the recent data of Collings, the paramagnetic susceptibilities for Li and Na can be much less than those used by Silverstein for comparison. Since all theoretical results depend on effective mass a precise comparison of theoretical results is difficult. However, in Fig. 1, we have compared our result on the paramagnetic susceptibility with Silverstein's.

In our numerical results we have chosen $g = 2$, but our theoretical formulas were derived for arbitrary g. In the past several years, accurate measurements of the electron g value have been made by conduction electron-spin resonance.[11] For alkali metals it has been found that g value is very nearly that of the free electron. The largest difference of 1.07×10^{-2} has been found for He while in Li the difference is $(-2\pm 2)\times 10^{-6}$.

The diamagnetic susceptibility reported by Kanazawa and Matsudaira needs two corrections. First, in their notation the correct ratio of the susceptibility to that of an ideal electron gas is

$$\frac{\chi}{\chi_0} = 1 + \frac{\alpha r_s}{6\pi}\left(\ln r_s + 4 + \ln\frac{\alpha}{\pi}\right).$$

The extra term $\ln\frac{1}{2}$ appearing in the bracket in their result is due to the effect of spin missing in their expression for the screening constant. Second, their numerical value 1.12 is correctly 0.86. This value is then not close to that which March and Donovan obtained, i.e., 1.51.

Figure 2 illustrates our results on the diamagnetic susceptibility in comparison with that of free-electron gas and also March and Donovan. The theoretical susceptibility curves for an interaction-electron gas cross with that of free electrons at $r_s = 2.75$ and the deviation becomes larger for larger r_s as expected. Our result (2.12) improves what Kanzawa and Matsudaira reported. It gives terms to the second order in r_s.

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Exchange Core-Polarization Contribution to the Spin Density in Liquid Metals

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A theory is developed for the exchange core-polarization (ECP) contribution to spin density S^{cp} in liquid metals in the framework of moment-perturbation (MP) procedure and pseudopotentials. The zero-order contribution to S^{cp} has been shown to be temperature independent while the first-order term depends on the temperature through the liquid-interference function. The results give a definite trend for convergence of the perturbation theory. In the specific case of liquid Mg the ECP contribution to the Knight shift K_s^{cp} is about 25% of the direct shift K_s^d and varies rather slowly with temperature in comparison to that of K_s^d. From the present results it seems that the Fermi-contact term is the most dominant term and determines the major change of the Knight shift with temperature in agreement with what has been predicted previously.

I. INTRODUCTION

Recently Rossini and Knight[1] have investigated a number of liquid metals to understand the various contributions to the Knight shift K_s and nuclear-spin relaxation rate, but in the absence of any theory they used some approximate results to represent the core-polarization contribution K^{cp} in their work. It is the purpose of this paper to show, by expounding the concept of pseudopotential and liquid-interference function, the relative and quantitative importance of both the magnitude and temperature dependence of K^{cp} in liquid metals.

The first and the most important contribution to the Knight shift usually comes from the Fermi-contact interaction K_s^d. To calculate K_s^d one evaluates the probability density of the conduction electrons directly at the nucleus. However, the conduction electrons with $l=0$ symmetry can only contribute to this mechanism. Thus, for a metal (as, for example, Be) where the conduction electrons are more like p electrons, the Fermi-contact term gives a vanishingly small contribution[2] to K_s, and "other" contributions to K_s may be of comparable importance.

The second important mechanism that contributes to K_s is the exchange interaction between the conduction and spin-polarized core electrons. This is usually known as the exchange core-polarization (ECP) contribution K^{cp}, and has been calculated in the solid state by both the exchange-perturbation[3] (EP) and moment-perturbation[4] (MP) methods, the latter being more flexible in its applications. For the solid alkali metals the ECP contribution to K_s is about 25% of K_s^d, while for Mg it is as much as 40% of K_s^d. In solid Be the ECP mechanism has played a very decisive role in canceling out a large portion of the positive direct contribution.[2] Besides its absolute magnitude, the temperature dependence of the ECP contribution to K_s is very interesting because the conduction electrons with angular momenta $l=0, 1, 2$ can contribute to K^{cp}. With the rise of temperature the s character of the conduction electron is expected to increase with a simultaneous decrease in the p, d angular components.[5] Thus, K_s^d is expected to rise with temperature. However, it is difficult to assess *a priori* the temperature dependence of K^{cp}, since the signs of the contributions to K^{cp} from various angular momenta cannot be determined without an explicit calculation.

Thirdly, there is the interaction between the nucleus and the non-s conduction electrons, which represents the orbital contribution K^o. The theory of the orbital contribution has been worked out for Bloch electrons in the solid state. However, a quantitative result of K^o for solids is rather difficult to obtain because of the complicated interband transitions. In the liquid state one does not have these discontinuities in the energy bands, and estimations of K^o indicate that, except for a very few metals, K^o can be regarded as small.[1]

Although the Knight shift in liquid metals has been measured quite satisfactorily both as a function of temperature and pressure,[6–8] a quantitative analysis of the various contributions to Knight shift in the liquid state has not yet been done. However, it has been concluded from those studies that the Fermi-contact interaction K_s is the most dominant contribution to the total Knight shift K_s. Most recently some good experiments[1,9,10] have also been made to study the temperature dependence of spin-relaxation rates, and attempts have been made to find a correlation between the Knight shift and spin-relaxation rate via the electron-electron interaction and exchange-enhancement phenomena. On the theoretical side, expressions have been worked out by several authors[11–15] for the Fermi-contact interaction, and the temperature dependence of K_s^d has been investigated. But for metals where K^{cp} is substantial (in particular, where its different component contributions have opposite signs) the temperature dependence of K^{cp} can importantly influence the temperature dependence of K_s. Such a calculation would require a knowledge of the temperature-dependent interference functions which are not readily available for the solid state. However, for the liquid state one can extract the information from the study of the liquid-interference functions available from elastic-scattering experiments. In view of this simplicity we have studied the temperature dependence of K^{cp} in liquid metals.

In Sec. II we will develop a theory for the ECP contribution to the spin density S^{cp} in the framework of pseudopotential formulation. In Sec. III this theory will be applied to the specific case of liquid Mg, and the effect of S^{cp} on K_s and spin-lattice relaxation time T_1T will be discussed. In Sec. IV we will summarize and relate these results to the earlier solid-state calculations.

II. THEORY FOR ECP CONTRIBUTION

The ECP contribution to Knight shift K_s can be written as

$$K_s^{cp} = \tfrac{8}{3}\pi\chi_s V S^{cp} , \tag{2.1}$$

where χ_s is the Pauli spin susceptibility and V is the volume of the entire liquid under consideration. The ECP contribution to spin density S^{cp} is expressed, as in the solid state,[2,4] by the equation

$$S^{cp} = \langle (1/N)\textstyle\sum_i |\Psi_k(\vec{R}_i)|^2\rangle^{cp} . \tag{2.2}$$

In Eq. (2.2), $\vec{R}_i$ defines the position vector of the ith dynamic nucleus, N is the number of nuclei in the liquid, and k is the magnitude of the Fermi momentum. The above average sign implies an "ensemble" average. The Fermi-surface averaging is not necessary here since the Fermi surface in the liquid state is assumed to be spherical.

The calculation of S^{cp} in Eq. (2.2) will be carried out in the spirit of MP procedure. Much has already been said about the MP procedure and we refer, in this regard, to earlier works.[2,4] As in the solid state, we write the spin density due to ECP mechanism at a single nuclear site as

$$|\Psi_k(\vec{R}_i)|^2 = 2\,\mathrm{Re}\left(\sum_{ns} \langle \delta\varphi_{ns}|\,H_E\,|\varphi_{ns}\rangle - \sum_{n's\neq ns} \langle \delta\varphi_{ns}|\varphi_{n's}\rangle\langle\varphi_{n's}|H_E|\varphi_{ns}\rangle\right). \quad (2.3)$$

The summation in Eq. (2.3) runs over all the cores of the metal. φ_{ns} is the atomic core function of the "ns" state and $\delta\varphi_{ns}$ is the corresponding MP core function. The second term in Eq. (2.3) arises because of nonorthogonality between $\delta\varphi_{ns}$ and $\varphi_{n's}$. This contribution has been found to be about 5–6% of the first term[5] in Eq. (2.3) and can be neglected. Thus,

$$|\Psi(\vec{R}_i)|^2 = 2\,\mathrm{Re}\sum_{ns} \langle \delta\varphi_{ns}|H_E|\varphi_{ns}\rangle \ . \quad (2.4)$$

The exchange Hamiltonian H_E which measures the difference in the exchange potential for the spin-up and spin-down core electrons can be written as

$$H_E\varphi_{ns}(\vec{r}_1) = -\Psi_k(\vec{r}_1)\int \Psi_k^*(\vec{r}_2)(e^2/r_{12})\varphi_{ns}(\vec{r}_2)\,d^3r_2 \ .$$

In terms of atomic units ($\hbar = 1$, $e^2 = 2$, and $m = \frac{1}{2}$) the above equation reads

$$H_E\varphi_{ns}(\vec{r}_1) = -\Psi_k(\vec{r}_1)\int \Psi_k^*(\vec{r}_2)(2/r_{12})\varphi_{ns}(\vec{r}_2)\,d^3r_2 \ . \quad (2.5)$$

The conduction-electron wave function Ψ_k is usually obtained in the solid state by variational procedures. Since the momentum states q in liquid metals are continuous, one cannot use the variational procedure. Instead, one resorts to the use of perturbation formalism in the framework of pseudopotential. In recent calculations[14,15] of K_s^d in liquid metals, it has been shown that the second-order contribution to spin density is small, and that perturbation theory in fact converges. Therefore, for our present calculation we express the conduction-electron wave function up to the first order in the perturbation, i.e., the pseudopotential

$$\Psi_k = \Psi_k^{(0)} + \Psi_k^{(1)} \ . \quad (2.6)$$

The zero-order function $\Psi_k^{(0)}$ is formed by making the plane wave (the basis function in the pseudopotential scheme) orthogonal to the core states. Thus $\Psi_k^{(0)}$ is a single orthogonalized plane wave (OPW),

$$\Psi_k^{(0)} = (1/\sqrt{V})e^{i\vec{k}\cdot\vec{r}} - \sum_t b_t(\vec{k})\varphi_t(\vec{k},\vec{r}) \ , \quad (2.7)$$

where the orthogonalization parameter is

$$b_t(\vec{k}) = (1/\sqrt{V})\langle\varphi_t(\vec{r})|e^{i\vec{k}\cdot\vec{r}}\rangle \ . \quad (2.8)$$

Expressing $e^{i\vec{k}\cdot\vec{r}}$ in terms of spherical harmonics, it can be shown that

$$\Psi_k^{(0)} = \frac{4\pi}{\sqrt{V}}\sum_{l,m}(i)^l Y_{lm}(\vec{r})Y_{lm}^*(\vec{k})R_l(kr)\frac{1}{r} \ , \quad (2.9)$$

with

$$R_l(kr) = rj_l(kr) - \sum_n T_{nl}(k)U_{nl}(r) \ . \quad (2.10)$$

In Eq. (2.10), $T_{nl}(k)$ is the Bessel transform of the radial atomic core functions,

$$T_{nl}(k) = \int_0^\infty U_{nl}(r)j_l(kr)\,r\,dr \ . \quad (2.11)$$

The first-order function $\Psi_k^{(1)}$ can be formed by orthogonalizing the first-order perturbed plane-wave function

$$\Phi_k^{(1)}(\vec{r}) = \sum_{k'}{}' \frac{\langle\vec{k}'|W|\vec{k}\rangle}{k^2-k'^2}\frac{1}{\sqrt{V}}e^{i\vec{k}'\cdot\vec{r}} \quad (2.12)$$

to the atomic core states in the same manner as Eq. (2.7). Therefore,

$$\Psi_k^{(1)}(\vec{r}) = \sum_{k'}{}' \frac{\langle\vec{k}'|W|\vec{k}\rangle}{k^2-k'^2} \times\left[\frac{4\pi}{V}\sum_{l,m}(i)^l Y_{lm}(\vec{r})Y_{lm}^*(\vec{k}')R_l(k'r)\frac{1}{r}\right] . \quad (2.13)$$

In Eqs. (2.12) and (2.13), $W(\vec{r})$ is the pseudopotential

$$W(\vec{r}) = \sum_\nu w(|\vec{r}-\vec{R}_\nu|) \ , \quad (2.14)$$

where $w(|\vec{r}-\vec{R}_\nu|)$ is the potential of the $\vec{R}_\nu$th ion and is assumed to be local. The Fourier transform of the pseudopotential $W(\vec{r})$ can now be expressed as

$$\langle\vec{k}'|W|\vec{k}\rangle = (1/N)\sum_\nu e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_\nu}w(|\vec{k}-\vec{k}'|) \ , \quad (2.15)$$

with

$$w(|\vec{k}-\vec{k}'|) = (1/\Omega_0)\int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}w(r)\,d^3r \ , \quad (2.16)$$

Ω_0 being the volume per ion. Using Eq. (2.15) in Eq. (2.13) and replacing the summation over k' by integration, the first-order wave function can be simplified to

$$\Psi^{(1)}(\vec{r}) = \frac{N\Omega_0}{(2\pi)^3}\,\mathcal{P}\int\frac{d^3k'}{k^2-k'^2}w(|\vec{k}-\vec{k}'|)\frac{1}{N}\sum_\nu e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_\nu} \times\left[\frac{4\pi}{V}\sum_{l,m}(i)^l Y_{lm}(\vec{r})Y_{lm}^*(\vec{k}')R_l(k'r)\frac{1}{r}\right] , \quad (2.17)$$

where $\mathcal{P}$ means the principal part. Using Eq. (2.6), the contributions from Eq. (2.5) can be separated into zero- and first-order terms in the following way.

A. Zero Order

The zero-order part of Eq. (2.5) can be seen to have the form

$$H_E\varphi_{ns}(\vec{r}_1) = -\Psi_k^{(0)}(\vec{r}_1)\int \Psi^{(0)*}(\vec{r}_2)(2/r_{12})\varphi_{ns}(\vec{r}_2)\,d^3r_2 \,. \tag{2.18}$$

Expressing $1/r_{12}$ in terms of spherical harmonics,

$$\frac{1}{r_{12}} = 4\pi\sum_l \frac{1}{2l+1}\frac{r_<^l}{r_>^{l+1}}\sum_m Y_{lm}^*(\vec{r}_1)Y_{lm}(\vec{r}_2) \,, \tag{2.19}$$

and using Eqs. (2.2), (2.4), (2.9), and (2.18), the zero-order contribution to S^{cp} can be calculated as

$$\begin{aligned}(S^{\mathrm{cp}})^{(0)} &= 2\,\mathrm{Re}\sum_{ns}\Big[-\frac{8\pi}{V}\sum_l\int_0^\infty r_1\,dr_1\,\delta U_{ns}(r_1) \\ &\qquad\times R_l(k, r_1)f_{l,ns}(k,r_1)\Big] \\ &= 2\,\mathrm{Re}\sum_{ns}\Big[-\frac{8\pi}{V}\sum_l\int_0^\infty \alpha_{l,ns}(k, r_1)\,dr_1\Big]. \end{aligned}\tag{2.20}$$

In Eq. (2.20), $\delta U_{ns}(r)$ is the radial part of the MP core functions $\delta\varphi_{ns}(r)$, and the exchange integral $f_{l,ns}(k, r_1)$ is given by

$$\begin{aligned}f_{l,ns}(k,r_1) &= \frac{1}{r_1^{l+1}}\int_0^{r_1} R_l(k, r_2)U_{ns}(r_2)\,r_2^{l+1}\,dr_2 \\ &\quad + r_1^l\int_{r_1}^\infty R_l(k, r_2)U_{ns}(r_2)\frac{1}{r_2^l}\,dr_2 \,. \end{aligned}\tag{2.21}$$

As can be seen, the zero-order contribution to S^{cp} is simply the one-OPW result and is temperature independent.

B. First Order

The first-order part of Eq. (2.5) has the form

$$\begin{aligned}H_E\varphi_{ns}(\vec{r}_1) = -\Big[&\Psi^{(0)}(\vec{r}_1)\int \Psi_k^{(1)*}(\vec{r}_2)\frac{2}{r_{12}}\varphi_{ns}(\vec{r}_2)\,d^3r_2 \\ &+\Psi^{(1)}(\vec{r}_1)\int \Psi_k^{(0)*}(\vec{r}_2)\frac{2}{r_{12}}\varphi_{ns}(\vec{r}_2)\,d^3r_2\Big] \,. \end{aligned}\tag{2.22}$$

From an inspection of the form of $\Psi_k^{(1)}$ and $\Psi_k^{(0)}$ it is evident that the above two terms of first-order contribution are different from each other. Therefore, we write the first-order contribution to S^{cp}, $(S^{\mathrm{cp}})^{(1)}$, as a sum of two terms:

$$(S^{\mathrm{cp}})^{(1)} = (S^{\mathrm{cp}})^{(1)}(\mathrm{I}) + (S^{\mathrm{cp}})^{(1)}(\mathrm{II}) \,. \tag{2.23}$$

With the use of Eqs. (2.2), (2.9), (2.17), (2.19), and (2.22), it can be shown that

$$\begin{aligned}(s^{\mathrm{cp}})^{(1)}(\mathrm{I}) &= 2\,\mathrm{Re}\sum_{ns}\Big[-\frac{8\pi}{V}\sum_l \mathcal{P}\int_0^\infty \frac{k'^2\,dk'\,G_{l,ns}(k, k')}{k^2-k'^2}\Big] \\ &\quad\times\frac{\Omega_0}{(2\pi)^2}\int_{-1}^1 w(|\vec{k}-\vec{k}'|)I(|\vec{k}-\vec{k}'|)P_l(x)\,dx \end{aligned}\tag{2.24}$$

and

$$\begin{aligned}(S^{\mathrm{cp}})^{(1)}(\mathrm{II}) &= 2\,\mathrm{Re}\sum_{ns}\Big[-\frac{8\pi}{V}\frac{\Omega_0}{(2\pi)^2} \\ &\qquad\times\sum_l \mathcal{P}\int_0^\infty \frac{k'^2\,dk'\,G_{l,ns}(k', k)}{k^2-k'^2}\Big] \\ &\quad\times\int_{-1}^1 w(|\vec{k}-\vec{k}'|)I(|\vec{k}-\vec{k}'|)P_l(x)\,dx \,. \end{aligned}\tag{2.25}$$

In Eqs. (2.24) and (2.25), x is the cosine of the angle between $\vec{k}$ and $\vec{k}'$ and $I(q)$ is the liquid-interference function

$$I(q) = \Big\langle \frac{1}{N}\sum_{l,\nu} e^{i\vec{q}\cdot(\vec{R}_l-\vec{R}_\nu)}\Big\rangle \,. \tag{2.26}$$

Information regarding $I(q)$ can be obtained experimentally from x-ray or neutron-diffraction studies, or theoretically by assuming the liquid metal to be a classical fluid of hard spheres. The quantity $G_{l,ns}(k', k)$ is given by

$$G_{l,ns}(k', k) = \int_0^\infty r_1\,dr_1\,\delta U_{ns}(r_1)\,f_{l,ns}(k', r_1)R_l(k, r_1) \,. \tag{2.27}$$

However, $G_{l,ns}(k,k')$ is similar to Eq. (2.27) except that k' and k have to be interchanged. It is only through the term $G_{l,ns}$ that $(S^{\mathrm{cp}})^{(1)}(\mathrm{I})$ and $(S^{\mathrm{cp}})^{(2)}(\mathrm{II})$ differ from one another. It is interesting to note that $(S^{\mathrm{cp}})^{(1)}$ is dependent on the structure of the liquid, and the temperature dependence is carried through the interference function $I(q)$.

As is well known, the direct contribution to Knight shift is explicitly described by

$$K_s^d = \tfrac{8}{3}\pi\chi_s V S^d \,, \tag{2.28}$$

where S^d is the Fermi-contact contribution to spin density. Therefore, combining the direct and ECP contribution, the quantity K_s is given by

$$K_s = \tfrac{8}{3}\pi\chi_s V S \,, \tag{2.29}$$

with

$$S = S^d + S_s^{\mathrm{cp}} \,. \tag{2.30}$$

From a knowledge of S^d and S_s^{cp}, the relaxation rate can be calculated from the expression[16]

$$1/T_1T = \tfrac{64}{9}\hbar^3\gamma_e^2\gamma_n^2 k_B g^2(E_F)V^2\mathcal{G} \,, \tag{2.31}$$

where γ_e and γ_n are the electron and nuclear gyromagnetic ratios, and k_B is the usual Boltzmann constant. $g(E_F)$ is the band density of states per electron spin; for the liquid metals (assuming $m^*/m = 1$) it can be taken as the free-electron den-

TABLE I. ECP contributions to spin density (in units of $1/N\,\Omega_0$) in liquid Mg from various atomic cores at 651 °C.

Order of perturbation	1s core		2s core		Total = 1s + 2s core	
	s	p	s	p	s	p
Zero order	6.841	−2.693	15.949	3.224	22.790	0.531
First order	−0.669	−0.089	−1.524	0.084	−2.193	−0.005
Total	6.172	−2.782	14.425	3.308	20.597	0.526

sity of states at the Fermi surface. Including the ECP effect, $\mathcal{G}$ is obtained as

$$\mathcal{G} = (S^d + S_s^{cp})^2 + \tfrac{1}{3}(S_p^{cp})^2 + \tfrac{1}{5}(S_d^{cp})^2 + \cdots , \qquad (2.32)$$

which is valid for the one-OPW approximation. For metals with $S_p^{cp} \to 0$, $\mathcal{G}$ can be conveniently expressed as

$$\mathcal{G} = (S^d + S_s^{cp})^2 . \qquad (2.33)$$

III. RESULTS AND DISCUSSIONS

Since we are mainly interested here in the temperature dependence of K^{cp}, we should look for a system where K^{cp} is substantial and its temperature variation distinct. In searching for such a system to apply the theory developed in Sec. II, we considered Mg to be an appropriate example for two strong reasons. Firstly, its direct contribution K_s^d has been calculated both in solid[5] and liquid[14] states in great deatil. Secondly, and more importantly, it has a large K^{cp} contribution (about 46% of the K_s^d) in the solid state. We believe that a study of this metal will give us an indication as to the importance of K^{cp} in liquid Mg and the behavior of K^{cp} with temperature in liquid metals in general.

In our calculations we have used the MP core states δU_{ns} obtained earlier for the solid-state calculation.[2] It has been argued[4] in general and shown for the specific case of Li that the MP functions, to a very good approximation, are independent of the environment they are in. This justifies our use of δU_{ns} from the earlier solid-state calculation in liquid Mg. For the atomic core functions U_{ns} we have used the wave functions tabulated by Clementi.[17]

For the temperature-dependent study of S^{cp} we need two additional pieces of information: the interference function $I(q)$ and the ionic potential $v(q)$. For $v(q)$ we have used the model-potential form factors of Animalu and Heine.[18] Unfortunately, no experimental measurement of the temperature-dependent $I(q)$ is available at present for liquid Mg. In view of this we have used the hard-sphere[19] $I(q)$ with temperature effects incorporated through a Debye-Waller-like approximation.[20] In Table I we have listed for the melting temperature (i.e., 651 °C) the ECP contributions to spin density from 1s and 2s cores separately. The following observations can be made from the results in Table I.

First, the contributions to S^{cp} from the 2s core is about twice as large as that of the 1s core. This is because the contribution from the individual cores depends both on their density at the nucleus and the strength of the exchange interaction. While the 1s core has a larger density at the nucleus than the 2s, the exchange interaction for the 2s core is stronger than the other. This can be clearly seen from Fig. 1, where we have plotted the exchange integrals [see Eq. (2.21)] involving the conduction electrons with $l = 0$ for the 1s and 2s cores. The magnitude of the height of the exchange integral at $r \to 0$ corresponding to the 1s core is slightly greater than that of the 2s core. On the other hand, the range of the integral for the 1s core is about five times smaller than that of the 2s core. The effect of these integrals on S^{cp} can be seen from Fig. 2, where the integrands of the zero-order contributions to S^{cp} with $l = 0$ [see Eq. (2.20)] for the 1s and 2s cores have been plotted. The oscillations in these integrands are partly due to the nodes in the atomic and MP core functions. It thus appears that in this case the exchange interaction plays the dominating

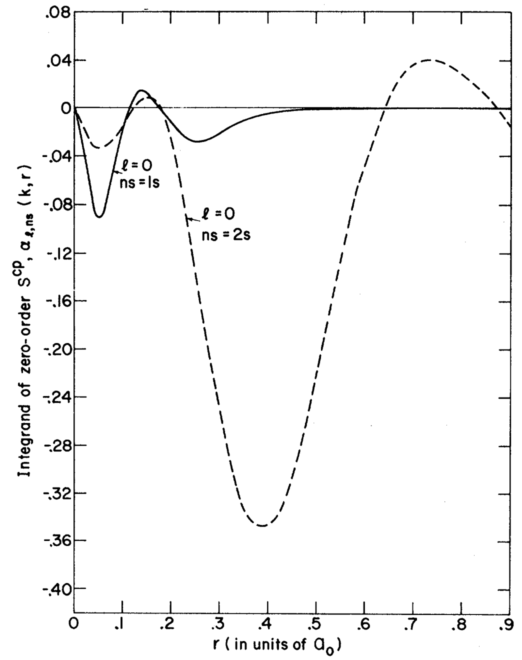

FIG. 1. Exchange integrals [Eq. (2.21)] of the $s(l=0)$ conduction electrons for the 1s and 2s cores of Mg.

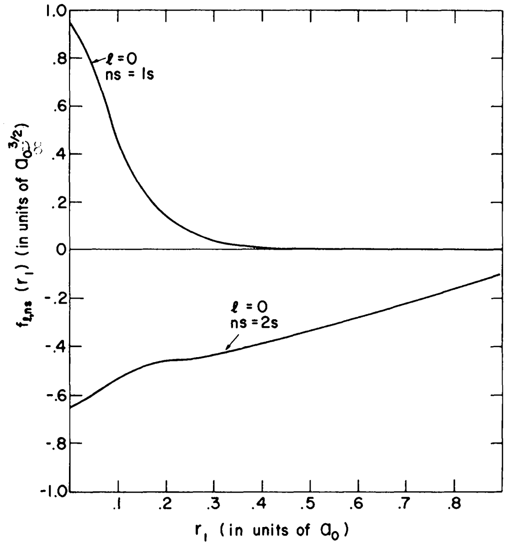

FIG. 2. Integrands $\alpha_{l,ns}(k, r)$ [Eq. (2.20)] of the zero-order contribution of S^{cp} in Mg. The integrands for the 1s and 2s cores are shown separately.

role.

Secondly, the contributions to S^{cp} from the $l=0$ part of the conduction electron (S_s^{cp}) are positive and of larger magnitude than the corresponding contributions from the $l=1$ part of the conduction electron (S_p^{cp}). This trend justifies the neglect of contributions to S^{cp} from the higher angular momenta ($l > 2$). The contributions to S^{cp} from S_p^{cp}, on the other hand, are negative for the 1s core and positive for the 2s core. Since these contributions are of comparable magnitude, the actual contribution to S_p^{cp} is even smaller due to the cancellation effect.

Thirdly, the first-order contribution to S^{cp} is found to be negative. This results in a reduction of the zero-order contribution to S^{cp}, which is not unexpected, since by including an additional plane wave one usually decreases the s content of the conduction-electron wave function with a simultanious increase in the p content.

Finally, and more importantly, we notice that the first-order contribution is an order of magnitude smaller than the corresponding zero-order result. Furthermore, the signs of these two contributions are opposite to each other. This indicates that the spin density S^{cp} is reduced by including an additional plane wave. This trend was also noticed in the calculation of K_s^d for many liquid metals.[21,22] From these results it can be concluded that perturbation theory converges, lending a strong support to the validity of the present approach in computing the hyperfine properties of liquid metals.

In Table II various contributions to S^{cp} from both the orders are given for five temperatures. The behavior of S^{cp} for various l and perturbation orders is found to be similar for all temperatures. As mentioned earlier, the zero-order contribution to S^{cp} is temperature independent; we are concerned only with the temperature dependence of the first-order contribution to S^{cp}. It can be seen from columns 5 and 6 of Table II that the magnitude of the s contribution to $(S^{cp})^{(1)}$ decreases (by about 20%) with a corresponding increase in the p contribution (by about 300%). Since these contributions are very small compared to the zero order, it is probably more meaningful to analyze the total contributions to S_s^{cp} and S_p^{cp} given in columns 8 and 9 of Table II. As the temperature rises, S_s^{cp} increases by about 4%, while S_p^{cp} decreases by about 3% within the temperature range of 350 °C. This indicates that the system becomes more free-electron-like with the rise of temperature. Since S_s^{cp} and S_p^{cp} are both positive and show opposite behavior relative to the temperature, the quantity S^{cp} in the last column of Table II exhibits only a 3% temperature dependence.

In Table III we have compared the calculated ECP contribution to Knight shift and nuclear spin-lattice relaxation time with the corresponding direct contributions. For the calculation of Knight shift we have used (at all temperatures) the free-electron exchange-enhanced susceptibility[22] $\chi_s = 1.32\times10^{-6}$ cgs volume units, assuming the density-of-states effective mass $m^*/m = 1$ for liquid Mg. Considering the uncertainties involved in the use of this χ_s, we have expressed the Knight shifts in Table III only up to the second significant figure. We will now comment on the temperature dependence of K^{cp} relative to K_s^d.

From Table III it can be seen that when K_s^d increases by about 25% with temperature, K_s^{cp} increases by only 3%, whereas K_p^{cp} practically re-

TABLE II. ECP contribution to spin density (in units of $1/N\Omega_0$) in liquid Mg at various temperatures.

Temp	Zero order, $(S^{cp})^{(0)}$			First order, $(S^{cp})^{(1)}$			Total, $(S^{cp})^{(0)} + (S^{cp})^{(1)}$		
(°C)	s	p	Total	s	p	Total	s	p	Total
651	22.790	0.531	23.321	−2.193	−0.005	−2.198	20.597	0.526	21.123
700	22.790	0.531	23.321	−2.111	−0.007	−2.118	20.679	0.524	21.203
750	22.790	0.531	23.321	−1.952	−0.007	−1.959	20.838	0.524	21.362
850	22.790	0.531	23.321	−1.709	−0.010	−1.719	21.081	0.521	21.602
1000	22.790	0.531	23.321	−1.532	−0.018	−1.550	21.258	0.513	21.771

TABLE III. Direct and ECP contributions to Knight shift and relaxation time in liquid Mg.

Temp (°C)	K_s^d (%)	K_s^{cp} (%)	K_p^{cp} (%)	K^{cp} (%)	K_s (%)	$(T_1T)^d$ (deg sec)	$(T_1T)^{c+cp,s}$ (deg sec)
651	0.064	0.0228	0.0006	0.0234	0.087	171.3	93.1
700	0.067	0.0229	0.0006	0.0235	0.091	156.3	86.8
750	0.072	0.0230	0.0006	0.0236	0.096	135.3	77.7
850	0.078	0.0233	0.0006	0.0239	0.102	115.3	68.4
1000	0.082	0.0235	0.0006	0.0241	0.106	104.3	63.0

mains constant. Thus we may conclude that the temperature dependence of K_s is carried mostly through the direct interaction and that the temperature dependence of K^{cp} is too small compared to K_s^d. The total Knight shift, as shown in column 5 of Table III, then shows about 15% rise in the temperature range studied. Since the temperature dependence of K_s is mainly due to the temperature dependence of $I(q)$, it is important that we assess the limit of uncertainty in $I(q)$. As we have mentioned earlier that there are no experimental $I(q)$ available for liquid Mg as functions of temperature, and that the theoretical $I(q)$ are derived from the hard-sphere model with temperature effects incorporated in an approximate way, it is possible that the magnitude of error in K_s may be about ± 0.005. Considering this limit of uncertainty and assuming χ_s to be temperature independent, the present K_s in Table III exhibits at least about 4% temperature dependence within the temperature range studied. An experimental measurement of K_s will be very helpful in deriving more definite conclusions about the temperature dependence of K_s and χ_s.

It is now appropriate to compare the liquid-state result with that of the earlier solid-state calculations.[2] It is interesting to note that K_s^{cp} in the solid was almost 46% of K_s^d, whereas in the liquid it is about 36% at the melting temperature. The reason for this is that in the solid state the conduction electrons in Mg had substantial p character, and K^{cp} was almost comparable to K_s^{cp} and of positive sign. However, with the increase of temperature it appears that the conduction electrons have become more s-like. This is reflected by the substantial increase in K_s^{cp} and almost negligible K_p^{cp} in the liquid state.

The spin-lattice relaxation time at these temperatures was calculated using the appropriate spin densities. Column 7 shows the relaxation time T_1T, obtained using the direct spin densities S^d. Since the p contribution to S^{cp} is very small compared to the s contribution, we have listed in column 8 T_1T as obtained by using $S^d + S_s^{cp}$. It is clear that the inclusion of the ECP effect considerably lowers the relaxation time. As regards the temperature dependence of T_1T, we again allow for an error of ±10 deg sec. This means that T_1T decreases by about 12% over the temperature range studied. Unfortunately there are no available experimental measurements of T_1T, and it will be interesting to see how these predictions agree with experimental measurements in the future.

IV. CONCLUSIONS

A first-principles theory of the ECP contribution to spin density has been developed for the liquid metals in the framework of MP procedure. The smallness of the first-order contribution to S^{cp} assures the convergence of perturbation theory. The temperature dependence of S^{cp} through the liquid-interference function is rather small compared to the temperature dependence of S^d. The contribution to the ECP effect to K_s and T_1T is appreciable and cannot be neglected. More definitive conclusions can be made if one can get some experimental information on K_s and T_1T in Mg. It will be worthwhile to apply this theory to other metals where S^{cp} is known to be substantial in the solid state and where experimental information on both K_s and T_1T is available.

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Electron-Phonon Umklapp Scattering Processes in the Low-Temperature Ultrasonic Attenuation and Electrical Resistivity of Potassium[*]

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The theoretical treatment by Rice and Sham of the electron-phonon contribution to the attenuation of ultrasound in the local limit and the ideal (phonon-limited) electrical resistivity of potassium is extended to include a careful evaluation of the role of umklapp scattering processes at low temperatures. The results have been explicitly separated into normal and umklapp scattering components and the rapid decrease of the umklapp components, and hence the total, at very low temperatures, is emphasized for both the attenuation and resistivity. The results obtained from a realistic phonon model are compared in one case with those from an isotropic Debye-like model with a quadratic dispersion relationship and purely longitudinal and transverse polarization vectors.

I. INTRODUCTION

Several recent developments in the study of the ultrasonic attenuation due to electron-phonon interactions and the ideal electrical resistivity at low temperature have suggested a more thorough examination of the role played by electron-phonon normal and umklapp scattering processes in potassium.

In a recent paper, Rice and Sham[1] calculated the amplitude attenuation constant by the pseudopotential method for a longitudinal ultrasonic wave in potassium in the local limit where the phonon-limited electron mean free path is short compared with the impressed ultrasound wavelength. They compared their calculations (corrected to account for sample dimensions as opposed to the infinite medium, and for the polycrystalline nature of the samples) to the experimental data taken by Natale and Rudnick[2] on polycrystalline potassium samples at three ultrasonic frequencies in the temperature region $T \approx 2-20\,^\circ\mathrm{K}$. Rice and Sham found that the theoretical values underestimated the measured attenuation constant by a factor approaching 2.

In recent years, measurements[3] of the electrical resistivity of potassium at very low temperatures have indicated that there are deviations from the T^5 temperature dependence predicted by the Bloch-Grüneisen formula which neglects electron-phonon umklapp scattering processes. Similar effects have been observed in sodium by Woods[4]; the interpretation in sodium, however, is somewhat obscured by the martensitic phase transformation. Very recently a quantitative comparison[5] of accurate resistivity measurements with accurate theoretical calculations (whose details are presented in this paper) has shown that the complicated temperature dependence in potassium at low temperatures can be completely accounted for in terms of a "freezing out" of umklapp processes.

Peierls[6] was the first to point out that for a metal in which the Fermi surface does not touch the Brillouin-zone boundary there exists a minimum phonon wave vector required for umklapp processes to be possible. At a temperature below the energy corresponding to this minimum wave vector, the umklapp component of the resistivity will decrease nearly exponentially owing to the effect of the Bose-Einstein distribution function for the thermal phonons. The relative importance of normal and umklapp processes has been estimated in the past.[7] In particular, Bailyn pointed out that owing to the anisotropy in the sound velocities the effect suggested by Peierls would occur at rather low temperatures in potassium.

In this paper a thorough analysis of the relative importance of electron-phonon normal and umklapp scattering processes in determining the low-temperature behavior of both the ultrasonic attenuation