

Solute Knight Shifts in Cu and Ag Base Solid Solutions*

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(Received 19 December 1963)

Measurements of the Knight shift of Al, P, Ga, Cd, and Sn in Cu base solid solutions, and of Cu, Ga, Cd, and Sn in Ag base solid solutions are reported. The change in solute Knight shift with composition and the dependence of linewidth on composition and external field strength are also discussed for selected alloys. The difference in the rate of change of relative Knight shift with composition for Sn and Ag in the Ag-Sn alloys indicates a tendency for the Sn atoms to avoid being nearest neighbors.

I. INTRODUCTION

WHEN foreign atoms are dissolved in a metal to form a dilute solid solution, a redistribution of conduction electrons takes place. Although this redistribution is reflected in many measurements including such diverse quantities as heat of solution, resistivity, and lattice-parameter changes, it is difficult to obtain data in which other than average bulk parameters are measured. Nuclear magnetic resonance was indispensable in establishing the character of the long-range oscillations caused by imperfections in metals^{1,2} and is unique in its ability to probe the scattering center when the latter is a foreign atom. There have been relatively few investigations in which the Knight shift of the solute has been emphasized and accordingly the characteristics of the solute resonance have not been well established. It is the purpose of this paper to present the results of an investigation of the nuclear magnetic resonance of various solute species in copper and silver base solid solutions. These same alloys have been the object of previous investigations^{2,3} in which the behavior of the solvent resonance has been studied. In the case of a solvent with spin $\frac{1}{2}$, such as silver, the resonance was found to broaden and shift as the solute concentration increased. For the Cu alloys, on the other hand, the major effect was a decrease in amplitude; practically no broadening or shift was found. This is a direct result of the electric quadrupole moment of the nuclei interacting with the field gradient caused by the long-range oscillations around the solute atoms. Similar characteristic behaviors of the resonances are observed for solute nuclei of $I = \frac{1}{2}$ and $I > \frac{1}{2}$, respectively.

The experimental results, to be presented in Sec. III, consist of the solute shift at infinite dilution, the rate of change of shift with solute concentration, and the linewidth versus concentration. These will be compared with existing theory. The "theory" of the solute shift at

infinite dilution consists of the suggestion of Knight⁴ as reconsidered by Daniel⁵ and has little beyond plausibility and some historical success to recommend it. The one clear improvement would be the calculation of the actual wave function at the solvent and solute nuclei in the metal. Even this would not allow a complete calculation of the absolute Knight shift. Section IV contains a brief discussion of the work presented.

II. EXPERIMENTAL METHOD

The data were obtained using the Bloch crossed-coil technique. A Varian rf unit fed a lock-in amplifier of standard design with an output time constant of about 35 sec, the output being recorded on a strip chart for analysis. An electromagnet with pole faces tapered to 5 in. in diameter and having a 1.5-in. gap supplied the field. Most of the measurements were made at a frequency near 16 Mc/sec and an appropriate magnetic field strength. The use of this high a frequency improved the signal-to-noise ratio and gave larger absolute Knight shifts. Only in the case of some dilute silver alloys were slight distortions noticed which probably reflected skin effects. The rf field was about 0.1 G and no saturation effects were observed. An audio modulation frequency of 20 cps was used; the modulation amplitude was kept between $\frac{1}{3}$ and $\frac{1}{2}$ of the linewidth.

In each case a reference substance whose absorption could be seen easily on an oscilloscope was chosen. The signal of the metal was recorded at a fixed frequency ν_m and sweeping magnetic field. The resonance frequency of the reference was measured during the field sweep immediately before and after the metal signal. With a linear variation of field during the recording, the resonance frequency of the reference nuclei was interpolated linearly to arrive at the frequency ν_{rm} of the reference at the resonance field of the metal. The relative Knight shift was then computed from the relation

$$\frac{\Delta\nu}{\nu} = \frac{\nu_m}{\nu_{rm}} \frac{\nu_r}{\nu_0} - 1,$$

where ν_r/ν_0 is the ratio of the resonance frequencies ν_r

* This work was supported by a grant from the U. S. Atomic Energy Commission.

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¹ A. Blandin, E. Daniel, and J. Friedel, *Phil. Mag.* **4**, 180 (1959); W. Kohn and S. H. Vosko, *Phys. Rev.* **119**, 912 (1960).

² T. J. Rowland, *Phys. Rev.* **125**, 459 (1962).

³ T. J. Rowland, *Phys. Rev.* **119**, 900 (1960).

⁴ W. D. Knight, *Solid State Phys.* **2**, 93 (1956).

⁵ E. Daniel, *Phys. Chem. Solids* **10**, 174 (1959); *J. Phys. Radium* **20**, 849 (1959).

of the reference, and ν_0 of the metal nuclei in a diamagnetic salt in aqueous solution. For Al^{27} and P^{31} the reference substances were an aqueous solution of AlCl_3 , and H_3PO_4 , 85%, respectively. In this case $\nu_r/\nu_0=1$. For the other measurements we used: (a) GaCl_3 and NaClO_3 , $\nu(\text{Na}^{23})/\nu(\text{Ga}^{71})=0.867157$; (b) CdCl_2 and NaClO_3 , $\nu(\text{Na}^{23})/\nu(\text{Cd}^{113})=1.192506$; (c) SnCl_4 and LiCl , $\nu(\text{Li}^7)/\nu(\text{Sn}^{119})=1.042855$; and (d) CuCl (solid) and NaClO_3 , $\nu(\text{Na}^{23})/\nu(\text{Cu}^{63})=0.997962$.

III. RESULTS

The Knight shifts of the various solute elements in Cu and Ag appear in Table I. These values are extrapolated to zero-percent solute and thus should give the solute shift at infinite dilution in Cu and Ag. A linear extrapolation was used. The symbol ${}^A K_B$ indicates the percentage shift of solute B in solvent A .

Also given in Table I are the ratios of the solute (B) to solvent (A) shifts and the ratios of the corresponding probability densities at the nuclei in the free atoms. P_{aA} is used for $|\Psi_a(0)|^2_A$. The values in these two columns would be equal if it were correct to think of the solute shift as⁴

$${}^A K_B = {}^A (\Delta H/H)_B = [a(s)_{B\chi_{PA}\xi_A}] A_A / 2g_I \beta \quad (1)$$

$$= (\Delta H/H)_A |\Psi_a(0)|^2_B / |\Psi_a(0)|^2_A, \quad (1a)$$

where $a(s)$ is the hyperfine interaction constant for s electrons, χ_{PA} is the Pauli susceptibility per unit mass, ξ_A is the ratio $\langle |\Psi_F(r_A)|^2 \rangle / |\Psi_a(0)|^2_A$ of the probability densities at an A nucleus in pure A (for electrons at the Fermi surface) and in the free atom, A is the atomic weight, g_I is the nuclear g factor and β is the Bohr magneton. We might expect a contribution to the solute Knight shift due to the accumulation of charge in the solute cell. This polarization P is defined by Daniel⁵ in the equation

$$\frac{\langle |\Psi_F(r_B)|^2 \rangle}{\langle |\Psi_F(r_A)|^2 \rangle} = P \frac{|\Psi_B(0)|^2}{|\Psi_A(0)|^2}, \quad (2)$$

where the Ψ 's on the right-hand side are bottom-of-the-band wave functions in A and in a hypothetical metal

TABLE I. Knight shifts (%) of solutes in Cu and Ag at infinite dilution, ratios of solute to solvent shifts and, for comparison, ratios of the estimated free atom wave functions at the nuclei. The polarization P multiplies the wave-function ratios.

Solvent (A)	Solute (B)	${}^A K_B$	${}^A K_B / K_A^a$	P_{aB} / P_{aA}	P
Cu	Al	0.113±0.003	0.487	0.255	1.06
	P	0.189±0.004	0.815	0.722	
	Ga	0.315±0.003	1.36	0.660	1.067
	Cd	0.518±0.003	2.23	2.18	1.091
	Sn	0.623±0.006	2.68	1.71	1.004
Ag	Cu	0.232±0.002	0.444	0.504	1.13
	Ga	0.428±0.003	0.820	0.333	1.077
	Cd	0.601±0.003	1.15	1.10	1.16
	Sn	0.797±0.005	1.53	0.862	1.006

^a $K_{Cu}=0.232$; $K_{Ag}=0.522$.

with the potential of B in A in each cell, and $\langle |\Psi_F(r_B)|^2 \rangle$ applies to an isolated B atom in A . Using a square-well model to estimate the polarization, it was found that for an impurity with positive excess charge, P has a value slightly greater than one as given in Table I. The inclusion of P in (1a) above just corresponds to multiplying $(\Delta H/H)_A$ by the left-hand side of (2). The inclusion of the polarization factor does not appear to improve the agreement between theory and experiment, and it seems probable that the square-well model is too crude to give useful results within the solute cell. The form of (1) also implies that the effective susceptibility at a B atom in A is not affected by correlation differently in the vicinity of the B and A atoms.

A second sort of test which can be applied to the data is the formation of ratios of the various solute Knight shifts in the same solvent. Representative pairs are given in Table II. It is implicitly assumed that the value of ξ is the same for all solutes and retains the value ξ_A characteristic of the pure solvent. This is tested later when we compute $\xi(B \text{ in } A)$ for these alloys.

TABLE IIa. Knight-shift ratios of pairs of solutes 1-2 in binary copper alloys.

1-2	${}^{Cu} K_1 / {}^{Cu} K_2$	$ \Psi_a(0) ^2_1 / \Psi_a(0) ^2_2$
Al-P	0.598	0.354
Al-Ga	0.359	0.387
Al-Cd	0.218	0.117
Al-Sn	0.181	0.149
P-Ga	0.600	1.09
P-Cd	0.365	0.331
P-Sn	0.303	0.422
Ga-Cd	0.608	0.303
Ga-Sn	0.506	0.386
Cd-Sn	0.898	1.27

In Tables I and II we have used values of the hyperfine constant $a(s)$ derived from the Goudsmit formula except in two cases, namely copper and silver, for which optical hyperfine⁶ and atomic beam⁷ measurements, respectively, were available for the neutral atoms in the ground state. The calculations were made using the term value for the ground state of the neutral atom to derive an effective quantum-number N_0 . This was used in conjunction with a Z_i and Z_0 appropriate to the neutral atom ($Z_i=Z$, $Z_0=1$) to arrive at a preliminary value to which a relativistic correction was applied. We believe the resulting $a(s)$ will approximate that for the free atom with the screening found in the metal. It is assumed that the atoms in the metal, solute or solvent, are neutral. This is not the procedure Knight⁴ used, but rather than make different corrections for various species as he did, it was decided to apply the above prescription consistently. A real difference occurs in the case of Cd where we believe Knight's value to be in

⁶ S. Tolansky and G. O. Forester, Proc. Phys. Soc. (London) **A50**, 826 (1938).

⁷ G. Wessel and H. Lew, Phys. Rev. **91**, 476 (1953).

error, applying to the 6s rather than the 5s electron. Using the Goudsmit formula, the value of $a(s)$ for a 5s electron on neutral Cd was found to be 0.259, which becomes 0.331 with the relativistic correction. This is significantly higher than Knight's value of 0.085 cm^{-1} , whereas our value for Sn is in almost exact agreement with his (see Table IV).

Unfortunately our values for the change in solute Knight shift with concentration can only be trusted to give results comparable with the theory in the cases in which the spin of the solute is one-half. For the other solutes it is quite possible that important contributions to the shift coming from the nearest-neighbor solutes will be lost because of quadrupole interactions. In this case only the more isolated solute atoms would contribute to the signal and the change of shift with concentration will appear to be absent or slight. Simultaneously a decrease in solute intensity (per solute atom) is to be expected. Only in the cases of Cd and Sn in Ag were good data obtainable. The dipolar width for solutes in Cu is of course much greater than it is for the same solutes in Ag. For Cd and Sn it is to be expected

TABLE IIb. Knight-shift ratios of pairs of solutes 1-2 in binary silver alloys.

1-2	${}^{\text{Ag}}K_1/{}^{\text{Ag}}K_2$	$ \Psi_a(0) ^2/ \Psi_a(0) _2^2$
Cu-Ga	0.542	1.51
Cu-Cd	0.386	0.459
Cu-Sn	0.291	0.584
Ga-Cd	0.712	0.303
Ga-Sn	0.537	0.386
Cd-Sn	0.754	1.27

that the theory of Blandin and Daniel⁸ should apply, i.e., the values of the change in shift with concentration should be the same for the solute as they are for the solvent. The percentage of solute atoms at any given radius from a solute atom is the same as it is for a solvent atom. Drain⁹ found the rate of change of the cadmium shift with concentration to be very nearly equal to that of the silver. Our data agrees with this. We find, however, that the position of the tin resonance in Ag rich Ag-Sn alloys shifts much less rapidly than the silver resonance. The value of $-\langle\Delta K\rangle_{\text{av}}/K_{\text{Ag}}C$ for silver was found² to be 0.82, while $-\langle\Delta K\rangle_{\text{av}}/{}^{\text{Ag}}K_{\text{Sn}}C$ for tin in the same alloys is only 0.19; the calculated value² is about 1.6.

The linewidths of the solute absorptions are interesting because of the diversity of the broadening mechanisms encountered. In the many alloys studied we have examples of large and small dipolar broadening upon which is superimposed the effects of both quadrupole splitting and inhomogeneous Knight shift. We will not examine each system in detail but will give arguments

⁸ A. Blandin and E. Daniel, Phys. Chem. Solids **10**, 126 (1959).

⁹ L. E. Drain, Phil. Mag. **4**, 484 (1959).

TABLE III. Derivative peak-to-peak width of Ga^{71} in Ag at various concentrations and field strengths.

At. % Ga	H_0	δH_{pp}
8.4	11 957	5.9 ± 0.3
6.0	12 013	5.2 ± 0.3
4.5	11 958	5.2 ± 0.3
4.5	8834	4.8 ± 0.3
4.5	5390	4.5 ± 0.3

for three situations, namely tin in silver and gallium in silver and copper. The first case is simplest because there are no quadrupole effects and the dipolar and exchange contributions are relatively small. At field strengths of 9600, 4774, and 2381 G, the linewidth of the tin was 6.1, 3.7, and 2.1 G, respectively. Assuming that the second moment of the line is the sum of the second moments of the various contributions, and using the approximation $\langle\delta H_{\text{exp}}^2\rangle = (\delta H_{pp}/2)^2$, where the left-hand side is the experimental second moment and δH_{pp} is the peak-to-peak linewidth of the derivative, we have

$$(\delta H_{pp}/2)^2 = [C(1-C)K^2 \sum_R (\Delta\rho(R)/\rho_0)^2] H_0^2 + \langle\delta H_c^2\rangle. \quad (3)$$

Here $\langle\delta H_c^2\rangle$ is the contribution to the second moment from the dipolar and exchange mechanisms and from field inhomogeneity. C is the solute concentration, K is the relative Knight shift of the solute extrapolated to $C=0$; $\Delta\rho(R)/\rho_0$ is the relative change in the electron density at a distance R from a scattering center as given by equation (4) of Blandin and Daniel⁸ and H_0 is the external magnetic field. A plot of $(\delta H_{pp}/2)^2$ vs H_0^2 gives the value 0.8 G^2 for $\langle\delta H_c^2\rangle$ and 0.032 for $\sum_R [\Delta\rho(R)/\rho_0]^2$, using $K=0.00797$. A plot of $(\delta H_{pp}/2)^2 - 0.8$ vs $C(1-C)$ (for $H_0=9600 \text{ G}$) provides a second way to evaluate $\sum_R [\Delta\rho(R)/\rho_0]^2$ and leads to a value 0.032 in agreement with the first and in fair agreement with the value 0.039 found experimentally² for the silver resonance in this alloy series. The major source of broadening in this case is the inhomogeneous Knight shift.

For Ga in Ag a very small dependence of Knight shift on composition together with the observation that the Ga^{71} resonance is slightly narrower and about three times larger than the Ga^{69} resonance at the same frequency indicates the large part played by the quadrupole interaction in this case. The natural abundance of Ga^{69} is 0.602 compared to 0.398 for Ga^{71} , their magnetic moments are 2.01 nm and 2.55 nm, respectively, but their quadrupole moments are $0.232 \times 10^{-24} \text{ cm}^2$ and $0.146 \times 10^{-24} \text{ cm}^2$, respectively. The linewidths for Ga^{71} given in Table III show the relatively small dependence on either composition or external field, which is apparently characteristic of the superposed inhomogeneous Knight shift and quadrupole broadening.

Since the δH_{pp} in Table III all greatly exceed the calculated dipolar width which is about 0.2 G, it is thought that both the above mentioned mechanisms

TABLE IV. Values of $a(s)$ in cm^{-1} and χ_P used to derive $\xi(B \text{ in } A)$ below.

Element	$a(s)$	$\chi_P(\text{cgs/mole}) \times 10^6$
Cu ⁶³	0.190	9.51
Ag ¹⁰⁹	0.0659	9.04
P ³¹	0.209	
Al ²⁷	0.0476	
Ga ⁷¹	0.144	
Cd ¹¹¹	0.331	
Sn ¹¹⁹	0.457	
$\xi(\text{Cu in Cu})=0.54$		$\xi(\text{Ag in Ag})=0.65$
$\xi(\text{Al in Cu})=1.03$		$\xi(\text{Cu in Ag})=0.57$
$\xi(\text{P in Cu})=0.61$		
$\xi(\text{Ga in Cu})=1.11$		$\xi(\text{Ga in Ag})=1.59$
$\xi(\text{Cd in Cu})=0.55$		$\xi(\text{Cd in Ag})=0.68$
$\xi(\text{Sn in Cu})=0.85$		$\xi(\text{Sn in Ag})=1.14$

contribute approximately equally to the observed width. When relatively probable configurations of atoms cause only moderate splitting (e.g. less than 5 kc/sec) of the central line ($m = -\frac{1}{2} \rightarrow \frac{1}{2}$), then this intensity distribution, rather than the dipolar width, determines the observed linewidth. The width of this absorption as a function of external field depends upon the particular electric gradient distribution and is not necessarily inversely proportional to the field as it is in the case of a homogeneous electric gradient. The slight decrease in width with decreasing field strength for the 4.5 at. % sample indicates that the inhomogeneous Knight shift is partially responsible for the width.

For Ga in Cu the calculated dipolar width is 3.5 G while the observed widths run from 4.5 to 5.9 G with a 1.5 to 6 at. % range of Ga content. This is indicative of an inhomogeneous Knight shift.

A single ternary alloy of silver with 2.99 at. % Ga and 5.1 at. % Cu was investigated to try to further understand the dominant broadening mechanism. In it the linewidth of the Cu⁶³ was 3.1 G (at $H_0 = 6940$ and 13 850 G) and that of the Ga⁷¹ 6.1 G. Since the quadrupole moments are nearly identical, the difference in linewidth appears to arise from the inhomogeneous Knight shift; the ratio of widths is approximately equal to the ratio of the Knight shifts of Cu and Ga in Ag. The insensitivity of linewidth to field indicates a quadrupole contribution also. In a binary 5 at. % Cu in Ag alloy, the linewidth was only 1.5 G. This relatively small value (compared to Ga in Ag) reflects the much smaller charge perturbation caused by the Cu (excess charge zero) than the Ga (excess charge +2).

Further insight into the factors comprising the Knight shift can be gained by computing the factor ξ for the various alloys assuming, as before, that χ_P in the alloy is the same as in the pure solvent metal but allowing $\xi(B \text{ in } A) \neq \xi_A$. $\xi(B \text{ in } A)$ assumes the meaning

$$\frac{\langle |\Psi_F(r_B)|^2 \rangle \langle |\Psi_F(r_A)|^2 \rangle}{\langle |\Psi_F(r_A)|^2 \rangle \langle |\Psi_A(0)|^2_A \rangle}$$

The values of χ_P used were computed from electronic specific heats¹⁰ by the usual formula (Knight's⁴ Eq. (5.2)). We have made previous reference to the method of obtaining the $a(s)$ values used in this paper. These are listed in Table IV along with the χ_P values used. The $\xi(B \text{ in } A)$ values given below have been computed using the relation⁴

$$\xi(B \text{ in } A) = [g_{IB}^4 K_B / 0.352 a(s)_B \chi_{PA}], \quad (4)$$

with 4K_B given in percent, $g_{IB} = (\mu_B / I_B)$ in nuclear magnetons, $a(s)$ in cm^{-1} and χ_P in cgs units per mole $\times 10^6$. There does seem to be a tendency for the solutes in silver to give a larger ξ value than the same solutes in copper. This indicates a correspondingly larger s character in silver.

IV. DISCUSSION

Perhaps the most surprising feature of the data is the relatively small change in Knight shift with composition for the Sn¹¹⁹ resonance in the Ag-Sn alloys. We expected $-\langle \Delta K \rangle_{av} / ^A g K_{\text{Sn}} C$ for Sn to be close to the value $-\langle \Delta K \rangle_{av} / K_{\text{Ag}} C$ for Ag, rather than approximately one-fourth of the latter. Unless there is a fundamental explanation for this behavior in terms of the electron redistribution around near-neighbor impurity atoms, it appears that the impurities prefer not to be neighbors. According to every theoretical estimate, there is a large negative change in the Knight shift of nuclei neighboring a solute atom with excess positive charge. Accordingly, if other solute atoms were to avoid these sites, their Knight-shift changes would be less negative than those of the solvent. Although the theoretical evidence for believing there may be short-range order in these alloys is largely qualitative, the interaction energy estimated by Blandin *et al.*¹¹ for Sn atoms in Ag amounts to about 0.3 eV and is repulsive. This is greater than the thermal energy of about 0.1 eV at the temperatures from which our alloys were quenched. Flynn¹² also remarks on the deviations from random positioning of solutes which would accompany the long-range oscillations. This tendency depends upon relative solute valence and lattice type.

Although it has not been possible in general to deal quantitatively with the data presented, we have attempted to make some comparisons which are helpful in demonstrating the characteristics of the solute resonance absorption in solid solution. We have noted the different resonance behavior to be expected of solutes depending upon their nuclear electric quadrupole moments and their excess charge in the matrix. The evaluation of the sum $\sum_R [\Delta\rho(R)/\rho_0]^2$ for Sn in Ag led to

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¹² C. P. Flynn and R. L. Odle, Proc. Phys. Soc. (London) **81**, 412 (1963).

reasonable agreement with the same quantity for the solvent; fair agreement was also found in the case of Cd in Ag, where the sum for the solute was 0.004, to be compared with the experimental value of 0.006 for the silver and a computed² (square-well) value of 0.003.

The linewidths of Al, Sn, and P in Cu were all 4.5 to 5.5 G and very slowly dependent upon solute concentration. The dipolar contribution accounted for the major part of the width and the inhomogeneous Knight

shift was probably responsible for the balance. Because of the errors involved in the measurement of total linewidth and the large proportion of dipolar width an analysis of the type carried out for the Sn and Cd in Ag alloys was not feasible.

ACKNOWLEDGMENT

We are grateful to Dr. C. P. Flynn for a discussion of the solute-solute interaction energies in these alloys.

X-Ray *K* Absorption Spectra of Cu-Ni Alloys*

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(Received 16 December 1963)

Copper and nickel *K* absorption spectra have been measured in the pure metals and in four alloys, respectively, containing 17.2, 26.0, 43.3, and 65.6 at. % copper. Variations in the absorption-edge fine structure of both metals were observed in the nickel-rich solid solutions. These variations are interpreted by considering the electronic configurations of the individual absorbing atoms and how they are altered by alloying. It is proposed that the *K* absorption spectrum of each constituent should be different and should not reflect a common density-of-states distribution for the alloy. It is also shown that this model can be applied to explain the x-ray emission spectra observed by others.

I. INTRODUCTION

THE difficulties associated with the selection of a suitable model for interpreting x-ray emission and absorption spectra in solids have been described previously.¹⁻³ In x-ray emission, the filling of an inner electron vacancy in an atom by one of the outer electrons is accompanied by the emission of an x-ray quantum having the corresponding energy. Conversely, in x-ray absorption, an incident x-ray quantum is absorbed provided its energy is sufficient to excite an inner electron to one of the normally unoccupied outer states. Thus, emission spectra of solids are related to the availability and energy distribution of valence-conduction electrons whereas their absorption spectra are related to the normally empty higher energy state distributions. The actual transitions are determined by quantum-mechanical transition probabilities which are usually too complicated to evaluate quantitatively except for determining the symmetries of the initial and final states (selection rules). The interpretation is further complicated by the fact that the excited atom may act as a perturbation, that is, it superimposes its own localized discrete states onto the energy bands of the solid. Despite these difficulties, which have prevented the development of a rigorous quantitative

theory, repeated efforts have been made to deduce the general features of energy bands in solids, such as their shapes, widths, and degree of occupation.

The present investigation was undertaken primarily to determine what correlations, if any, could be established between the fine structure observed in x-ray absorption spectra of alloys and their electronic structure. To date, essentially three kinds of correlations have been proposed. In 1939, Beeman and Friedman⁴ demonstrated quite clearly that the absorption-edge structure of copper and nickel could be explained by the then recently calculated energy-band model of these metals.^{5,6} The validity of this correlation has been re-emphasized by Burdick⁷ who found that it agreed with his recalculation of the energy-band structure of copper. Nemnonov⁸ has extended this approach by attempting to correlate the presumed electronic structures of transition metals, their alloys, and their compounds, to displacements (along the energy scale) of certain portions of the absorption edge. As pointed out below, the exact location of inflections or other characteristics of the absorption-edge curves along the energy scale is subject to considerable error so that the efficacy of this procedure is uncertain. Similarly, specific correlations of the fine structure to plasma oscillations

* This research was supported by U. S. Navy, Office of Naval Research.

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