powder-pattern structure at 4.2 K. Only when a field is applied at 4.2 K is there direct evidence of randomization of the magnetization directions, indicated by the more rapid disappearance of the multiplet structure compared to the total resonance. Therefore we would rule out zero-field 3-dimensional powder pattern insofar as it is produced by shape anisotropy. However, within the c plane the ^{11}B NMR cannot distinguish between a 2-dimensional powder pattern and a model of only two magnetically inequivalent sites.

The appearance of the dispersion mode in the ^{11}B NMR at $T=4.2$ K in zero applied field is likely due to the absorption derivatives saturating out more rapidly with increasing T_1 than the dispersion derivatives at a fixed level of rf field.[24] An admixture of dispersion-dependent upon T_1 and the effective rf field will always be present at the marginal oscillator detector because of the electronic mechanism driving the nuclear resonance.[24] This effect is demonstrated in Figs. 3(a) and 3(b), where upon increasing the rf level by approximately a factor of two, the dispersion component becomes evident. The possibility that the enhancement of the applied rf field goes up with decreasing temperature cannot be ruled out, but this seems unlikely in view of the fact that magnetocrystalline anisotropy field increases at lower temperatures[14] (decreasing the enhancement factor). There is nothing to suggest that the multiplet and background resonances come from two different sources. For example, no difference in temperature dependence of the two resonances has been observed.

ACKNOWLEDGMENTS

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[24] R. L. Streever and L. H. Bennett, Phys. Rev. 131, 2000 (1963).

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Knight Shifts in Liquid Alloys from the Pseudopotential Formalism

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The fractional changes of Knight shift $\Delta S/S$ for solvent and solute atoms in liquid In-Tl, Pb-Sn, Hg-In, and Ga-In alloys have been calculated from the pseudopotential formalism. It is shown that the Faber theory developed for the substitutional dilute liquid alloys can be extended to include the nonsubstitutional liquid alloys of any concentration within the first-order approximation. The experimental and hard-sphere-model interference functions $I(K)$ have been used, and it is pointed out that small errors in $I(K)$, particularly with respect to its peak shape and peak position, are rather unimportant as far as the qualitative results for $\Delta S/S$ are concerned. The calculations predict the right sign and right trend of the $\Delta S/S$-versus-c plots of the above liquid alloys. Quantitatively, however, there exists some disagreement, which may easily be interpreted in terms of the variation of the spin paramagnetic susceptibility and perhaps the Fermi diameter with the solute concentrations; these effects were not considered in the basic theory. The present findings strongly suggest that the pseudopotential approach leads to encouraging results if the pseudopotentials are correctly evaluated and necessary corrections are applied.

I. INTRODUCTION

THIS paper will deal with some calculations of Knight shifts in liquid In-Tl, Pb-Sn, Hg-In, and Ga-In alloys, which form a practical test of the application of the nearly free-electron model. The calculations are based on the pseudopotential formalism and the interference functions of the liquid metals.

The theory that we propose to use is an extension of Faber's[1] theory developed for very dilute substitutional alloys. The fractional change of Knight shift $\Delta S/S$ of the solvent and solute atoms with concentration will be evaluated using the hard-sphere-model and experimental interference functions. Although the theory has some limitations, it will be shown that the present approach is moderately adequate in interpreting the behavior of the above liquid alloys over the whole composition range. No attempt will be made to discuss the concentration dependence of the spin susceptibility term.

II. NUCLEAR MAGNETIC RESONANCE SHIFTS

If a small amount of impurity is introduced in a pure metallic specimen, two things may happen whenever there is a nuclear magnetic resonance[2] (NMR). First,

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[1] T. E. Faber, Advan. Phys. 16, 637 (1967).

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

there occurs a broadening of the resonance line, and second, the position of the resonance line is usually shifted. In this paper we will be concerned with the impurity shifts of NMR lines in liquid alloys.

The shift of an NMR line represents the interaction of the nuclei and the conduction electrons.[3] The shift may be caused by either of the two possible magnetic interactions between the nuclei and the electrons, which are known as the Knight shift and chemical shift according to their origin. The former shift represents the coupling of the electrons to the nucleus due to the magnetic moment associated with the electron spin; the latter, that due to magnetic fields originating from the motion of the electron charges. Thus, the Knight shift in metals is quite different from the chemical shift. Furthermore, the Knight shift is observed to be larger than the chemical shift in metals.

We will, at present, deal with Knight shifts only, and therefore, all other resonance phenomenona will be excluded from further discussions. We will first briefly describe the situations in the solids, and then pass on to liquids—in particular the liquid alloys. Our final approach will involve an application of the nearly free-electron model[4] and the use of an appropriate atomic-distribution function[5] of the crystal lattice. We begin by writing down the equation for pure metals. For a given nuclear spin, the strength of the resonance magnetic field is characterized by the surrounding constituents of the nucleus. It has been shown[6] that the relative change of the resonance magnetic field ΔH for two different environments of a particular nucleus is

$$\Delta H/H=(8\pi/3)\Omega_0\chi_P\langle|\psi(0)|^2\rangle_F, \qquad (1)$$

where Ω_0 is the atomic volume, χ_P is the spin paramagnetic susceptibility per unit volume, and $\langle|\psi(0)|^2\rangle_F$ is the density of the s electron, i.e., the conduction electron, at the site of the nucleus averaged over the Fermi surface. χ_P is proportional to the density of states at the Fermi surface and can be measured experimentally. Most important of all is the term $\langle|\psi(0)|^2\rangle_F$, which depends primarily on the atomic volume and the atomic structure of the metal. Experimentally one may achieve the above resonance condition also by changing the radio frequency of the applied magnetic field, and in that case the above equation reduces to

$$\Delta\nu/\nu=(8\pi/3)\Omega_0\chi_P\langle|\psi(0)|^2\rangle_F.$$

If we make use of the electron density function $\langle|\psi_A(0)|^2\rangle$ of the free atom at the site of the nucleus we may write[2]

$$\langle|\psi(0)|^2\rangle_F=\xi\langle|\psi_A(0)|^2\rangle. \qquad (2)$$

Denoting $\langle|\psi(0)|^2\rangle_F$ by P_F and $\langle|\psi_A(0)|^2\rangle$ by P_A we get

$$S=\Delta H/H=\Delta\nu/\nu=(8\pi/3)\Omega_0\chi_P\xi P_A. \qquad (3)$$

The factor $\xi=P_F/P_A$, as measured[3] for solid alkali metals, is about 0.5–0.8, and agrees very well with the theoretical calculation of Kjeldaas and Kohn.[7] The above theory has been reasonably successful in explaining the Knight shifts in solid metals.

The fact that the solid loses its long-range periodicity upon melting, causing an enhancement of the atomic volume, was considered to be a strong indication that the Knight shift for solids should change appreciably at the melting temperature.[2,8] Although Eq. (3) is valid for both solids and liquids, it failed to predict the experimental observations (see Table I in Ref. 2), i.e., practically no change in S upon melting was observed in Li, Hg, Al, and In. Thus, one is led to suspect the foundation of the theory. Nevertheless, later experiments have yielded results in the cases of Na,[2] Cs,[2] Sb,[9] Cu,[9] Bi,[10] and Cd [11] restoring some order in the theory, and thus encourage more faith in the use of the nearly free-electron model for liquid metals. Subsequently Watabe *et al.*[12] advanced a theory describing the temperature dependence of S in liquid metals and applied the theory to liquid Na. The results of their theory and experiment were in good agreement for liquid Na. In their theory, while the basic form of Eq. (3) was still intact, the quantity P_F for liquid metals was treated by the first-order perturbation method, and the electron wave functions were written in terms of pseudo-wave functions as outlined by Phillips and Kleinman.[13] The structural disorders were accounted for by the introduction of the interference function of the liquid.

The above is a general outline of the Knight shifts in pure solid and liquid metals. As we are interested here in the study of liquid alloys, in Sec. III we shall elaborate on the mechanism of Knight shift in liquid alloys, introducing some alternative arguments to those given above.

III. LIQUID-ALLOY THEORIES

The effect of an impurity atom in a metal is to alter the Knight-shift spectrum through changes at all nuclear positions. If the structure of the crystal is known (as in solid solutions), the exact solution of the problem is not difficult. The problem of the Knight shift in alloys was first attacked by Blandin and Daniel,[14] who

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[3] C. P. Slichter, ***Principles of Magnetic Resonance*** (Harper and Row Publishers, New York, 1963).

[4] J. M. Ziman, Phil. Mag. **6**, 1013 (1961).

[5] C. N. J. Wagner and N. C. Halder, Advan. Phys. **16**, 241 (1967).

[6] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

[7] T. Kjeldass and W. Kohn, Phys. Rev. **101**, 66 (1956).

[8] W. D. Knight, Solid State Phys. **2**, 132 (1956).

[9] R. L. Odle and C. P. Flynn, J. Phys. Chem. Solids **26**, 1685 (1965).

[10] R. R. Hewitt and B. F. Williams, Phys. Rev. Letters **12**, 216 (1964).

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

[12] M. Watabe, M. Tanaka, H. Endo, and B. K. Jones, Phil. Mag. **12**, 347 (1965).

[13] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[14] A. Blandin and E. Daniel, J. Phys. Chem. Solids **10**, 126 (1959).

considered that the changes in Knight shift originate in the changes of electron density at the Fermi surface caused by a spherically symmetric scattering center. Odle and Flynn[15] extended this idea to study liquid alloys by adding the modification terms generated by the short-range periodicity of the atomic arrangements and the true potentials of the liquids. Their theory depended on the radial-density function (also called the pair-probability function) of the solvent atoms and on the phase-shift data on the solute atoms at the given concentration of the solutes. Unfortunately, the latter values are not known with a great degree of certainty except for some recent calculations on the monovalent metals.[16,17] Besides, the Odle-Flynn theory is applicable to very dilute alloys.

Recently Faber[1,18] has developed a theory for calculating the Knight shifts in liquid alloys, using the pseudopotentials of the atoms and the interference functions of the solvent. It is the idea of this theory which will be useful to us. The original Faber theory is limited to a certain class of liquid alloys that are known as the substitutional alloys.[19] In these alloys the atomic constituents are supposed to have the same valences and same atomic volumes, so that the Fermi radius at the two extremities of the concentration range does not differ. Also, the Faber theory is satisfied by the very dilute alloys. Here we will rewrite his theory in a manner suitable for our calculations and carry it one step further to study both substitutional and nonsubstitutional alloys at any solute concentration.

We have seen earlier that the density of electrons at the site of a nucleus, i.e., the probability density of finding an electron at a nucleus, is

$$P_F=\langle|\psi(0)|^2\rangle_F.$$

If there are N ions present in a given volume of the liquid, then

$$P_F=\left\langle\frac{1}{N}\sum|\psi(\mathbf{r}_i)|^2\rangle\right\rangle_F, \tag{4}$$

where $\mathbf{r}_i$ is the position of an ith ion, the angular brackets mean the average over the Fermi surface. The conduction-electron wave function in the OPW approximation[13] is given by

$$\psi_k(\mathbf{r})=C_k[\phi_k(\mathbf{r})-\sum_\alpha(\phi_\alpha,\phi_k)\phi_\alpha(\mathbf{r})], \tag{5}$$

where

$$|C_k|^{-2}=(\phi_k,\phi_k)-\sum_\alpha|(\phi_\alpha,\phi_k)|^2. \tag{6}$$

$\phi_k(\mathbf{r})$ is the pseudo-wave function, and $\phi_\alpha(\mathbf{r})$ is the core electron wave function. The summation indicates inclusion of all ion sites as well as that of core states, and

$$(\phi_\alpha,\phi_k)=\int\phi_\alpha^*\phi_k d\Omega \tag{7}$$

indicates integration over the whole volume. The wave function $\phi_k(\mathbf{r})$ is a smoothly varying function, as in the orthogonalized-plane-wave treatment. The orthogonality condition [to make $\psi_k(\mathbf{r})$ orthogonal to $\phi_\alpha(\mathbf{r})$] is usually satisfied by writing the potential term of the wave equation in ϕ_k as V_R+V, where V_R is a repulsive potential added to the true potential V. This sum V_R+V is the pseudopotential, which is weak enough to be treated by the perturbation theory.

Let us now consider the following scattering problem. Suppose that an electron in a liquid metal passes from a state ψ_1 to another state ψ_2 under the action of a potential $v(\mathbf{r})$. The incident wave ψ_1 will be modulated both in amplitude and phase by the same potential of the adjacent ions, and may be represented by ψ, where this ψ really represents the incident plus all the scattered waves. Therefore, the probability of scattering from state ψ_1 to ψ_2 of an electron due to the potential $v(\mathbf{r})$ is proportional to the mean potential energy and can be determined[18] from

$$\int\psi_2^*v(\mathbf{r})\psi d\mathbf{r}.$$

We write the modulation factor as $1+\gamma_1(\mathbf{r})$, then it will be seen

$$\psi(\mathbf{r})=[1+\gamma_1(\mathbf{r})]\psi_1(\mathbf{r}). \tag{8}$$

The above result therefore becomes

$$\int\psi_2^*[1+\gamma_1(\mathbf{r})]v(\mathbf{r})\psi_1 d\mathbf{r}.$$

Writing $w(\mathbf{r})=[1+\gamma_1(\mathbf{r})]v(\mathbf{r})$, we find that this result is now equivalent to

$$\int\psi_2^*w(\mathbf{r})\psi_1 d\mathbf{r}.$$

This $w(\mathbf{r})$ is the effective potential that is causing scattering. If it is a nearly free-electron scattering, $w(\mathbf{r})$ may be expressed in terms of the pseudopotential $u(\mathbf{r})$. When the potential is very weak and the Born approximation is accepted, $\gamma_1(\mathbf{r})$ is very small and it may be neglected, that is, $w(\mathbf{r})\simeq u(\mathbf{r})$. Consider further that had we calculated the pseudopotential $u(\mathbf{r})$ of *an isolated ion* as done by Animalu and Heine (see Ref. 37), then of course we should have

$$w(\mathbf{r})=[1+\gamma(\mathbf{r})]u(\mathbf{r}), \tag{9}$$

where the term $1+\gamma(\mathbf{r})$ is introduced to represent some

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

[16] W. H. Young, A. Meyer, and G. E. Kilby, Phys. Rev. **160**, 482 (1967).

[17] J. M. Dickey, A. Meyer, and W. H. Young, Phys. Rev. **160**, 490 (1967).

[18] T. E. Faber, Advan. Phys. **15**, 547 (1966).

[19] T. E. Faber and J. M. Ziman, Phil. Mag. **11**, 153 (1965).

additional modulation due to the potential set up by the adjacent ions.

We saw before that the Knight shift S is proportional to $\langle|\psi(0)|^2\rangle_F$; hence it is also proportional to $[1+\gamma(0)_F]^2$ [see Eq. (8)]. If we disregard the variation of χ_P and omit the constant of proportionality terms, then it is easily seen, retaining the first order terms in $\gamma(0)_F$, that

$$S \simeq 1+2\gamma(0)_F. \tag{10}$$

Equation (10) is derived for liquid metals, i.e., for ions in the presence of the same kind of ions. The above argument is equally valid even when the surrounding ions are replaced by an impurity. Let c atomic percent of the impurity atoms be present in a liquid metal. The Knight shift now becomes

$$S_0 \simeq 1+2\gamma_0(0)_F. \tag{11}$$

The fractional change of Knight shift for the liquid alloy will be simply

$$\Gamma=(S_0-S)/S=2[\gamma_0(0)_F-\gamma(0)_F]/[1+2\gamma(0)_F]. \tag{12}$$

Faber[1] has clearly shown that when $u_0(0)$ goes to $-\frac{2}{3}E_F$, then to a good approximation in u, for an electron at the Fermi surface, one has

$$\gamma(0)_F=Z_0(m/m^*)\int_0^\infty [I(K)-1]\frac{u_0(K)}{u_0(0)} \times\left[\tfrac{1}{2}\ln\frac{(K+2k_F)^2+m^2/(4\hbar^2\tau^2K^2)}{(K-2k_F)^2+m^2/(4\hbar^2\tau^2K^2)}\right] \times\left(\frac{K}{2k_F}\right)d\left(\frac{K}{2k_F}\right), \tag{13}$$

where τ is the lifetime of an electron in a free-electron traveling-wave state, $I(K)$ is the solvent interference function, and $u_0(K)$ is the matrix element of the solvent pseudopotential $u_0(\mathbf{r})$. We will now discuss two cases.

Case I: Substitutional Alloys

For a substitutional alloy we may write $u_0(0)=u_1(0)$ and $\rho_1(r)=\rho_{10}(r)/c_1=\rho_{01}(r)/c_0=\rho_0(r)$. The subscripts 0 and 1 denote the solvent and solute atoms, respectively, and $\rho_{ij}(r)$ are called the partial distribution functions. It then immediately follows from Eqs. (10), (12), and (13) that

$$\Gamma=-\frac{2Z_0(m/m^*)}{1+2\gamma(0)_F}\int_0^\infty \frac{u_0(K)-u_1(K)}{u_0(0)}[I(K)-1] \times\left[\tfrac{1}{2}\ln\frac{(K+2k_F)^2+m^2/(4\hbar^2\tau^2K^2)}{(K-2k_F)^2+m^2/(4\hbar^2\tau^2K^2)}\right] \times\left(\frac{K}{2k_F}\right)d\left(\frac{K}{2k_F}\right). \tag{14}$$

Case II: Nonsubstitutional Alloys

In the case of nonsubstitutional but very dilute alloys, the effect of dilatation, i.e., the size effect, is significant. All that is now necessary is to replace $u_1(K)$ (the pseudopotential element of the solute atoms) by the reduced solute pseudopotential[19] element

$$u_1'(K)=u_1(K)-u_0(K)\delta F(K), \tag{15}$$

where δ is the dilatation term defined by

$$\delta=\frac{\text{change in volume caused by the impurity}}{\text{mean atomic volume}}, \tag{16}$$

and $F(K)$ is a function of K, which is related to the pair probability function $P(r)$ by

$$\begin{aligned} F(K)&=\int_0^\infty \frac{dP(r)}{dr}\frac{\sin Kr}{Kr}dr \\ &=\frac{1}{\rho_0}\int_0^\infty \frac{d\rho(r)}{dr}\frac{\sin Kr}{Kr}dr, \end{aligned} \tag{17}$$

where ρ_0 is the average atomic density of the liquid. Then the formula for Γ becomes

$$\Gamma=-\frac{2(m/m^*)}{1+2\gamma(0)_F}\int_0^\infty\left[\frac{Z_0u_0(K)}{u_0(0)}-\frac{Z_1u_1'(K)}{u_1'(0)}\right] \times[I(K)-1]\left[\tfrac{1}{2}\ln\frac{(K+2k_F)^2+m^2/(4\hbar^2\tau^2K^2)}{(K-2k_F)^2+m^2/(4\hbar^2\tau^2K^2)}\right] \times\left(\frac{K}{2k_F}\right)d\left(\frac{K}{2k_F}\right). \tag{18}$$

Equations (14) and (18) are still valid for nonsubstitutional alloys with large c if the functions $I(K)$ are independent of the concentration, i.e., when the pure-solvent radial distribution function is indistinguishable from the solvent-solvent distributions. Such liquid alloys are Ag-Sn,[20] Au-Sn,[21] and Cu-Sn.[22] It is, therefore, natural to expect that in these alloys $\Delta S/S$ will be approximately linear in c. Hence the only factor that determines the change of $\Delta S/S$ in these alloys is δ. For small enough δ $\Delta S/S$ will be exactly linear in c.

Nevertheless one can use the present theory if one replaces the term $I(K)-1$ by $I_{00}(K)-1$ at the desired concentration. The partial interference function $I_{00}(K)$ has the form[20,23]

$$I_{00}(K)=1+\int_0^\infty [\rho_{00}(r)/c_0-\rho_0]\frac{\sin Kr}{Kr}d^3r.$$

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[20] N. C. Halder and C. N. J. Wagner, J. Chem. Phys. **47**, 4385 (1967).

[21] C. N. J. Wagner, N. C. Halder, and D. M. North, Phys. Letters **25A**, 663 (1967).

[22] D. M. North and C. N. J. Wagner (unpublished).

[23] N. C. Halder and C. N. J. Wagner, Z. Naturforsch. **22A**, 1489 (1967).

It is well known that $I_{00}(K)$ is a function of the alloy, solute-solute, and solvent-solute interference functions,

$$I(K)=\frac{c_0^2f_0^2}{\langle f\rangle^2}I_{00}(K)+\frac{c_1^2f_1^2}{\langle f\rangle^2}I_{11}(K)+\frac{2c_0c_1f_1f_2}{\langle f\rangle^2}I_{01}(K), \quad (19)$$

where the f's are the atomic scattering factors, and $\langle f\rangle$ is the weighted average of f. There is no way of determining these quantities except by means of three-radiation experiments, as suggested in the work of Keating.[24] The three-radiation experiment involves practical problems not yet surmounted, and has not yet been enthusiastically pursued except in the case of liquid Cu_6Sn_5 alloy.[25] Fortunately, however, a theoretical computation[26,27] of $I_{00}(K)$ is possible using the Percus-Yevick equation for the hard-sphere (HS) model. Recently both HS $I(K)$ and HS $I_{ij}(K)$ have been successful in explaining the electrical resistivities in liquid metals and alloys. Finally, after adding the dilatation term we may, to a good approximation, take the interference function term for a nonsubstitutional alloy as

$$I_{00}(K)-\delta F(K)-1.$$

Writing $I'(K)$ for $I_{00}-\delta F(K)$, we have in this case

$$\Gamma=-\frac{2(m/m^*)}{(1+2\gamma(0)_F)}\int_0^\infty\left[\frac{Z_0u_0(K)}{u_0(0)}-\frac{Z_1u_1'(K)}{u_1'(0)}\right]\times[I'(K)-1]\left[\tfrac{1}{2}\ln\frac{(K+2k_F)^2+m^2/(4\hbar^2\tau^2K^2)}{(K-2k_F)^2+m^2/(4\hbar^2\tau^2K^2)}\right]\times\left(\frac{K}{2k_F}\right)d\left(\frac{K}{2k_F}\right). \quad (20)$$

IV. ACTUAL COMPUTATION OF KNIGHT SHIFTS

Choice of the Systems

Four liquid alloy systems—In-Tl, Pb-Sn, Hg-In, and Ga-In—were chosen, for which experimental data are available from NMR measurements.[28–30] In In-Tl and Pb-Sn alloys both the solvent and solute atoms are equivalent and have nearly the same Fermi radii (within about 4%). These two systems more or less satisfy the existing requirements of Eq. (14). Hg-In and Ga-In alloys fall in the group of nonsubstitutional alloys and can be fitted well within the first order approximation laid out in Eq. (20). In addition, the data on $I(K)$ of the elements of the above four alloys have been measured with sufficient accuracy, and also their $u(K)$'s have been calculated with reasonable success. Thus these systems constitute very interesting alloys which seem to present problems amenable to practical solution and leading to useful results based on the pseudopotential theory.

Interference Functions

Several interference functions were used. It is important that they should be defined clearly. The experimental interference function is defined [20] by

$$I(K)=[I_{eu}^{\text{coh}}-\langle f^2\rangle+\langle f\rangle^2]/\langle f\rangle^2=1+\int_0^\infty[\rho(r)-\rho_0]\frac{\sin Kr}{Kr}d^3r. \quad (21)$$

The coherently scattered intensity I_{eu}^{coh} is obtained from x-ray or neutron-diffraction experiments. The HS $I(K)$ is written[31] as

$$I(K\sigma)=1/[1-\rho_0c(K\sigma)], \quad (22)$$

where the function

$$c(K\sigma)=-4\pi\sigma^3\int_0^1(\alpha_0+\beta s+\gamma s^3)\frac{\sin(sK\sigma)}{(sK\sigma)}s^2ds, \quad (23)$$

and the packing density

$$\eta=\pi\rho_0\sigma^3/6.$$

α_0, β, and γ are constants depending on η, and σ is the hard-sphere diameter. For alloys,[32] however, the distribution function is

$$\rho(r)=\sum_i\sum_j c_if_if_j\rho_{ij}(r)/\langle f\rangle^2, \quad (24)$$

which yields the partial interference functions of the type

$$I_{ij}(K)=1+\int_0^\infty[\rho_{ij}(r)/c_j-\rho_0]\frac{\sin Kr}{Kr}d^3r. \quad (25)$$

These are related as shown in Eq. (19). The HS $I_{ij}(K)$ for alloys[27] are

$$I_{ij}^H(K)=\delta_{ij}+(\rho_i\rho_j)^{1/2}\int_0^\infty(g_{ij}-1)\frac{\sin Kr}{Kr}d^3r, \quad (26)$$

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[24] D. T. Keating, J. Appl. Phys. **34**, 923 (1963).

[25] J. E. Enderby, D. M. North, and P. A. Egelstaff, Phil. Mag. **14**, 961 (1966).

[26] N. W. Ashcroft and D. C. Langreth, Phys. Rev. **156**, 685 (1967).

[27] J. E. Enderby and D. M. North, Phys. Chem. Liquids **1**, 1 (1968).

[28] D. J. Moulson and E. F. W. Seymour, Advan. Phys. **16**, 449 (1967).

[29] W. Van Der Lugt and S. B. Van Der Molen, Phys. Status Solidi **19**, 327 (1967).

[30] D. J. Moulson and G. A. Styles, Phys. Letters **24A**, 438 (1967).

[31] N. W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).

[32] N. C. Halder and C. N. J. Wagner, J. Chem. Phys. **45**, 482 (1966).

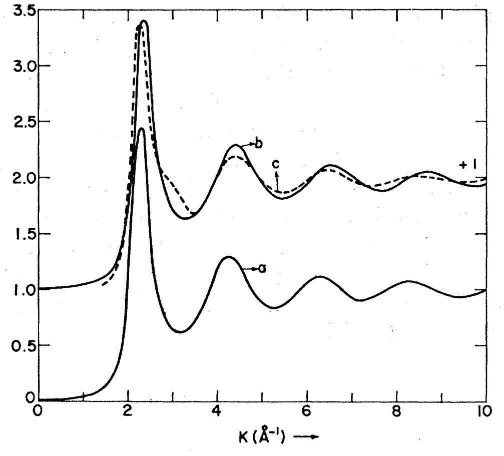

FIG. 1. Plots of the interference functions $I(K)$ for liquid Pb (330°C) and Sn (335°C). The experimental $I(K)$ for Pb was identical to the hard-sphere (HS) $I(K)$, as shown in curve a. Curves b and c, respectively, denote the HS and the experimental $I(K)$ for liquid Sn.

where δ_{ij} is the Kronecker delta, and

$$g_{11}=1+[c_{11}(1-\rho_2c_{22})+\rho_2c_{12}^2]P^{-1},$$
$$g_{22}=1+[c_{22}(1-\rho_1c_{11})+\rho_1c_{12}^2]P^{-1}, \qquad (27)$$

and

$$g_{12}=g_{21}=1+c_{12}P^{-1},$$

with

$$P=1-\rho_1c_{11}-\rho_2c_{22}+\rho_1\rho_2c_{11}c_{22}-\rho_1\rho_2c_{12}^2.$$

The coefficients c_{ij} are given by Enderby and North.[27]

The experimental $I(K)$ for liquid Tl (350°C) and Hg (25°C) were taken from Halder and Wagner,[32] In (170°C) from Ocken and Wagner,[33] Sn (335°C) from Wagner *et al.*,[34] and Ga (50°C) from Ascarelli.[35] All experimental $I(K)$ were from x-ray data except that for Ga, which was measured by neutron diffraction. The HS $I(K)$ and $I_{ij}(K)$ were calculated as discussed by Ashcroft and Lekner,[31] and Enderby and North.[27] Some of these $I(K)$ and $I_{ij}(K)$ are displayed in Figs. 1–3.

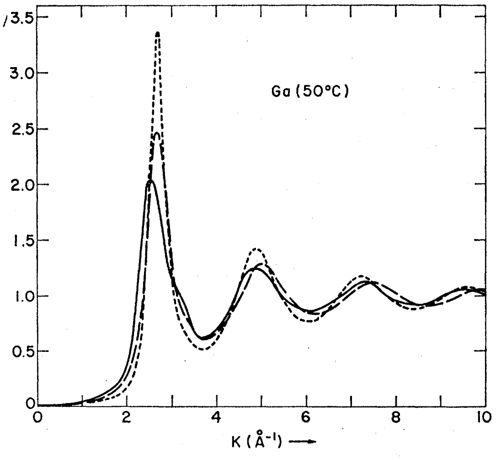

FIG. 2. Plots of the interference functions $I(K)$ for liquid Ga (50°C). The solid line gives the experimental $I(K)$; the dotted line, the HS $I(K)$ with packing density 0.50; and the dashed line, the HS $I(K)$ with packing density 0.45. Attempts at generating HS $I(K)$ with packing density below 0.45 to match the experimental $I(K)$ were unsuccessful. The experimental $I(K)$ was obtained by inverting the radial distribution function of Ga (50°C) reported by Ascarelli (Ref. 35).

Determination of δ and $F(K)$

The dilatation effects in the alloys were considered according to Eqs. (16) and (17). Let us write

$$\delta=(\Omega'-\Omega)/\bar{\Omega}, \qquad (28a)$$

where Ω' and Ω are the atomic volume of the element in the presence and absence of the impurity atom, respectively. $\bar{\Omega}$ represents the mean atomic volume. The above equation in the approximation becomes

$$\delta=(\rho_0^2-\rho'^2_0)/2\rho_0\rho'_0 \qquad (28b)$$

where ρ_0 and ρ'_0 are known from the density measurements.

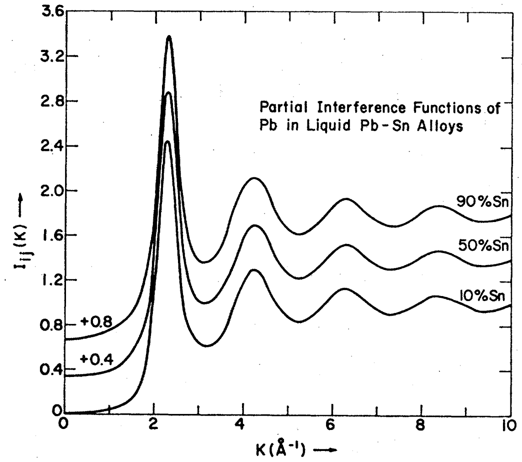

FIG. 3. Plots of the partial interference functions $I_{ij}(K)$ for liquid Pb(330°C) at different Sn concentrations. These partial functions were computed as discussed in the paper of Enderby and North, Ref. 27. These $I_{ij}(K)$ are somewhat different from HS $I(K)$ (see Fig. 1), particularly below the first peak; but no significant change was observed in the calculated $\Delta S/S$.

The function $F(K)$ of Eq. (17) was obtained from the derivatives $dP(r)/dr$. To get $P(r)$, the functions $I(K)$ were inverted:

$$P(r)=1+\frac{1}{2\pi^2\rho_0 r}\int_0^\infty K[I(K)-1]\sin Kr dK. \qquad (29)$$

The derivatives of $P(r)$ were computed numerically

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[33] H. Ocken and C. N. J. Wagner, Phys. Rev. **49**, 122 (1966).

[34] C. N. J. Wagner, H. Ocken, and M. L. Joshi, Z. Naturforsch. **20A**, 325 (1965).

[35] P. Ascarelli, Phys. Rev. **143**, 36 (1966).

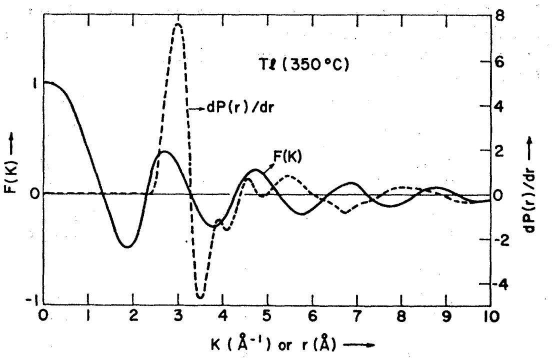

Fig. 4. Plots of the derivative $dP(r)/dr$ and the function $F(K)$ as defined in Eq. (17). These were obtained using Tl (350°C) data.

with the method of five-point approximation[36] at intervals of 0.1 Å. Incidentally, it is interesting to note that when $K\rightarrow 0$

$$F(K)=\int_0^\infty \frac{dP(r)}{dr}dr=1, \tag{30}$$

which result fixes the value of $F(K)$ for all elements at 1 for $K=0$. Figures 4 and 5 show the plots of $F(K)$ and $dP(r)/dr$ for liquid Tl (350°C) and In (170°C).

Pseudopotential Elements

The pseudopotential elements $u(K)$ due to Animalu and Heine (AH)[37] were used for all elements. The AH $u(K)$ for Hg, are, however, unsatisfactory, as has been pointed out previously.[38] Therefore, Ashcroft's[39] $u(K)$ for Hg, which were obtained somewhat empirically, were also employed. The AH $u(K)$, which were given as functions of $K/2k_F$, were first expressed as functions of K and then normalized—i.e., for all K, the $u(K)$ were divided by the AH $u(0)$ and then multiplied by the appropriate $u(0)$ corresponding to the temperature considered. This helped include the effect of temperature through the equation $u(0)=-\frac{2}{3}E_F$, where E_F is the Fermi energy. Two necessary corrections were made before these functions were used. The first step was to account for the screening of the ions. When solute atoms are dissolved in any solvent, we must evaluate the $u(K)$ of the solute embedded in the electron gas existing in the solvent atom. One may write[40]

$$u(K)_{\text{solute in solvent}}=u^{\text{AH}}(K)[\epsilon(K)_{\text{solute}}/\epsilon(K)_{\text{solvent}}], \tag{31}$$

where $\epsilon(K)$ is the dielectric function given by

$$\epsilon(K)=1+(4\pi e^2/K^2)N(E_F). \tag{32}$$

The quantity $N(E_F)$ is the density of states of the liquid at the Fermi surface, and is usually expressed[41] as

$$N(E_F)=4\pi k^2/(8\pi^3)[1/(dE/dk)],$$

which for a free-electron liquid becomes

$$N(E_F)=[m/(2\pi^2)](k_F/\hbar^2). \tag{33}$$

The second correction was made to absorb the dilatation effect,[42] as described in Eq. (15).

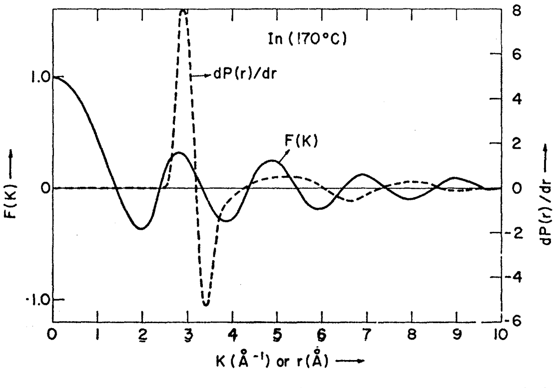

Fig. 5. Plots of the derivative $dP(r)/dr$ and the function $F(K)$ as defined in Eq. (17). These were obtained using In (170°C) data.

Electron Lifetime τ

The logarithmic term in Eq. (18) contains the quantity τ, the electron lifetime in the free-electron traveling-wave state, which needs some attention. Faber[18] writes

$$\frac{1}{\tau}=\frac{mk_0}{\pi\hbar^3\Omega}\int_0^1 \langle|u(K)|^2\rangle\times 2\left(\frac{K}{2k_0}\right)d\left(\frac{K}{2k_0}\right), \tag{34}$$

where

$$\langle|u(K)|^2\rangle=|u(K)|^2I(K).$$

τ is little different from the electronic relaxation time as defined by Ziman.[4] We set $k_0=k_F$ as an approximation and evaluated the integral. For metals those are under discussion here, we have $\tau\simeq 10^{-15}$ sec. In the work of Moulson and Seymour[28] the τ-dependent part of the logarithmic term was completely neglected.

We are now ready to compute $\gamma(0)_F$ and hence Γ. A program was written in FORTRAN language for a CDC 3100-3300 computer to solve Eqs. (14), (18), and (20). Provision was made to accept various $I(K)$ and $u(K)$. Table I shows the basic data on the solvent atoms which were used to calculate what follows.

V. DISCUSSIONS OF THE KNIGHT-SHIFT PARAMETERS

The calculated results are shown in Figs. 6–9. For comparison the experimental values are also reproduced

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[36] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1967), p. 883.

[37] A. O. E. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965).

[38] N. C. Halder and C. N. J. Wagner, Z. Naturforsch. **23A**, 992 (1968).

[39] N. W. Ashcroft, Phys. Letters **23**, 48 (1966).

[40] S. H. Kellington and J. M. Titman, Phil. Mag. **15**, 137 (1967).

[41] N. F. Mott, Advan. Phys. **16**, 49 (1967).

[42] T. E. Farber (private communication).

TABLE I. Solvent data used to calculate Knight shifts in liquid alloys. Note that in Hg-In alloys two different sets of pseudopotentials for Hg were used. I and II refer to the calculations based on Ashcroft and Animalu-Heine pseudopotentials of Hg, respectively. Both experimental (expt) and hard-sphere (HS) interference functions $I(K)$ were used to evaluate τ, $\gamma(0)_F$, and $\Gamma_{c=0}$, which are defined in Eqs. (34), (13), and (18), respectively. Z is the valence and k_F is the Fermi momentum.

Alloy	Solvent	Z	$k_F(\text{Å}^{-1})$	$I(K)$	τ(sec)	$[1+2\gamma(0)_F]$	$\Gamma_{c=0}$
In-Tl	In	3	1.484	expt HS	1.865×10^{-15} 0.928	0.890 0.813	−0.004 −0.049
Tl-In	Tl	3	1.432	expt HS	0.587 0.520	0.833 0.833	+0.010 +0.0001
Pb-Sn	Pb	4	1.548	HS	0.315	0.840	−0.033
Sn-Pb	Sn	4	1.607	expt HS	0.649 0.533	0.771 0.818	+0.038 +0.046
Hg-In(I)	Hg	2	1.340	expt	0.576	0.872	−0.346
Hg-In(II)	Hg	2		expt	1.850	0.555	+0.022
In-Hg(I)	In	3	1.484	expt	1.865	0.890	−0.207
In-Hg(II)	In	3		expt	1.865	0.890	+0.045
Ga-In	Ga	3	1.671	expt HS	0.702 0.718	0.804 0.807	−0.070 −0.086
In-Ga	In	3	1.484	expt HS	1.865 0.928	0.890 0.813	−0.054 +0.021

(Figs. 10–12). $\Delta S/S$ for the pure liquid metal in each case was adjusted to zero after the integration was performed, and consequently all the alloy data scaled with respect to this point.

Interpretation of the Results

As can be seen from Figs. 6 and 10, the shapes of the $\Delta S/S$ curve for In and Tl in In-Tl alloys agree well with that of the experimental curve. The calculated $\Delta S/S$ refer to liquid Tl at 350°C and liquid In at 170°C. The $\Delta S/S$ obtained with HS $I(K)$ are a little smaller than those obtained with the measured $I(K)$. A calculation with the HS partial $I_{ij}(K)$ did not yield results strikingly different from those with HS $I(K)$ for this alloy. The predicted values of $\Delta S/S$ for Tl and In are about ten times smaller and four times larger than the respective experimental values. The results for Pb and Sn in Pb-Sn alloys as shown in Fig. 7 do not seem to predict the right curvature of the experimental curves (Fig. 10), although the magnitudes of $\Delta S/S$ are now much closer to the measured values than for In-Tl alloys. Both the predicted and measured values fall with increasing Pb percentage. In Ga-In alloys the predicted $\Delta S/S$ for Ga is linear in c, and for In it is nonlinear, which agrees with one of the experimental observations,[29] as is evident from Fig. 11. Of course, there exists a temperature difference of 40°C between the two experimental findings; we do not believe that this temperature difference is really responsible for the discrepancy. Our results are based on Ga data[35] at 50°C and In data[33] at 170°C, and both temperatures are close to the respective melting temperatures. The case of Hg-In alloys is different. First,

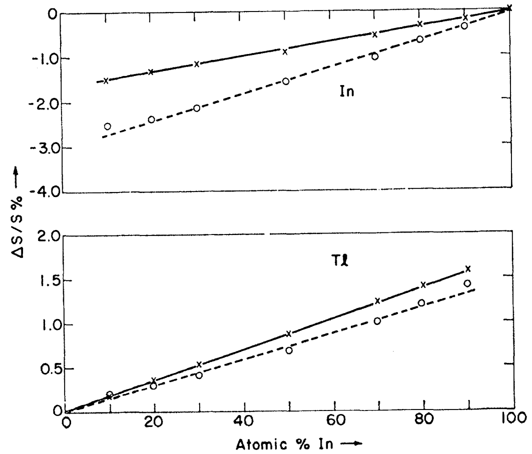

FIG. 6. Plots of the predicted $\Delta S/S$ as a function of atomic percent of In. × are obtained with measured $I(K)$ and ○ are obtained with HS $I(K)$. Partial $I_{ij}(K)$ gave almost the same values of $\Delta S/S$ as HS $I(K)$; thus those results are not shown here.

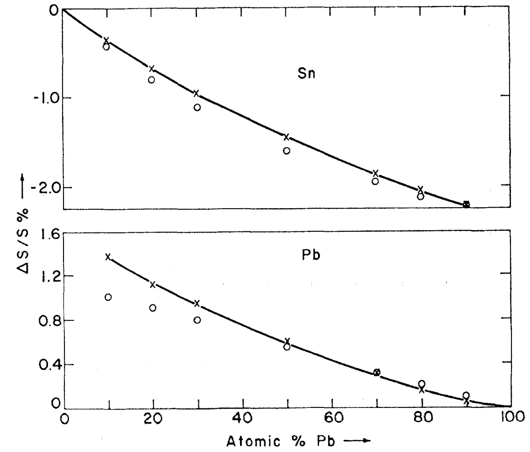

FIG. 7. Plots of the predicted $\Delta S/S$ as a function of atomic percent of Pb. The × line is obtained with measured $I(K)$; the ○ line is obtained with HS $I(K)$. Partial $I_{ij}(K)$ gave almost the same values of $\Delta S/S$ as HS $I(K)$; thus those results are not shown here.

Hg-In is not an equivalent alloy, and secondly, liquid Hg shows some anomalous behavior within the framework of the nearly free-electron model.[38,43] The predicted graphs for Hg and In in the alloy do not quite give the qualitative picture of the experimental trend. In particular, two differences are apparent. One is the missing hump of the In plot, and the other is the curvature of the Hg plot, which is concave downward rather than convex.

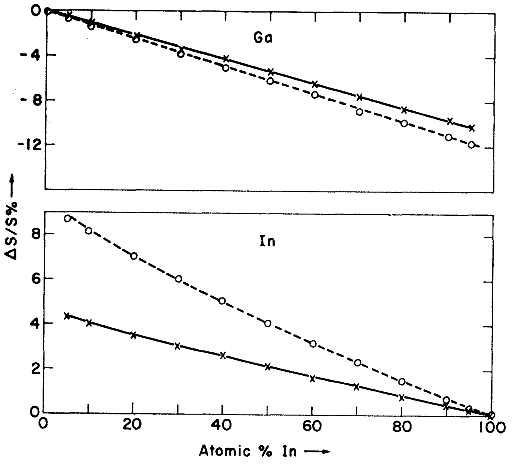

FIG. 8. Plots of the predicted $\Delta S/S$ as a function of atomic percent of In. The × line is obtained with measured $I(K)$; the ○ line is obtained with HS $I(K)$.

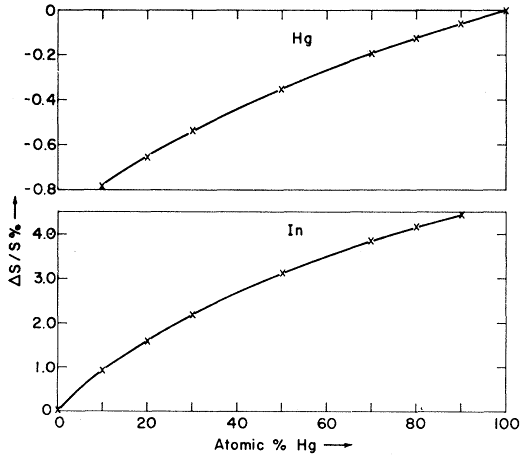

FIG. 9. Plots of the predicted $\Delta S/S$ as a function of atomic percent of Hg. These points were obtained with experimental $I(K)$ and AH (Ref. 37) $u(K)$ for In, but Ashcroft (Ref. 39) $u(K)$ for Hg.

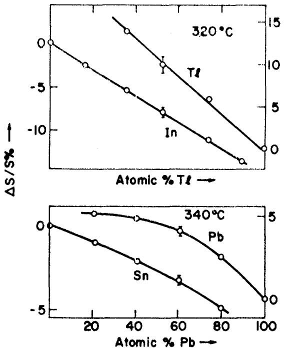

FIG. 10. Plots of the experimental $\Delta S/S$ of solvent and solute atoms in liquid In-Tl and Pb-Sn alloys. These were taken from Moulson and Seymour (Ref. 28).

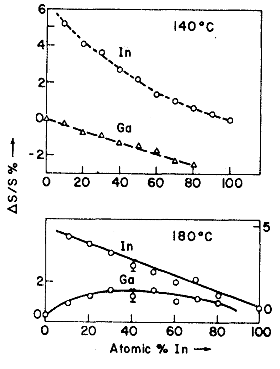

FIG. 11. Two experimental plots of $\Delta S/S$ for Ga and In in liquid Ga-In alloys. The upper results were taken from Van Der Lugt and Van Der Molen (Ref. 29), and the lower ones from Moulson and Seymour (Ref. 28). Note that the two measurements do not give consistent results, particularly for Ga in the region of low In concentration.

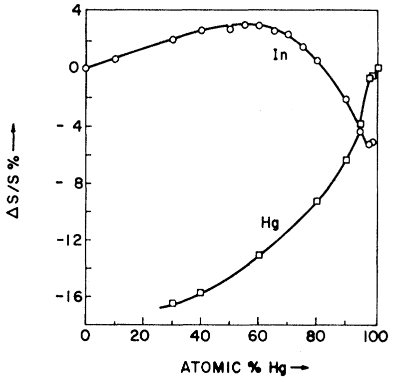

FIG. 12. Experimental plots of $\Delta S/S$ for Hg and In in liquid Hg-In alloys. These data were taken from Moulson and Styles (Ref. 30).

From Table I it is evident that $1+2\gamma(0)_F$ is almost constant (0.8–0.9) for the various solvents, except for Hg in Hg-In(II) alloy and Sn in Sn-Pb alloy. The value 0.555 for Hg obtained with AH $u(K)$ cannot be trusted.[38] Similarly the AH $u(K)$ for Sn are also doubtful; they are discussed in Ref. 22. We then find that $\gamma(0)_F$ is about $-(0.1\text{–}0.05)$ for Hg, Tl, In, Ga, and Pb, compared to -0.23 for Li obtained by Faber.[1] This result implies that the effective pseudopotentials $w_0(K)$ in these metals are about 10 to 5% less than the computed $u_0(K)$ when K is large. But how large this K should be before this conclusion becomes effective is a matter of guesswork—most likely, larger than $2k_F$.

Qualitative Prediction of $\Delta S/S$

To give any meaning to the present results and to understand their importance one must return to Eqs. (13) and (20). Obviously, in these equations there are three principal terms upon which the whole analysis

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[43] N. E. Cusack, P. Kendall, and M. Fielder, Phil. Mag. **10**, 871 (1964).

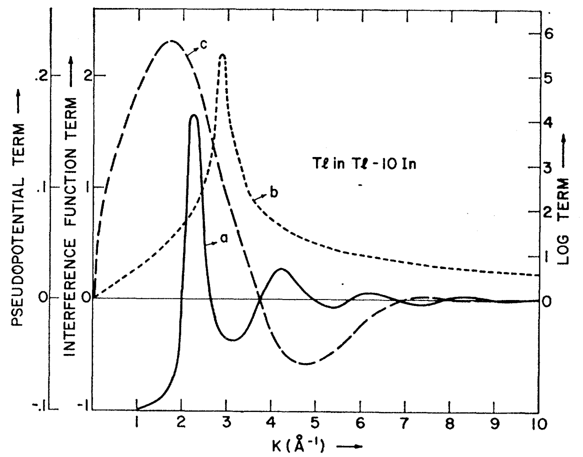

FIG. 13. Plots of the interference-function term, the logarithmic term, and the pseudopotential term of Eq. (18) for Tl in liquid Tl–10 at.% In alloy. Curve a: interference-function term; curve b: logarithmic term; curve c: pseudopotential term.

was centered. These are the pseudopotential term

$$[Z_0u_0(K)/u_0(0)-Z_1u_1'(K)/u_1'(0)],$$

the interference function term $[I'(K)-1]$, and the logarithmic term

$$\left[\tfrac{1}{2}\ln\frac{(K+2k_F)^2+m^2/(4\hbar^2\tau^2K^2)}{(K-2k_F)^2+m^2/(4\hbar^2\tau^2K^2)}\right].$$

We show the behavior of these terms in Figs. 13 and 14 for liquid Tl and In, respectively. The limits of the integrations in both equations extend up to ∞. It must be emphasized here that beyond $K=7$ Å^{-1} the pseudopotential term does not contribute to the integration, and therefore any structure at $K>7$ Å^{-1} may be unimportant. The only region that is of any relevance to us is approximately 2 Å$^{-1}<K<7$ Å^{-1}. Small errors in the measurement of either the peak height or the peak position of $I(K)$ should have practically no effect in the process of integration. For this reason it is not surprising at all that reasonably good agreement (Figs. 7 and 8) was found between $\Delta S/S$ obtained with measured and HS $I(K)$ for liquid Sn, Ga, and Hg, which do not quite resemble HS liquids (Figs. 1 and 2). The sign of $\Delta S/S$ is mainly determined by the pseudopotential term. In the present investigation perhaps the most encouraging and significant contribution is the prediction of the right sign and qualitative trend of the $\Delta S/S$-versus-c curve in the liquid alloys.

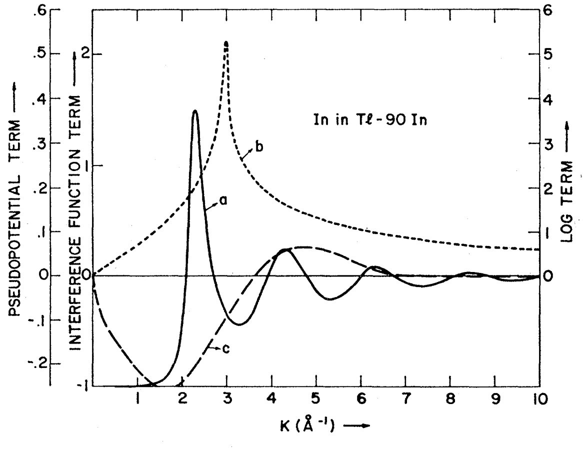

FIG. 14. The plots of the interference-function term, the logarithmic term, and the pseudopotential term of Eq. (18) for In in liquid Tl–90% In alloy. Curve a: interference term; curve b: logarithmic term; curve c: pseudopotential term.

C. Limitations for Quantitative Agreement

We should not be disappointed at the lack of quantitative agreement of $\Delta S/S$ with the experimental result. We know that in the theory we made a number of approximations; most serious of all is our reluctance to distinguish the $2k_F$ of the solute atom from that of the solvent atom, which was due to mathematical complexities. Perhaps this restriction can be disposed of without too much difficulty when the two atomic species have quite dissimilar $2k_F$. Additional reason can be found if we recall Eq. (3) and Eq. (18). Admittedly, there are two other factors Ω_0 and χ_P, both of which depend upon the concentration of the elements. In the present theory we have completely ignored any contributions from these two variations. One could, however, add these two extra features to the present results to observe somewhat better quantitative agreement.

VI. CONCLUDING REMARKS

We have made attempts here to establish that a treatment of the electron density function $\langle|\psi(0)|^2\rangle_F$ in terms of the pseudopotentials alone predicts qualitatively the fractional change of Knight shift, $\Delta S/S$, in liquid alloys. The procedure also gives the right sign of the shift. Thus, the results of this study apparently disagree with the conclusions of Moulson and Seymour,[28] who do not seem to have found support for the theory. Kellington and Titman[40] applied the Faber[1] theory to the case of dilute Na alloys and found qualitative agreement between their experimental and theoretical answers, although the equation (see Ref. 40, p. 1047) they gave in their note is not the same as that given by Faber (see Ref. 1, Eq. 15).

ACKNOWLEDGMENTS

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