

the enhancement theory for the present. Our results imply that the additional mechanisms (orbital and dipolar interactions and differential chemical shifts) mentioned (and dismissed) by Narath and Weaver⁴ do not play a dominant role in Korringa

enhancement. However, until this is demonstrated by explicit calculations, we would caution against using a Korringa enhancement calculation to test the suitability of a particular exchange-correlation potential.

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Many-Electron Effects on the Enhancements of the Korringa Constants and Spin-Lattice Relaxation Rates in Alkali Metals*

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A quantitative explanation of the observed enhancements of the Korringa product and the ratio of Zeeman to dipolar spin-lattice relaxation times in sodium is given. The explanation is based on an extension of the theories of Moriya and Wolff, using for the generalized paramagnetic susceptibility the expression given by the self-consistent theory of Singwi *et al.* of spin correlations in a low-density interacting electron gas. The theory also predicts that the Korringa constant in the alkali metals is almost constant – a result in agreement with experiment.

I. INTRODUCTION

It is well known¹ that the many-body effects of electron-electron interactions are manifested in a direct way, at least in simple metals, via the enhancement of the paramagnetic susceptibility over its free-electron value through the so-called Stoner factor $(1 - \alpha)^{-1}$. It is also known that these correlations lead to an enhancement of the Knight shift K_s and the nuclear spin-lattice relaxation rates T_1^{-1} , thereby giving a value for the Korringa constant² which is again different from its free-

electron value $[K_s^2 T_1 T = (g\mu_B/\nu_n)^2 (\hbar/4\pi k_B) \equiv K_0^0]$. The Korringa relation is valid provided the dominant hyperfine coupling between the conduction electrons and the nuclear spins is of the *s* type. Recently Narath and Weaver³ have made a careful experimental investigation of the Korringa relation in the alkali and noble metals. These authors have attempted to understand their data in terms of Moriya's theory⁴ which is based on several assumptions: (i) the existence of a spherical Fermi surface, (ii) a δ -function electron-electron interaction potential, and (iii) the random-phase approxi-

mation (RPA); they find that they are unable to explain their results quantitatively. The values of the parameter α they obtain are not consistent with the values obtained directly from the susceptibility measurements. Narath and Weaver,³ after examining several alternative explanations for the discrepancy between theory and experiment, were led to postulate a nonzero electron-electron interaction-potential range, and hence a q -dependent α of the form $\alpha(q) = \alpha/(1 + q^2/\lambda^2)$, where α is determined from the paramagnetic susceptibility data and λ is an arbitrary parameter. For sodium, for which the theory is expected to be most applicable, Narath and Weaver find that agreement with experiment is obtained for $\lambda/2k_F = 1.1$. These authors also comment in their paper that the most surprising result of their experimental study is the observation that the Korringa constant stays almost constant ($\sim 1.6K_0^0$) for all five alkali metals – a result which they did not anticipate and is not yet understood.

Another physical quantity in whose calculation many-body electron-electron interaction effects enter in an analogous manner is the ratio δ of the Zeeman spin-lattice relaxation time T_1 to the dipolar spin-lattice relaxation time T_2 . For a noninteracting electron gas, this ratio has the value ~ 2.01 . The observed departure of this ratio denoted by $\epsilon = \delta - 2$ from its value in a noninteracting electron gas is an order of magnitude larger both in sodium and aluminum. A very critical discussion based on Wolff's theory⁵ for these two metals has very recently been given by Tunstall and Brown.⁶ The basic assumptions of Wolff's theory are the same as those of the theory of Moriya.⁴ Here we shall be mainly concerned with sodium, since the theory is best applicable to it. The theory of Wolff with a δ -function interaction gives for ϵ for sodium a value of 0.06 using a constant $\alpha = 0.42 \pm 0.03$, whereas the experimental value is 0.12 ± 0.03 , where the value of α is fixed from an independent spin-susceptibility measurement. In an attempt to account for this remaining discrepancy, these authors following Narath and Weaver³ assume a q -dependent α of the form as mentioned before. They find that for a certain value of the parameter λ ($\lambda = 0.42 \times 2k_F$), it is possible to obtain a reasonable agreement between theory and experiment as far as the value of ϵ is concerned, but then, unfortunately, agreement is lost between the theoretical prediction and experiment for the Korringa constant. The discrepancy to date remains unresolved.

From the foregoing discussion it is clear that we are here faced with the problem of explaining in a consistent manner the observed facts regarding the spin susceptibility, the Korringa constant, and the ratio δ of the two relaxation times in alkali metals and in particular for sodium for which the the-

ories of both Moriya and Wolff should be most applicable. From the analysis of Narath and Weaver³ and of Tunstall and Brown,⁶ and also from the neutron inelastic scattering data on paramagnetic nickel of Allan and his co-workers,⁷ it seems clear that what is chiefly lacking in the theoretical treatment is the proper q dependence of the effective exchange correlation potential and hence the q dependence of $\alpha(q)$. As far as the value of α is concerned, it is most reliably given by the measured value of the spin susceptibility.

The purpose of this paper is to demonstrate by explicit numerical calculations that it is possible to account quantitatively and in a consistent manner for the observed Korringa product and for the observed ϵ for sodium. It is somewhat unfortunate that experimental values for ϵ are not available for other alkali metals. The observed constancy of the Korringa constant in the alkali metals is also predicted by the theory. Our explanation is based on the theories of Moriya⁴ and Wolff,⁵ with the modification that instead of having a δ -function electron-electron interaction, we have a q -dependent effective exchange correlation potential. The latter is determined by the self-consistent theory of spin correlations of Singwi *et al.*⁸ for a low-density interacting electron gas and not in an *ad hoc* manner. The relevant formulas and the results of calculations are presented in Sec. II.

II. MATHEMATICAL FORMULAS AND RESULTS

A. Spin Susceptibility

The central quantity in discussing the hyperfine effects in simple metals (alkali metals) is the generalized spin susceptibility of an interacting electron gas. Many equilibrium correlation functions of spin densities can also be expressed⁹ in terms of generalized spin susceptibilities. We shall give here a very brief discussion of the spin susceptibility of an interacting electron gas for the sake of completeness and introduce the relevant formulas which we shall be using. The electron spin-density operator is defined as

$$\vec{s}(\vec{q}) = \frac{1}{2} \sum_{\vec{k}} \alpha_{\vec{k}+\vec{q}}^\dagger \vec{\sigma} \alpha_{\vec{k}}, \quad (1)$$

where $\alpha_{\vec{k}}^\dagger$ and $\alpha_{\vec{k}}$ are, respectively, the two component creation and annihilation operators, and the σ 's are the Pauli spin matrices. The spin susceptibility is determined by the linear response of an electron gas to an infinitesimal external magnetic field. We define the following retarded response function⁹:

$$\begin{aligned} \chi^*(\vec{q}, t) &= \langle \langle s^*(\vec{q}, t); s^*(-\vec{q}, 0) \rangle \rangle \\ &= i\theta(t) \sum_{\vec{k}} \langle [\alpha_{\vec{k}+\vec{q}}^\dagger, \alpha_{\vec{k}}, s^*(-\vec{q}, 0)] \rangle \\ &= \sum_{\vec{k}} G_{\vec{k}}(\vec{q}, t), \end{aligned} \quad (2)$$

where $\theta(t)$ is the Heaviside unit step function. The

angular brackets denote the equilibrium ensemble average with respect to the total Hamiltonian

$$H = H_0 + H_1 = \sum_{\mathbf{k}, \sigma} \omega_{\mathbf{k}} \alpha_{\mathbf{k}\sigma}^\dagger \alpha_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\mathbf{k}, \sigma} \sum_{\mathbf{k}', \sigma'} v(\mathbf{q}) \alpha_{\mathbf{k}\sigma}^\dagger \alpha_{\mathbf{k}+\mathbf{q}, \sigma'}^\dagger \alpha_{\mathbf{k}+\mathbf{q}, \sigma'} \alpha_{\mathbf{k}, \sigma}, \quad (3)$$

where $s^\pm(\mathbf{q}, t)$ are the circular components of the spin-density fluctuation. $G_{\mathbf{k}}(\mathbf{q}, \omega)$, the Fourier transform of the response function $G_{\mathbf{k}}(\mathbf{q}, t)$, satisfies the following exact equation:

$$(\omega - \omega_{\mathbf{k}} + \omega_{\mathbf{k}+\mathbf{q}}) G_{\mathbf{k}}(\mathbf{q}, \omega) = (n_{\mathbf{k}} - n_{\mathbf{k}+\mathbf{q}}) + \langle \langle [\alpha_{\mathbf{k}+\mathbf{q}}^\dagger, \alpha_{\mathbf{k}}^\dagger, H_1]; s^-(\mathbf{q}, 0) \rangle \rangle, \quad (4)$$

where $n_{\mathbf{k}\sigma} = \langle \alpha_{\mathbf{k}\sigma}^\dagger \alpha_{\mathbf{k}\sigma} \rangle$.

In Eq. (4) the main problem in proceeding further is to make a suitable approximation for the last term. If one breaks the Green's function appearing in the last term of Eq. (4) using the random-phase-approximation (RPA) decoupling scheme, one obtains the following integral equation:

$$G_{\mathbf{k}}(\mathbf{q}, \omega) = G_{\mathbf{k}}^0(\mathbf{q}, \omega) + G_{\mathbf{k}}^0(\mathbf{q}, \omega) \sum_{\mathbf{k}'} v(\mathbf{k} - \mathbf{k}') G_{\mathbf{k}'}(\mathbf{q}, \omega), \quad (5)$$

where $G_{\mathbf{k}}^0(\mathbf{q}, \omega)$ is the free-particle Green's function. It has been shown by Wolff¹⁰ that Eq. (5) can be solved exactly in (i) the static case and the limit $q \rightarrow 0$, and (ii) when $v(\mathbf{k} - \mathbf{k}') = \text{const} \times (2\bar{v})$. In the latter case, the result for the paramagnetic spin susceptibility is

$$\chi(\mathbf{q}, \omega) = \frac{1}{2} g^2 \mu_B^2 \frac{\chi_0(\mathbf{q}, \omega)}{1 - 2\bar{v} \chi_0(\mathbf{q}, \omega)}, \quad (6)$$

where

$$\chi_0(\mathbf{q}, \omega) = \sum_{\mathbf{k}} \frac{n_{\mathbf{k}+\mathbf{q}} - n_{\mathbf{k}}}{\omega - \omega_{\mathbf{k}} + \omega_{\mathbf{k}+\mathbf{q}} + i\eta}, \quad \eta = 0^+ \quad (7)$$

where g is the electron Landé factor ($g=2$ for a free electron) and μ_B is the Bohr magneton. In case (i), the uniform paramagnetic spin susceptibility is given by

$$\chi \equiv \chi(\mathbf{q} = 0, \omega = 0) = \frac{1}{2} g^2 \mu_B^2 \frac{D(E_F)}{1 - (\lambda r_s / 2\pi) \ln(1 + \pi / \lambda r_s)}, \quad (8)$$

where $2D(E_F)$ is the electron density of states at the Fermi energy and $\lambda = (4/9\pi)^{1/3}$. In obtaining Eq. (8), the Coulomb potential is screened by the Thomas-Fermi dielectric function.

Recently Lobo, Singwi, and Tosi¹¹ have developed a theory of paramagnetic spin susceptibility of an interacting electron gas by suitably breaking the higher-order Green's function such that the susceptibility becomes a functional of the difference between the correlation functions for a pair of electrons with parallel and antiparallel spins. In their

theory, the expression for $\chi(\mathbf{q}, \omega)$ is the same as that given by Eq. (6) except that \bar{v} is replaced by

$$I(q) = \frac{1}{n} v(\mathbf{q}) \int \frac{\mathbf{q} \cdot \mathbf{q}'}{q'^2} [\tilde{S}(\mathbf{q} - \mathbf{q}') - 1] \frac{d\mathbf{q}'}{(2\pi)^3}, \quad (9)$$

where

$$\tilde{S}(\mathbf{q}) - 1 = \frac{n}{2} \int [g_{+,+}(\mathbf{r}) - g_{+,-}(\mathbf{r})] e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r}, \quad (10)$$

and $g(\mathbf{r})$ is the usual pair correlation function. The pair correlation function is determined in a self-consistent manner using the fluctuation-dissipation theorem:

$$\tilde{S}(\mathbf{q}) = \frac{4}{\pi n g^2 \mu_B^2} \int_0^\infty d\omega \text{Im} \chi(\mathbf{q}, \omega), \quad (11)$$

n being the electron density. It is important to note here that although the formal structure of $I(q)$ [Eq. (9)] is the same as that of $G(q)$ of the dielectric-screening theory of Singwi *et al.*,⁸ there is one fundamental difference in that in the latter $[\tilde{S}(q) - 1]$ of (9) is replaced by $[S(q) - 1]$, the Fourier transform of the full pair correlation function $g(r) - 1$. In the theory of Lobo *et al.*,¹¹ the susceptibility sum rule is violated by a factor of 2 and the internal field $I(q)$ decreases rapidly as a function of q . Since this theory yields satisfactory pair distribution functions for small values of the inter-electronic distance, it is believed to be better for larger values of q . In a more recent publication, Singwi *et al.*⁸ have modified their theory by introducing a screening of the Coulomb potential $v(q)$ appearing in Eq. (9) for the internal field with a static self-consistent dielectric function. This improved version of the theory gives much better values for the uniform static spin susceptibility and is, therefore, more trustworthy for small values of q . In the Hubbard and modified Hubbard approximations the internal field is given by

$$I(q) = \frac{1}{2} \frac{4\pi e^2}{q^2 + q_F^2}, \quad (12a)$$

$$I(q) = \frac{1}{2} \frac{4\pi e^2}{q^2 + q_F^2 + q_{FT}^2}, \quad (12b)$$

respectively. In the static and $q \rightarrow 0$ limit, the exchange-enhanced paramagnetic susceptibility is defined in terms of the Stoner parameter α as

$$\chi = \chi_P / (1 - \alpha), \quad (13)$$

where

$$\alpha = \lim_{q \rightarrow 0} 2I(q) \chi_0(q, \omega = 0) = 2D(E_F) I(q = 0)$$

and

$$\chi_P = \frac{1}{2} g^2 \mu_B^2 D(E_F) \quad (14)$$

is the Pauli spin susceptibility of a free-electron

gas. Also Brueckner and Sawada¹² have obtained in the RPA from energy considerations the result

$$\alpha = 0.166r_s - 0.204r_s^2(0.225 - 0.0676 \ln r_s). \quad (15)$$

In Table I we have given the values of α obtained in various theories for three different values of r_s . It is interesting to note that in the theory of Singwi *et al.* α almost remains constant in the entire metallic density range. It is, of course, understood that complications resulting from the non-sphericity of the Fermi surface are ignored in the theory. For calculations of interest, we need $I(q)$ for all values of q . As mentioned before, although in the revised version of the theory of Singwi *et al.*⁸ the susceptibility sum rule is improved considerably, there is still some discrepancy left. In order to rectify this discrepancy for small values of q in $I(q)$, we have scaled it by a constant factor, the latter being determined to give correctly the experimental static susceptibility of sodium. Sodium was chosen for the reason that band effects in this metal are negligible. The same scale factor is used for other values of r_s . The scaling of $I(q)$ was continued till it smoothly joined the $I(q)$ of the theory of Lobo *et al.*¹¹ which is believed to be reliable for large values of q . In practice, they smoothly join around $q \approx q_F$. The values of $I(q)$ thus determined are plotted in Fig. 1.

Localized magnetic fields in a metal, such as those due to a magnetic impurity, induce spin polarization in the conduction electrons which can be calculated by taking the Fourier transform of the susceptibility function $\chi(q, \omega=0) \equiv \chi(q)$. From Eq. (6), replacing \bar{v} by the self-consistent $I(q)$ of Eq. (9), we have

$$\chi(q) = \frac{\chi_F U(q/q_F)}{1 - 2D(E_F)I(q)U(q/q_F)}, \quad (16)$$

where

$$U(x) = \frac{1}{2} + \frac{1 - \frac{1}{4}x^2}{2x} \ln \left| \frac{2+x}{2-x} \right|. \quad (17)$$

The Fourier transform of Eq. (16) is given by

$$\chi(r) = \frac{q_F^3}{2\pi^2(q_F r)} \int_0^\infty dx x \sin(q_F r x) \chi(x). \quad (18)$$

In the absence of exchange enhancement, i.e.,

TABLE I. Comparison of α in various theories for three values of r_s .

r_s	Sum rule ^a	Values of α from				Landau theory ^b
		Eq. (8)	Eq. (12a)	Eq. (12b)	Eq. (15)	
2	0.22	0.231	0.332	0.143	0.187	0.235
4	0.25	0.305	0.663	0.182	0.236	0.28
6	0.224	0.346	0.995	0.272	0.233	...

^aReference 8.

^bReference 13.

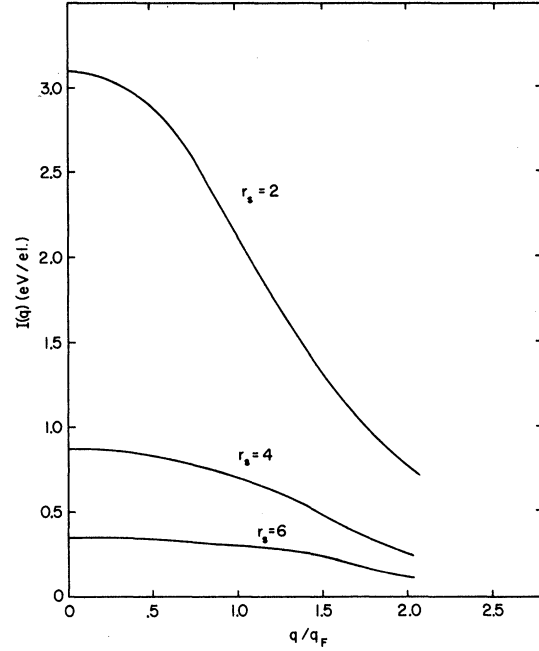


FIG. 1. Function $I(q)$ (eV/electron) vs q/q_F for $r_s = 2, 4$, and 6 .

$I(q) = 0$, one obtains from Eq. (18) the well-known expression

$$\chi_0(r) = \frac{\chi_F q_F^3}{8\pi} \frac{(\sin 2q_F r - 2q_F r \cos 2q_F r)}{(q_F r)^4}, \quad (19)$$

which is often referred to as the Rudermann-Kittel function. In Fig. 2 the dimensionless quantity $\chi(r)/\chi_F q_F^3$ is plotted as a function of r for sodium using the $I(q)$ of Fig. 1. For the sake of comparison the Rudermann-Kittel function is also plotted. It is seen from Fig. 2 that the effect of enhancement due to Coulomb interaction is sizable only for small distances.

B. Korringa Constant and Nuclear Relaxation Rates

1. Korringa Constant

The contact hyperfine interaction between the conduction electron spin \vec{s} and the nuclear spin \vec{I} is¹⁴

$$H_{en} = -\frac{8}{3} \pi g \mu_B \gamma_n \vec{I} \cdot \vec{s} \delta(\vec{r}), \quad (20)$$

where γ_n is the nuclear gyromagnetic ratio and \vec{r} is the position of the electron relative to the nucleus. The nuclear spin-lattice relaxation rate due to the fluctuating internal magnetic field $\delta \mathcal{H}$ is given by¹⁵

$$T_1^{-1} = \frac{1}{4} \gamma_n^2 \int_{-\infty}^{\infty} dt \cos \omega_0 t \langle \{ \delta \mathcal{H}^+(t), \delta \mathcal{H}^-(0) \} \rangle, \quad (21)$$

where ω_0 is the nuclear resonance frequency and curly brackets denote the anticommutator. Equation (21) can be rewritten in terms of the circular components of spin density fluctuation as

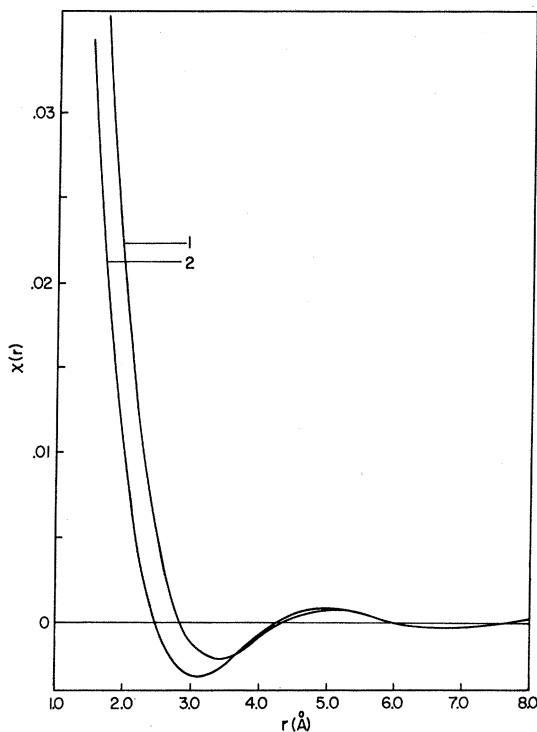


FIG. 2. Susceptibility $\chi(r)$ (units of $\chi_P q_F^3$) vs r (in Å): curve 1, as obtained from Eq. (18); curve 2, the Rudermann-Kittel function as defined in Eq. (19).

$$T_1^{-1} = \frac{1}{4} \gamma_n^2 \sum_q |A_q|^2 \int_{-\infty}^{+\infty} dt \cos(\omega_0 t) \times \langle \{s^+(\vec{q}, t), s^-(\vec{q}, 0)\} \rangle, \quad (22)$$

where

$$A_q = \frac{8}{3} \pi g \mu_B |u_q(0)|^2, \quad (23)$$

$u_q(0)$ is the amplitude of the conduction-electron wave function at the nucleus. Using the fluctuation-dissipation theorem, Eq. (22) can also be written as

$$T_1^{-1} = \frac{2\gamma_n^2 k_B T}{g^2 \mu_B^2 \omega_0} \sum_q |A_q|^2 \text{Im} \chi(q, \omega_0). \quad (24)$$

Since $\omega_0 \ll k_B T$, we have from Eq. (6) with $I(q)$ replacing \bar{v} and using Eq. (7):

$$\text{Im} \chi(q, \omega_0) = \frac{g^2 \mu_B^2 \omega_0}{8\pi q} \left[1 - 2D(E_F) I(q) U\left(\frac{q}{q_F}\right) \right]^{-2} \quad (25)$$

for $q \leq 2q_F$ and 0 otherwise. Equation (24) then becomes

$$T_1^{-1} = \pi \gamma_n^2 k_B T D^2(E_F) \langle |A_q|^2 \rangle_{q_F} \times \frac{1}{2} \int_0^2 dx \frac{x}{[1 - 2D(E_F) I(x) U(x)]^2}. \quad (26)$$

The angular bracket average is to be taken over the entire Fermi surface. The expression for the

Knight shift K_s is given by

$$K_s = g \mu_B D(E_F) \langle A_q \rangle_{q_F} / 2(1 - \alpha). \quad (27)$$

Finally, using Eqs. (26) and (27), we obtain for the Korringa constant K_c the expression

$$K_c = K_s^2 T_1 T = K_c^0 \left(\frac{1}{2} (1 - \alpha)^2 \int_0^2 dx \frac{x}{[1 - 2D(E_F) I(x) U(x)]^2} \right)^{-1}, \quad (28)$$

where $K_c^0 = g^2 \mu_B^2 / 4\pi k_B \gamma_n^2$ is the Korringa constant for the free-electron gas. For the case $I(q) = \bar{v}$, Eq. (28) reduces to that given by Moriya,⁴

$$K_c = K_c^0 \left(\frac{1}{2} (1 - \alpha)^2 \int_0^\infty dx \frac{x}{[1 - \alpha U(x)]^2} \right)^{-1}. \quad (29)$$

Numerical results obtained from Eqs. (28) and (29) are presented in Table II for $r_s = 2, 4$, and 6. Notice that K_c/K_c^0 as given by Eq. (28) remains like α , almost constant (~ 1.63) over the entire metallic density range. This feature is borne out by experiments in the alkali series.³ It is worth remembering that in the earlier attempts,⁶ where α was treated as a constant adjustable parameter, it was not possible to fit both the susceptibility and the Korringa constant. The present calculation thus demonstrates that in the calculation of the Korringa constant, it is necessary to take the q dependence of the effective exchange correlation potential into account. Numerical agreement with experiment also justifies *a posteriori* our scaling procedure for $I(q)$.

2. Relaxation Rates

It was first pointed out by Hebel and Slichter¹⁶ that the ratio of the Zeeman relaxation time T_1 to the dipolar relaxation time T_2 is sensitive to the degree of correlation between electron spin densities on adjacent nuclear sites. Following Wolff,⁵ this ratio can be written as

$$\delta = 2 + \epsilon, \quad (30a)$$

where

$$\epsilon = \frac{\sum_{i,j} (K_{ij}/r_{ij}^6)}{\sum_{i,j} (1/r_{ij}^6)}, \quad (30b)$$

$$K_{ij} = \alpha_{ij}/\alpha_{ii}. \quad (30c)$$

α_{ij} is the time integral of the spin-density correlation function and is given by⁵

$$\alpha_{ij} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \langle \vec{s}(\vec{r}_i, t) \cdot \vec{s}(\vec{r}_j, 0) \rangle, \quad (31)$$

which again on using the fluctuation-dissipation theorem can be written as

$$\alpha_{ij} = \frac{m^2 q_F^2 k_B T}{4\pi^4} \frac{1}{2q_F r_{ij}} \int_0^2 dx \frac{\sin(q_F r_{ij} x)}{[1 - 2D(E_F) I(x) U(x)]^2}. \quad (32)$$

TABLE II. Comparison of the experimental values of K_c/K_c^0 and ϵ with theoretical predictions.

r_s	α	K_c/K_c^0			Eq. (34)		ϵ		Expt
		Eq. (29)	Eq. (28)	Expt	$I(q)$ of Fig. 1	$I(q)=\bar{v}$	Eq. (33)	$I(q)=\bar{v}$	
2	0.370	1.24	1.69						
4	0.420	1.29	1.71	1.60 ± 0.08^a	0.094	0.061	0.054	0.026	0.12 ± 0.03^b
6	0.376	1.24	1.50	...					

^aReference 3.^bReference 17.

Using Eq. (32) in Eq. (30c), we have

$$K_{ij} = \frac{1}{q_F r_{ij}} \int_0^2 dx \frac{\sin(q_F r_{ij} x)}{[1 - 2D(E_F)I(x)U(x)]^2} \cdot \int_0^2 dx \frac{x}{[1 - 2D(E_F)I(x)U(x)]^2} \quad (33)$$

However, Wolff⁵ has argued that Eq. (32) should be used to calculate the spin density when $i \neq j$. For $i = j$, one should neglect the exchange enhancement in Eq. (32). In this approximation, K_{ij} becomes

$$K_{ij} = \frac{1}{2q_F r_{ij}} \int_0^2 dx \frac{\sin(q_F r_{ij} x)}{[1 - 2D(E_F)I(x)U(x)]^2} \quad (34)$$

In Fig. 3 we have plotted K_{ij} for sodium as a function of r_{ij} using Eqs. (33) and (34). The corresponding result for the free-electron case is also plotted. Also, using the same equations and carrying out the lattice sum in Eq. (30b) up to five neighbors, we have calculated ϵ for sodium ($r_s = 4$). Our results are presented in Table II.

Unfortunately, the only available value⁵ for ϵ in the alkali series is for sodium. It is gratifying to see that the calculated value for ϵ from Eqs. (34) and (30a) for sodium is within the experimental error. The agreement with experiment that we have obtained both for the Korringa constant and ϵ for sodium leads us to believe that our function $I(q)$ is a reasonable one. From a comparison of the values of ϵ in columns six and eight of Table II, it is clear that the suggestion of Wolff for the evaluation of \mathcal{Q}_{ii} is the correct one as we should expect on physical grounds. For a constant value of $I(q)$ such that $\alpha = 0.42$ at $r_s = 4$, Eq. (34) gives for ϵ a value of 0.061. This again emphasizes the importance of the q dependence of $I(q)$. The free-electron value of ϵ for sodium is 0.01.

Disregarding, for the moment, the fact that the applicability of the theory in its present form to aluminum is of somewhat doubtful validity, we have calculated both the Korringa constant and ϵ using for $I(q)$ the values as given in Fig. 1 for $r_s = 2$. Our results are $K_c/K_c^0 = 1.69$ and $\epsilon = 0.056$, whereas the corresponding experimental values⁶ are

1.26 ± 0.08 and 0.15 ± 0.07 . If we believe in the analysis of Tunstall and Brown,⁶ it is hard to understand this discrepancy between our theory and experiment.

III. CONCLUSION

Extending the theories of Moriya⁴ and Wolff,⁵ by using the expression for the generalized paramagnetic susceptibility of an interacting low-density electron gas as given by the self-consistent theory of Singwi *et al.*,⁸ we have been able to account for the experimentally observed enhancements of the Korringa product and the ratio of Zeeman to dipolar spin-lattice relaxation times in sodium. We have also been able to give a semiquantitative explanation of the observation of Narath and Weaver³ that

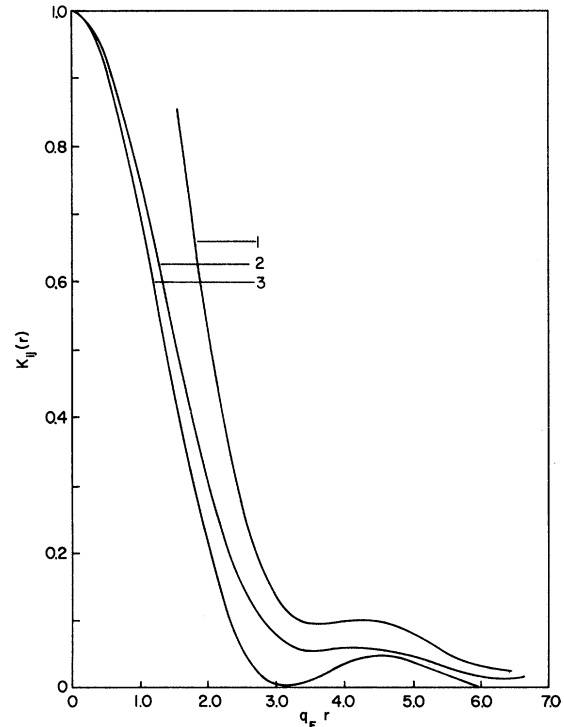


FIG. 3. The function $K_{ij}(r)$ vs $q_F r$: curve 1, as obtained from Eq. (34); curve 2, as obtained from Eq. (33); curve 3, for the free-electron case.

the value of the Korringa product in the alkali metals is almost constant. As a further test of the theory, it would be desirable to have experimental data for the ratio of Zeeman to dipolar spin-lattice relaxation times in other alkali metals. Applicabil-

ity of the theory in its present form to metals for which band effects are significant is somewhat questionable. For such cases a crude approximation is to assume an effective band mass for the electrons.

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Pressure Dependence of the Knight Shift in Al and Nb Metal

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The pressure dependence of the Knight shift K of Al and Nb metals was measured with a digitally slaved signal averager. The maximum hydrostatic pressure utilized was 8000 kg/cm². The observed value of $d\ln K/d\ln V$ is -1.01 ± 0.02 and -0.29 ± 0.02 for Al and Nb, respectively. Since it is essential to know the volume dependence of the (electron-electron-enhanced) spin susceptibility $d\ln \chi_{sp}^*/d\ln V$ in order to analyze the observed $d\ln K/d\ln V$, the theoretical implication of the previously proposed methods to estimate $d\ln \chi_{sp}^*/d\ln V$ was explored. The linearly temperature-dependent thermal expansion at low temperature α_e gives rise to the volume dependence of electron-phonon-enhanced density of states at the Fermi surface. α_e includes only a temperature-independent part of the enhancement factor $1+\lambda$. The pressure dependence of the superconductor parameters renders the volume dependence of the density of states clothed with a full electron-phonon interaction, which includes the temperature-independent part as well as a possible temperature-dependent part. A semiempirical scheme to deduce the volume dependence of $1+\lambda$, the density of states for the bare electrons $N(E_F)_{BS}$, and the band-structure effective mass m^* is proposed. These values are derived from the pressure dependence of the superconducting transition temperature and α_e . The volume dependence of χ_{sp}^* is deduced from $d\ln N(E_F)_{BS}/d\ln V$ by taking into account the effect of the electron-electron enhancement factor. The volume dependence of the density of wave function at the Fermi surface $\langle |\psi(0)|^2 \rangle$ was deduced for Al as $d\ln \langle |\psi(0)|^2 \rangle / d\ln V = -2.12$. The volume dependence of the orbital Knight shift K_0 for Nb is estimated as $d\ln K_0/d\ln V \approx 0.4$ (or 0.1). The possible origin of the discrepancy between the density of states derived from α_e and from the pressure dependence of the superconductor parameters is discussed. The origin of inconsistency in the previously reported temperature dependence of K for Al is also suggested.

I. INTRODUCTION

The Knight shift K and the spin-lattice relaxation

time T_1 of metals are directly associated with the properties of the electronic wave functions. The three main contributions to K and T_1 are the con-