solute-solvent valence difference. This almost inevitably implies a decrease in the fraction of s character in the Fermi-surface electron orbitals.[2] One might extend the argument by asserting that Cu, with its increased interband mixing relative to Ag, effectively has a larger pure metal n_e and has more d character in the Fermi-level orbitals (in the host metal) and that this will encourage a larger range in ξ. While we believe that arguments of this type have more validity here, than when both solute and solvent are monovalent, they are obviously grossly oversimplified. For example, a Fermi-level electron orbital will tend to build up its density at the solute site relative to that in the solvent. In addition to questions concerning the amount of s character in the orbital at the solute site, a density build up of s character need not be reflected in an increased contact interaction due to interference in core-density cross terms (a matter we intend exploring in the future). At this point it becomes clear that there is some uncertainty as to what this traditional argument actually predicts, though one rather expects it to be consistent with the ξ reductions seen for Cu and Ag hosts.

There are two ways to scan the results of Table VII and Fig. 7. One may note significant valence effects for the ξ's in Cu which are reduced in Ag and cross over by the time Au is reached. In this view one must ask why the ξ's drop for some (Cu, Ag, and Cd) solutes and rise for others (notably Ga and Sn) with the slopes reflecting solute vacancy. The other view, which we have already invoked, orders the solvents so as to account for the variation in the character of the conduction-electron bands. Then Ag, being considered the most free-electron-like metal, displays valence effects and these increase on going to Cu, a trend which we believe can be rationalized in terms of interband mixing. On going to the least free-electron-like metal Au, there is then a reversal. Given either way of viewing the results, they are difficult to rationalize in terms of a picture where the similarity of the noble metals is emphasized. Unfortunately, lack of experimental data for the Au alloy system hinders such an analysis. Susceptibility and specific-heat results are meager and it does not appear that solvent Knight shifts will be obtained for Au alloys. While the valence effects may be attributable to the various factors already considered in this paper, we believe something essential is missing. We believe local effects are present involving the combined susceptibility and hyperfine interaction in much the sense of Eq. (13). One can, of course, invoke a whole variety of new terms.

Sorting this out requires more data, particularly for the Au systems.

VIII. SOLVENT KNIGHT SHIFTS

While our primary concern is with solute Knight shifts in this paper, it is of some interest to consider the implications of Eq. (4) and Fig. 5 for solvent shifts in Ag, Cu, and other alloys. Valence effects were first seen in the Ag solvent Knight-shift results.[1] These effects are normally attributed to oscillatory charge screening. Let us see what an alternative model, the rigid free-electron band theory, predicts. Replotting the results of Eq. (4) for pure Ag and pure Cu (with fixed lattice volumes), we obtain the ratios (normalized to $n_e=1$) of the conduction-electron contact terms plotted as a function of n_e in Fig. 8. These are labeled P_F(Cu) and P_F(Ag). Any comparison of these with the change in Knight shift ΔK observed for a particular alloy requires accounting for the changes in lattice volume and in χ_p, appropriate to that alloy. We will estimate the effects of this for the Cu-Zn and Ag-Cd systems. The choice of these two systems, while somewhat arbitrary, relies on having relatively good data for them.

Using the observed change in lattice volume[38] with n_e (and again assuming Cu and Ag have a valency of 1 and Zn and Cd of 2), Eq. (4) has been reevaluated, yielding the curves P_F(Cu-Zn) and P_F(Ag-Cd), also plotted in Fig. 8. These volume effects have significantly steepened the hyperfine field curves for the alloys at hand.

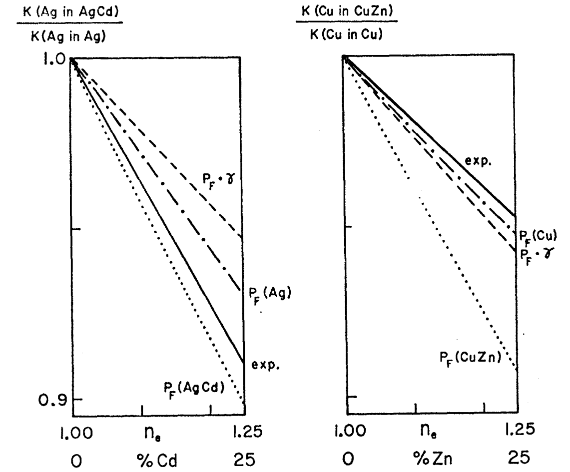

FIG. 8. Comparison of the rigid-band hyperfine field calculation (Fig. 5) with solvent NMR data. The experimental lines (——) are the fractional changes in solvent Knight shift for AgCd (from Rowland, Ref. 1) and CuZn (from Odle and Flynn, Ref. 2). P_F(Ag) (–·–·) is a normalized segment of the Ag in Ag curve of Fig. 5; P_F(Cu) (–·–·) is from the Cu in Cu curve. P_F(AgCd) (····) is P_F(Ag) modified by lattice expansion due to Cd; P_F(CuZn) (····) is P_F(Cu) modified due to Zn. Theory (– – –) is P_F(AgCd) or P_F(CuZn) multiplied by appropriate changes in χ_p, as explained in the text.

The variation in χ_p upon alloying is more difficult to obtain than were the pure metal χ_p's considered in Sec. VI. Henry and Rogers have reported[39] extensive results for the variation in susceptibility for various Cu and Ag alloys and these too display valence effects. The metals become increasingly diamagnetic on alloying, the more so, the greater the valence of the solute, for given solute concentration. Henry attributes this to diamagnetism arising from the localized impurity screening charge and to a decline in χ_p with increasing n_e (there are, of course, also contributions from the differing $\chi_{\text{dia}}{}^{\text{core}}$ of solute and solvent). A drop in χ_p is consistent with rigid band estimates of the density of states of these metals.[39,40] It differs with observed specific heats γ's which increase on alloying.[40] Given the uncertainties involved in extricating the χ_p variation from Henry and Rogers' results, we will use the observed γ's. (Their χ_{expt} results are, in principle, invaluable to understanding the solute behavior of the preceding section. As a matter of practice, the above-mentioned uncertainties must first be resolved.)

Differing specific-heat γ results are to be found for some of the alloy systems in the literature. We will use recent, apparently reliable, results which have appeared[40] for Ag-Cd and Cu-Zn. We do not require the absolute values of the χ_p but only their fractiona change with alloying, and we will use

$$\chi_p(n_e)/\chi_p(1)=\gamma(n_e)/\gamma(1).$$

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[38] W. B. Pearson, *Handbook of Lattice Spacing and Structure of Metals and Alloys* (Pergamon Press, Inc., New York, 1968), Vol. I. We have assumed that the change in lattice volume in the solid alloy is relevant to liquid Cu-Zn.

[39] W. G. Henry and J. L. Rogers, Can. J. Phys. 38, 908 (1960).

[40] H. Montgomery, G. P. Pells, and E. M. Wray, Proc. Roy. Soc. (London) **A301**, 261 (1967) (Ag-Cd); and B. W. Veal and J. A. Rayne, Phys. Rev. **130**, 2156 (1963) (Cu-Zn). Both papers indicate increases on alloying. Unfortunately the error in data points is large compared to the change in γ, and in Knight shifts, with alloy composition. Since the observed Knight shifts display a linear dependence (within their error) on concentration, we have chosen to use linear (least square) fits of the γ. In the case of Ag-Cd the fit was made over the entire composition range (0–29.1%) for which data was recorded and for Cu-Zn over a partial range (0–23.93%). The fits lie within the experimental error but the results are by no means unique. Fits to higher Cu-Zn concentrations (which were used in Ref. 5) would flatten γ (i.e., steepen our $P_F\cdot\gamma$ curve) whereas much steeper initial slopes could be inferred for either dilute Cu-Zn or dilute Ag-Cd. Electron-phonon effects on changes in γ may be most severe in this dilute region. More serious, we have had to assume that the specific heat γ for the solid-alloy is relevant to the susceptibility appropriate to the liquid Cu alloy ΔK. *Note added in proof*. L. Clune [(private communication); also see, L. C. Clune and B. A. Green, Jr., Bull. Am. Phys. Soc. **13**, 643 (1968); H. Wu and B. A. Green, Jr., *ibid.* **13**, 643 (1968)] has estimated the effects of the electron-phonon enhancement on the change of γ upon alloying. He finds that, for Pb alloys, the *sign* of the observed changes of γ is opposite to the *signs* of the change in the band structure density of states $N(E_F)$. In the case of Pb alloys, tunneling experiments are used to estimate the electron-phonon enhancement factor. For the noble metals, Clune also concludes that the sign of the observed changes in γ is opposite to the sign of $N(E_F)$ upon alloying, but the conclusion is less certain because the electron-phonon enhancement has not been measured directly. If the slope of $N(E_F)$ is negative, the predicted Knight shifts would lie considerably below the experimental values.

This makes the unwarranted[40] assumption that the electron-phonon (and virtual magnon) enhancement of γ as well as the exchange enhancement of χ_p do not change appreciably with alloying. Multiplying the resulting variation in χ_p by the P_F(Cu-Zn) and P_F(Ag-Cd) hyperfine field results, we obtain the theoretical predictions labeled $P_F \cdot \gamma$ for ΔK appearing in Fig. 8. In addition to other assumptions, these results assume that core-polarization contributions to the Knight shift simply scale the contact term, an assumption already invoked when obtaining the H_{eff} of Table II and discussed in Sec. IV. The chief uncertainty remains the estimate of χ_p (with vertical error bars of the order of dimensions of the figures,[40] or larger[39]). This situation is similar to what has been seen for the solute Knight shifts.

The agreement between the rigid-band predictions and experiment (which are also in the figure) is remarkable in view of the assumptions of the model. It is doubly remarkable in that there are no adjustable parameters. We should note that if Henry is correct and the χ_p does fall with alloying, the theoretical ΔK would lie below experiment for both alloy systems. More important than any detailed agreement, or lack thereof, is the fact that rigid free-electron band theory may yield ΔK of the correct sign and magnitude. Behavior of wrong sign has been attributed to the model and this attribution has sometimes been cited when asserting the validity of the charge screening model. Figure 8 suggests that the screening model is not unique in its ability to reproduce experiment. We believe that screening effects are important to solvent (as well as solute) Knight shifts, but that a description relying on screening effects alone is incomplete, that the true situation in alloys is more complicated. We might note that standard application of the screening model omits the effect on the hyperfine field of orthogonalization of the conduction electrons to the ion cores of a metal (a factor we intend investigating). Also omitted[41] are changes in χ_p. All that is considered is the (very important) effect of conduction-electron screening of the impurity charge and the so-called Friedel charge oscillations as manifested in the Fermi-surface electron orbitals.

Unfortunately, given their nature, the results of the present model and of screening theory cannot simply be added together. Most important to this is the differing character of the Fermi-surface orbitals (and their associated hyperfine fields) incorporated into the two models. In the rigid-band model, the Fermi-surface orbital charge distribution is the same from solvent site to solvent site in the alloy irrespective of their position relative to the solute. The solute contact density differs from that of the solvent due to factors that have been neglected in the screening model. In this latter, the distribution piles up at or near the solute and varies from site to site in the solvent.[42] While over-all charge screening does indeed occur, note that only its manifestation in the Fermi-surface character is relevant here.

Although rigid-band theory is not universally successful,[43] many of its results have validity even in the presence of screening effects.[44,45] For example, as Stern[45] has indicated, the concent of n_e (or an effective n_e) remains useful when considering some experimental data. We believe hyperfine fields are among these. We also believe that, though derived for the rigid-band model, the hyperfine fields plotted in Figs. 5 and 8 are relevant to how the ion cores more generally affect the results; in other words, that these figures give a qualitative indication of core contributions to a unified description of the Knight shifts. Such a model has yet to be developed. Elsewhere[5] we have discussed some of the experiments which might shed light on what must be predicted by a unified model. In view of the solute results of Sec. VIII, it is too bad that solvent data is not available for Au alloys. Such data might provide a severe test of one's model.

IX. SUMMARY

We have measured a number of Knight shifts of solute nuclei in dilute alloys of the noble metals. Using these and all other previous results, we have uncovered a surprising valence effect, separating Au from Cu on the one hand and Ag from Cu on the other. In order to inspect the results, it became necessary to estimate new values for the atomic hyperfine fields for the nuclei of interest. We have also considered in quite some detail the somewhat unsatisfactory state of knowledge of the spin susceptibility χ_p. Values of the Knight parameter ξ were derived for all the results in as consistent a way as possible, using Eq. (1) as a definition of ξ. The valence effects persist in the ξ. These valence effects are inconsistent with application of a charge screening description common to Cu, Ag, and Au together. Both the ξ results and considerations of the electronic properties of these metals suggest that the ξ values are appreciably perturbed by factors outside the original compass of Eq. (1). We cannot claim to understand the

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[41] For example, a recent phase shift analysis omitting changes in χ_p is given by Alfred and Van Ostenburg [Phys. Rev. **161**, 569 (1957)]. The screening theory assumes noninteracting impurities and therefore is most applicable to the dilute alloys. For present purposes, it may be useful to define the alloys as nondilute when χ_p differs significantly from the pure metal value. Alfred and Van Ostenburg claim good agreement for their analysis with Knight-shift data appropriate to this nondilute region where χ_p variation cannot be ignored. It is thus most appropriate to compare their results with our P_F curves directly.

[42] In the liquid alloys, the effect of the spatial distribution (causing satellite lines and line broadening in solid alloys) is, of course, motionally averaged.

[43] A recent example of a failure of rigid-band analysis is described by N. Lang and H. Ehrenreich, Phys. Rev. (to be published).

[44] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 344.

[45] E. A. Stern, Phys. Rev. **157**, 544 (1967).

ξ behavior; a unique determination of its origin requires more information than we currently have at hand, particularly for the Au alloys. We favor local effects involving the combined hyperfine field and susceptibility at solute sites.

Simple calculations, estimating conduction-electron hyperfine interactions, were done employing free-electron bands properly orthogonalized to ion cores. Three facts of interest emerged. First, changes in Knight shift with lattice volume are much smaller than a naively assumed V^{-1} factor. This improves agreement between theory and experiment. Secondly, the observed ξ of Table VII are much smaller than free-electron estimates for pure Cu and Ag. In some senses this is a measure of the breakdown of Eq. (1). Thirdly, and of greatest interest, we saw that rigid-band theory predicts solvent Knight shift changes of the right sign and magnitude. We thus see that the charge screening model, which is traditionally invoked for solvent effects, is not unique in its ability to reproduce them. While screening effects are important, there arises the question of exactly what is the proper description of the solvent Knight shifts, i.e., an accurate unified model is badly needed for the problem.

Perhaps the greatest value in the present results is in the questions they raised. The noble metals are not as "simple" as sometimes presumed and considerable experimental and theoretical work is needed before the existing body of experimental data for the alloys is truly understood.

Theoretical efforts ranging from estimates of exchange enhancement (as part of an effort to improve knowledge of χ_p), to energy band calculations, to the development of a unified alloy model of the solvent shifts are needed. Some efforts are straightforward. Consistent sets of energy band results for Cu, Ag, and Au should be available in the not too distant future. The effective atomic configurations of the bands and, more particularly, the character of the Fermi-surface electron orbitals, will be of great interest. Comparison with the pure metal Knight shifts should provide an interesting test for the energy band results.

Additional susceptibility and specific-heat data would be most valuable, particularly for the Au alloys where it is lacking.[46] The fact that the origins of the susceptibilities are as complicated as the Knight shifts does not reduce the value of Au alloy results. The extent to which they are the same, or differ, with the Cu and Ag systems is of great interest.[46] Solvent hyperfine data for Au systems would be even more valuable, but far harder to obtain. Experiments revealing satellites in noble-metal alloys and providing quantitative measurements of local effects would be helpful as would further solute Knight-shift measurements on dilute alloys not yet measured. In a number of cases, rapid quenching techniques would increase the percent solute to high enough values for easy measurement and low temperatures could be used to increase the Boltzmann factor as well.

We have not exhausted the list of what can and/or should be done. Without some of these data, the implications of Figs. 7 and 8 and of other results in the literature cannot truly be claimed to be understood.

Note added in proof. D. O. Van Ostenburg and L. C. R. Alfred [Phys. Rev. Letters **20**, 1484 (1968)] have, unfortunately, misinterpreted our work and incorrectly described what we said in Ref. 5 (and elaborated on here) concerning the physics of the model employed. In addition, the two theoretical models, when compared, should be treated on an equal basis. The "unmatched success" of Alfred and Van Ostenburg would be destroyed (see Ref. 41) if their phase-shift calculations included either their same estimate for the susceptibility from the raw specific-heat data *or* our estimates of the susceptibility from the specific heat (which are preferable to the use of the raw data for the reasons described in this paper) *or* the negative slope of the susceptibility suggested by Clune and Green.

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[46] T. A. Will and B. A. Green, Jr., Phys. Rev. **150**, 519 (1966), find that the slope of the specific heats γ versus n_e is $\frac{2}{3}$ the free-electron value for either CuSn or AgSn, but is $2\frac{1}{2}$ times it for AuSn (the one Au alloy for which there is data). They dismiss dilatation effects and this may not be valid (see our Sec. V B). They suggest the possibility that mass differences change the phonon enhancement. This is best tested with results for other solutes. If not due to phonon enhancement, these results are of vital interest to the problems at hand.