PHYSICAL REVIEW VOLUME 161, NUMBER 3 15 SEPTEMBER 1967

New Scheme for the Construction of Phase Shifts with Application to Nuclear Magnetic Resonance*

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(Received 23 February 1967)

A semiempirical scheme is developed for the construction of phase shifts of unlimited order for the investigation of properties depending on the electron redistribution in alloys. The method utilizes a generalized free-electron potential around the solute atom, residual-resistivity data, and the Friedel sum rule. Application to the Knight shifts in a series of dilute alloys with liquid copper and solid silver as hosts leads to much better agreement with experiment than obtained previously.

THERE are currently two sets of phase shifts in extensive use in problems related to the electronic structure of dilute alloys, particularly in the study of NMR (nuclear magnetic resonance). The first set, proposed by Blatt[1] (B), assumes a square-well potential for the solute atom; the second, due to Kohn and Vosko[2] KV, is derived semiempirically utilizing resistivity data and the Friedel sum rule. Blatt's method has been mainly criticized for adopting an arbitrary form for the solute potential, and that of KV for giving phase shifts only for $l \leq 1$. In the present investigation, we attempt to remedy these shortcomings with a scheme which generates phase shifts of unlimited order utilizing a generalized free-electron potential and an extension of the semiempirical approach of KV. These phase shifts are found to lead to better agreement with experiment for the Knight shift of dilute Ag and liquid Cu alloys than had been obtained previously.

Since phase shifts of high order are known to depend almost entirely on the potential in the region away from the vicinity of the solute nucleus,[3] we will not be concerned with the precise potential form at or near the origin in their determination. We can utilize in the evaluation of those phase shifts a potential known in the outer region only and we will adopt for this potential a form generally consistent with the free-electron framework,[4] viz.,

$$V = \frac{1}{r} \sum_{n=1}^{\infty} C_n \exp(-nqr), \tag{1}$$

where the C_n's are numerical coefficients with $C_1 \gg C_2$, $C_3, \cdots$; and q is a screening constant. In the Born approximation,[3] it can be shown that the lth-order phase shift corresponding to the potential in Eq. (1) is given by

$$\eta_l = -\frac{m}{\hbar^2 k_F} \sum_{n=1}^{\infty} C_n Q_l(1+n^2q^2/2k_F^2), \tag{2}$$

where Q_l is a Legendre polynomial of the second kind, and k_F is the Fermi wave number of the solvent. For $q \sim 1$ atomic unit (a.u.), it can be shown that to a good approximation,

$$\frac{\eta_l}{\eta_{l+1}} = \frac{Q_l(1+q^2/2k_F^2)}{Q_{l+1}(1+q^2/2k_F^2)}. \tag{3}$$

Equation (3), for $l \geq 1$, can now be combined with (a) the Friedel sum rule [corrected for atomic size factor (see Ref. 1)], viz.,

$$Z_I = \frac{2}{\pi} \sum_l (2l+1)\eta_l, \tag{4}$$

where Z_I is the effective residual nuclear charge of a solute atom, and (b) the free-electron expression for the residual resistivity in a dilute alloy,[5]

$$\Delta\rho = \frac{4\pi\hbar c}{Ze^2k_F} \sum_{l=1}^{\infty} l \sin^2(\eta_{l-1}-\eta_l), \tag{5}$$

where Z is the solvent valence, and c the atomic fraction of solute, to give a set of simultaneous equations which can be solved for phase shifts of unlimited order.

Figure 1 displays the phase shifts obtained by the present method for Zn and Se in copper, when Mott's[6] screening constant (i.e., $q^2 = 4me^2k_F/\hbar^2\pi$) is used in the calculations. The corresponding phase shifts obtained by B and KV are shown for comparison. We have used phase shifts obtained by the three methods to estimate the relative change in the average Knight shift K with atomic fraction of solute for dilute Ag and liquid Cu alloys. The calculations were carried out utilizing Daniel's[7] Knight-shift expression:

$$\frac{1}{K}\frac{\partial K}{\partial c} = \sum_l \{A_l \sin^2\eta_l + B_l \sin 2\eta_l\}, \tag{6}$$

where A_l and B_l are coefficients depending on the atomic distribution in the host metal. These coefficients were obtained by revising the estimates of Odle and Flynn[8]

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* Work performed under the auspices of the U. S. Atomic Energy Commission.

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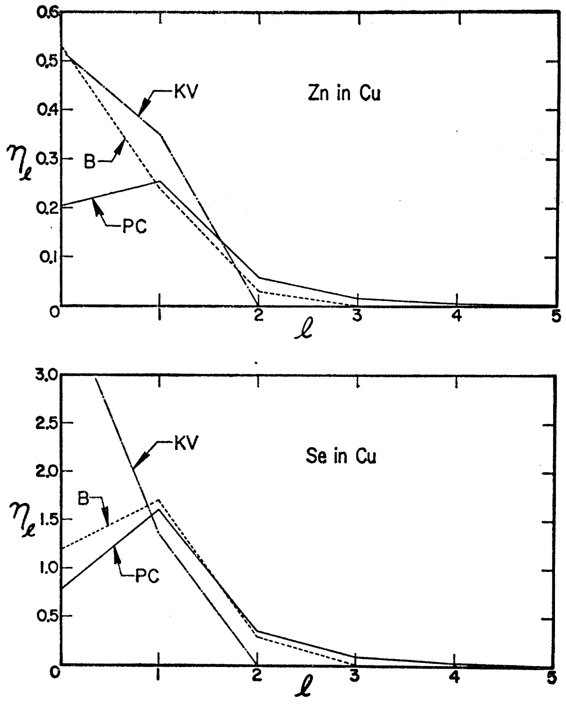

FIG. 1. Comparison of the three sets of phase shifts for Zn and Se in copper. Legend: dashed line, B; dot dash line KV; and solid line PC (present calculation).

for Cu, and from Van Ostenburg and Alfred[9] for Ag. Figure 2(a) shows a comparison of the measured[10] $(1/K)/(\partial K/\partial c)$ with the calculated values for Cu, and Fig. 2(b) for Ag.

We find that the agreement between theory and experiment is improved very significantly when the new phase shifts are used, indicating that they describe the scattering of conduction electrons in dilute copper and silver base alloys better than previous sets of phase shifts. The present results also serve to correct the impression, obtained from earlier work,[8,11] that the free-electron theory of Knight shift in dilute alloys with a fcc monovalent host only leads to qualitative agreement with experiment. We have shown that it can yield good theoretical estimates when proper phase shifts and Knight-shift coefficients are used.

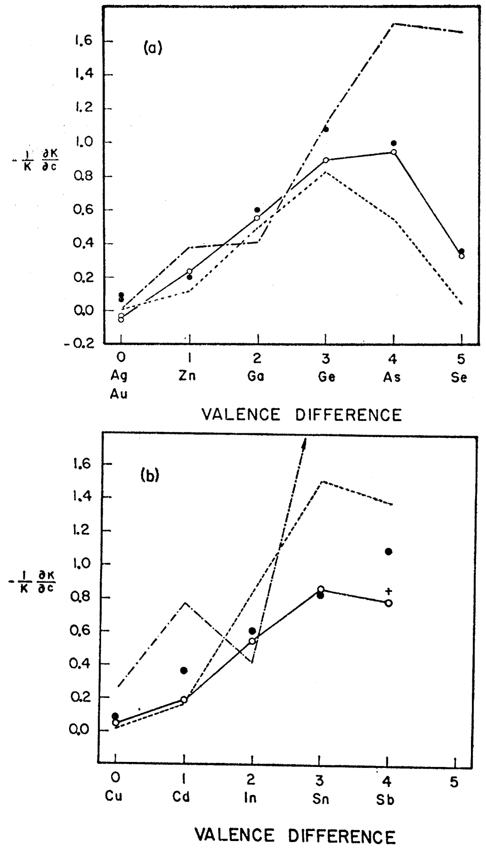

FIG. 2(a) The fractional Knight-shift change for unit solute concentration, $K^{-1}\partial K/\partial c$, for various impurities in liquid copper. Data points are denoted by ●. (Ref. 8). Curves denote theoretical values using different sets of phase shifts, dashed line, B; dot-dash line, KV; and solid line, PC. (b) Same as (a) but for silver as the host. Data points from Ref. 11. The value + was obtained from Ref. 11 by weighting more heavily the data at low concentration.

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