Effect of Core Polarization on Knight Shift and Relaxation Time in Metallic Cadmium*

P. JENA AND T. P. DAS
Department of Physics, University of Utah, Salt Lake City, Utah 84112

AND

G. D. GASPARI
Department of Physics, University of California, Santa Cruz, California 95060

AND

S. D. MAHANTI
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 11 August 1969)

The core-polarization contributions to spin density in cadmium have been obtained using the moment-perturbed (MP) procedure and leads to increases of 10 and 17% in the isotropic Knight shift (K_s) and the relaxation rate $(T_1T)^{-1}$ at 0°K. The core-polarization effect is dominated by the s part of the wave functions of the conduction electrons on the Fermi surface, and therefore produces only a small departure (1.8%) of the Korringa ratio, $R=(K_s^2T_1T)_{\text{expt}}/(K_s^2T_1T)_{\text{ideal}}$. Additionally, the small importance of the p-type core polarization indicates that the p component of the conduction-electron wave function has no significant influence on the Knight shift. A comparison of our theoretical results for K_s and $(T_1T)^{-1}$ leads to empirical enhancement factors of $\eta_s=1.89$ and $\eta_M=3.10$, which are factors 1.6 and 2.4 larger than the predictions from the current-exchange enhancement theories for susceptibility. Possible sources for the origin of this discrepancy are discussed.

I. INTRODUCTION

THE divalent hcp metals (Be, Mg, Cd) present interesting trends[1] in their structural, band and hyperfine properties. Beryllium and magnesium have nearly equal c/a ratios, whereas the c/a ratio of cadmium is much larger. On the contrary, beryllium resembles cadmium more closely in its effective mass (related to density of state) than magnesium, which has an effective mass close to the free-electron value. The isotropic Knight shift K_s and the exchange enhancement effects on Pauli paramagnetic spin susceptibility for these three systems also present a very interesting comparison. The isotropic Knight shift in beryllium[2] is very small (−0.0025%) and negative whereas it is significant and positive for magnesium[3] and cadmium.[4,5] The Pauli spin susceptibility χ_p for beryllium, measured experimentally[6] from the area under the spin-resonance curve, is a factor of 3 smaller than the theoretical value, χ_{band}, obtained from the density of states[7] at the Fermi surface. This suggests a deenhancement on the theoretical value of spin susceptibility χ_{band}. The situation in magnesium[1] appears to be opposite in this respect. An enhancement over χ_{band} is needed if our attempts fit the experimental Knight shift.[3] The differences in the nature of the isotropic Knight shift in beryllium[8] and magnesium[1] have been explained by a combination of differences in the angular momentum character of wave functions on the Fermi surface and opposite signs for the p-type core-polarization effect for the two metals, the latter playing a rather crucial role.

The purpose of this paper is to present the results of our investigation on the effects of core polarization on the isotropic Knight shift and relaxation time in cadmium. From this analysis, one can make inferences about the importance of exchange enhancement effects on the paramagnetic spin susceptibility and relaxation rate. It is also interesting to compare the Korringa[9] constants in the three metals. The two major sources which alter the Korringa constant from its ideal non-interacting value are core-polarization (CP) and exchange-enhancement effects. A study of the Korringa constant in beryllium is not very meaningful, since we do not understand the sign of K_s as yet. The Korringa constant in magnesium[1] was predicted to be quite different from the free-electron value, this departure being mainly due to a combination of non-s core-polarization and exchange-enhancement effects. It is

* Work supported by a grant from the National Science Foundation.

[1] P. Jena, T. P. Das, and S. D. Mahanti, Phys. Rev. (to be published).

[2] D. E. Barnaal, R. G. Barnes, B. R. McCart, L. W. Mohn, and D. R. Torgeson, Phys. Rev. **157**, 510 (1967); W. T. Anderson, Jr., M. Ruhlig, and R. R. Hewitt, *ibid.* **161**, 293 (1967).

[3] T. J. Rowland, in *Progress in Material Science*, edited by Bruce Chalmers (Pergamon Press, Inc., New York, 1961), Vol. IX, p. 14; P. C. Dougan, S. N. Sharma, and D. L. Williams, Can. J. Phys. **47**, 1047 (1969); E. M. Dickson and E. F. W. Seymour, J. Physics (England) (to be published).

[4] E. F. W. Seymour and G. A. Styles, Phys. Letters **10**, 269 (1964); F. Borsa and R. G. Barnes, J. Chem. Phys. Solids **27**, 567 (1966); S. N. Sharma and D. L. Williams, Phys. Letters **25A**, 738 (1967).

[5] E. M. Dickson, Ph.D. thesis, University of California, Berkeley, California, 1968 (unpublished); Phys. Rev. **184**, 294 (1969).

[6] G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).

[7] W. M. Shyu, G. D. Gaspari, and T. P. Das, Phys. Rev. **141**, 603 (1966).

[8] P. Jena, S. D. Mahanti, and T. P. Das, Phys. Rev. Letters **20**, 544 (1968).

[9] J. Korringa, Physica **16**, 601 (1950).

interesting to find out if the observed departure of the Korringa constant in cadmium from its noninteracting value is due more to a core polarization or exchange enhancement. For these reasons, a CP investigation of cadmium is very important.

There is a further important reason for studying the CP effect in cadmium. A strong temperature dependence has been observed[4,5] for K_s in cadmium. Kasowski and Falicov[10] have recently proposed an explanation of the large temperature dependence of metallic cadmium based on the influence of electron-phonon interaction on the pseudopotential and through this on the wave functions. Kasowski and Falicov have considered the direct contribution to the spin density from the s components of the wave function. A substantial contribution to K_s from non-s components through the CP mechanism can lead to an additional source of temperature dependence.

II. PROCEDURE AND RESULTS

We shall briefly describe our procedure for evaluating the direct and CP contribution to the spin density and then present our results for the Knight shift and relaxation time at 0°K. The direct contribution to the Knight shift, $K_s{}^d$, is given by the well-known expression[11]

$$K_s{}^d=\frac{8\pi}{3}\chi_p V\langle|\psi_{\mathbf{k}_F}(0)|^2\rangle_{\mathrm{av}}, \tag{1}$$

where χ_p is the Pauli-spin susceptibility per unit volume, V, the volume of the entire crystal over which the conduction-electron wave functions are normalized and $\langle|\psi_{\mathbf{k}_F}(0)|^2\rangle_{\mathrm{av}}$ is the averaged direct spin density at the nuclear site $\mathbf{R}_j$ of conduction electrons at the Fermi surface. This average is carried out by the usual procedure[1,8] using the local density of states.

The conduction-electron wave functions can be written as a linear combination of orthogonalized plane waves[1,12,13] (OPW) in the form

$$\psi_{\mathbf{k}}(\mathbf{r})=\sum_{\mathbf{K}} C(\mathbf{k}+\mathbf{K})\mathrm{OPW}(\mathbf{k}+\mathbf{K},\mathbf{r}). \tag{2}$$

In our earlier calculations on beryllium[8] and magnesium,[1] the coefficients $C(\mathbf{k}+\mathbf{K})$ were obtained by solving the requisite secular equation using the actual potential.[14,15] Since no actual potential calculations are available for cadmium, we have instead made use of the coefficients $C(\mathbf{k}+\mathbf{K})$ derived for plane-wave basis sets[16] using the nonlocal pseudopotentials obtained by Stark and Falicov.[17]

With these wave functions, the spin density at the nuclear site $\mathbf{R}_j$ may be expressed in the form

$$|\psi_{\mathbf{k}}(\mathbf{R}_j)|^2=|\sum_{\mathbf{K}}\alpha(\mathbf{k}+\mathbf{K})e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{R}j}|^2/\langle\psi_{\mathbf{k}}(\mathbf{r})|\psi_{\mathbf{k}}(\mathbf{r})\rangle, \tag{3}$$

where

$$\alpha(\mathbf{k}+\mathbf{K})=C(\mathbf{k}+\mathbf{K})[1-\sum_t \Theta_t(0)b_t(\mathbf{k}+\mathbf{K})]. \tag{4}$$

$\Theta_t(\mathbf{r})$ is a core wave function belonging to core state t and Ω_0 is the volume of the Wigner-Seitz cell. The orthogonalization parameter $b_t(\mathbf{k}+\mathbf{K})$ is expressed in the form

$$b_t(\mathbf{k}+\mathbf{K})=\langle\Theta_t(\mathbf{r})|e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}\rangle. \tag{5}$$

For purposes of simplification one may be tempted to neglect the variation of $b_t(\mathbf{k}+\mathbf{K})$ with $\mathbf{K}$. This approximation reduces $|\psi_{\mathbf{k}}(\mathbf{R}_j)|^2$ to the form

$$|\psi_{\mathbf{k}}(\mathbf{R}_j)|^2_{\mathrm{approx}}=O^2|\Phi_{\mathbf{k}}(\mathbf{R}_j)|^2, \tag{6}$$

where

$$O^2=\frac{1}{1-(1/\Omega_0)\sum_t b_t{}^2(\mathbf{k}_F)}[1-\sum_t \Theta_t(0)b_t(\mathbf{k}_F)]^2 \tag{7}$$

and

$$\Phi_{\mathbf{k}}(\mathbf{R}_j)=\sum_{\mathbf{K}} C(\mathbf{k}+\mathbf{K})e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{R}j}. \tag{8}$$

In Eq. (7), k_F, the Fermi momentum in the free-electron approximation, is 0.747 $a_0{}^{-1}$, a_0 being the Bohr radius. Such an approximation has been utilized in recent liquid-alloy work.[18] While it may be justified in the liquid where $\mathbf{K}$ varies continuously, its validity in solid is questionable because $\mathbf{K}$'s are now restricted to be reciprocal-lattice vectors. In Fig. 1 we have presented $[1/(4\pi)^{1/2}]b_{ns}(\mathbf{k})$ as a function of k using neutral-atom Hartree-Fock wave functions[19] for the core states. While $b_{ns}(\mathbf{k})$ changes very little with k for the tightly bound inner core states, for the outermost 4s core state, the variation with k is considerable. The influence of this approximation on the spin density for cadmium will be discussed while considering our results.

For the evaluation of the CP contribution to Knight shift, arising from the exchange polarization of the core electrons at the Fermi surface in the presence of a magnetic field, we have utilized the moment-perturbation (MP) procedure.[20] The pertinent expression for

[10] R. V. Kasowski and L. M. Falicov, Phys. Rev. Letters **22**, 1001 (1969).

[11] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963); W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. II, p. 93; C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

[12] C. Herring, Phys. Rev. **57**, 1169 (1940); T. O. Woodruff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957); J. Callaway, *Energy Band Theory* (Academic Press Inc., New York, 1964).

[13] S. D. Mahanti and T. P. Das, Phys. Rev. **170**, 426 (1968).

[14] T. L. Loucks and P. H. Cutler, Phys. Rev. **133**, A819 (1964).

[15] L. M. Falicov, Phil. Trans. Roy. Soc. (London) **A255**, 55 (1962).

[16] R. W. Stark and L. M. Falicov, Phys. Rev. Letters **19**, 795 (1967).

[17] A similar approximation has been used in the Knight-shift and Ruderman–Kittel calculation on lead by L. Tterlikkis, S. D. Mahanti, and T. P. Das, Phys. Rev. Letters **21**, 1796 (1968), and in Ref. 10.

[18] N. C. Halder, Phys. Rev. **177**, 471 (1969).

[19] J. B. Mann, Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico, Report, 1968 (unpublished).

[20] G. D. Gaspari, W. M. Shyu, and T. P. Das, Phys. Rev. **134**, A852 (1964).

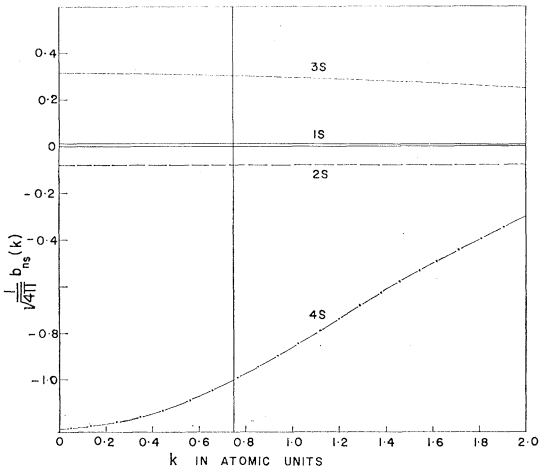

FIG. 1. Plot of orthogonalization parameters $\{[1/(4\pi)^{1/2}]b_{ns}(\mathbf{k})\}$ corresponding to the four s cores of cadmium in units of $a_0^{3/2}$ as a function of k.

this contribution to Knight shift is given by

$$K_s^{\mathrm{CP}} = \frac{8\pi}{3}\chi_p V \langle|\psi_{k_F}(\mathbf{R}_j)|^2\rangle_{\mathrm{av}}^{\mathrm{CP}}, \tag{9}$$

where

$$\langle|\psi_{k_F}(\mathbf{R}_j)|^2\rangle_{\mathrm{av}}^{\mathrm{CP}} = 2\,\mathrm{Re}\sum_t [\langle\delta\phi_t|H_E(\mathbf{k}_F)|\phi_t\rangle - \sum_{t,t'}\langle\delta\phi_t|\phi_{t'}\rangle\langle\phi_{t'}|H_E(\mathbf{k}_F)|\phi_t\rangle]. \tag{10}$$

In Eq. (10), the summations t and t' extend over all the s core states. $H_E(\mathbf{k}_F)$ is the difference in the exchange potential for spin-up and spin-down core electrons when there is a surplus of one conduction electrons at the Fermi surface in the spin-up state and is given by

$$H_E(\mathbf{k}_F)\phi_t(\mathbf{r}_1) = \psi_{k_F}(\mathbf{r}_1)\int \psi_{k_F}^*(\mathbf{r}_2)\phi_t(\mathbf{r}_2)\frac{2}{r_{12}}d\tau_2. \tag{11}$$

The function $\delta\phi_t$ represents the perturbation in the core function produced by the Fermi-contact interaction with the nuclear moment. The perturbation equation for $\delta\phi_t$ and the procedure for its solution are described in the literature[1,7,20,21] and will not be repeated here. The terms $t\neq t'$ in Eq. (10) arise out of the nonorthogonality effects[22] involving the perturbed core states. The Fermi-surface average in Eq. (10) has to be carried out in the same manner as that for the direct Knight shift K_s^d. The CP spin density in Eq. (10) can be shown to have contributions from various angular components ($l=0, 1, 2$) of the conduction-electron wave function. The notations $\langle|\psi_{k_F}(R_j)|^2\rangle_{\mathrm{av}}^{\mathrm{CP},s}$, $\langle|\psi_{k_F}(R_j)|^2\rangle_{\mathrm{av}}^{\mathrm{CP},p}$, and $\langle|\psi_{k_F}(R_j)|^2\rangle_{\mathrm{av}}^{\mathrm{CP},d}$ will be used for the s-, p-, and d-type CP contributions to spin density.

[21] W. M. Shyu, T. P. Das, and G. D. Gaspari, Phys. Rev. **152**, 270 (1966).

[22] K. J. Duff, and T. P. Das, Phys. Rev. **168**, 43 (1968); A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 282 (1959).

For the actual calculation of the spin density in cadmium, we have considered the two major segments of the Fermi-surface, called the "lens" and the "monster."[16] The averaging over the Fermi surface for the direct spin density was carried out as a first step by a proper scanning of 1/24th of the surface of lens and monster. The contributions to the spin density from a distribution of points on each of the two segments of the Fermi surface were then combined through the local density of states.[1,8] The resulting spin densities in units of $1/V$ from lens and monster are

$$\langle|\psi_{k_F}(R_j)|^2\rangle_{\mathrm{av}}^{d,\mathrm{lens}} = 258.7 \tag{12}$$

and

$$\langle|\psi_{k_F}(R_j)|^2\rangle_{\mathrm{av}}^{d,\mathrm{monster}} = 397.6. \tag{13}$$

Next these individual contributions have to be combined according to the relative surface areas[1,8] of lens and monster. An examination of the relative surface areas through Harrison construction[23] gives a ratio of 5:1 for the surface areas of monster and lens. An examination of the Fermi surface dimensions from the radio-frequency size-effect measurements,[24] however, indicates that the ratio is somewhat smaller and is probably closer to 4:1. Using the latter ratio and Eqs. (12) and (13) the final averaged direct spin density in units of $1/V$ is

$$\langle|\psi_{k_F}(R_j)|^2\rangle_{\mathrm{av}}^{d} = 369.9. \tag{14}$$

If the ratio 5:1 had been taken, the corresponding value for the spin density would be equal to 374.4836, which is not substantially different. For the analysis of the Knight-shift K_s and relaxation time T_1 we prefer to use the spin density in Eq. (14). For the approximation of constant $b(\mathbf{k})$, the important quantities for the evaluation of the approximate direct spin density in Eq. (6) are

$$O^2 = 534.9 \tag{15}$$

and

$$\langle|\phi_{k_F}(R_j)|^2\rangle_{\mathrm{av}} = 0.7576. \tag{16}$$

Thus, the resulting approximate spin density is

$$\langle|\psi_{k_F}(R_j)|^2\rangle_{\mathrm{av,\ approx}} = 405.2. \tag{17}$$

This approximation is seen to produce a substantial overestimation of the spin density over the value in Eq. (14) (by about 10%).

The second important quantity in the evaluation of K_s is the Pauli paramagnetic spin susceptibility χ_p in Eq. (1). Kasowski and Falicov,[10] from an earlier calculation[25] of the band density of states, have obtained a value for the spin susceptibility.

$$\chi_{\mathrm{band}} = 0.54\times10^{-6}\ \mathrm{cgs\ vol\ units}. \tag{18}$$

[23] W. A. Harrison, *Pseudopotential in Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

[24] R. C. Jones, R. G. Goodrich, and L. M. Falicov, Phys. Rev. **174**, 672 (1968).

[25] P. B. Allen, M. L. Cohen, L. M. Falicov, and R. V. Kasowski, Phys. Rev. Letters **21**, 1794 (1968).

TABLE I. Core-polarization contributions to Knight shift (in %) from the s, p, and d angular components of the conduction-electron wave function from each of the four s cores of cadmium.

Segment of the Fermi surface	Angular component	Individual core contributions to K_s^{CP} (in %) 1S	2S	3S	4S	Total	Direct Knight shift K_s^d (in %)
Monster	s	0.0023	0.0030	0.0077	0.0044	0.0174	
	p	−0.0016	−0.0001	0.0009	0.0027	0.0019	0.1799
	d	0.0	−0.0006	0.0	0.0005	−0.0001	
Lens	s	0.0014	0.0018	0.0045	0.0026	0.0103	
	p	−0.0017	−0.0001	0.0010	0.0029	0.0021	0.1170
	d	0.0	−0.0009	0.0	0.0005	−0.0004	
Averaged over the fermi surface	s	0.0021	0.0027	0.0070	0.0040	0.0158	
	p	−0.0016	−0.0001	0.0009	0.0027	0.0019	0.1673
	d	0.0	−0.0007	0.0	0.0005	−0.0002	

Combining this with the direct spin density in Eq. (14), the direct Knight shift turns out to be

$$K_s^d = 0.1673\%. \tag{19}$$

The CP contribution to the Knight shift K_s^{CP} was calculated using the same choice of χ_{band}, and the appropriate results are displayed in Table I. In Table I we have listed the contributions to Knight shift from the various angular components ($l=0, 1, 2$) of the conduction-electron wave functions resulting from the polarization of each of the four s-core states of cadmium. In order to understand the relative angular character of the conduction electrons on monster and lens, we have also listed in Table I the CP contributions to K_s for both the segments. The last column presents the direct contribution to Knight shift to facilitate comparison with the CP contribution. The contributions from the individual segments, monster and lens, are then weighted by their relative surface areas 4:1 to yield the final averaged direct and CP contribution to Knight shift. For the CP calculations, as in the case of direct Knight shift, we have again made use of the Hartree-Fock core wave functions[19] for the neutral atom.

K_s^{CP} from the s part of the conduction-electron wave function ($K_s^{CP,s}$) is seen to be composed of comparable contributions from the various core states with the same sign. The relative contributions from various core states is determined by the combination of two factors, the strength of the exchange with the conduction electrons which is stronger for the outer cores and the density of the nucleus which is larger for the inner cores. The combination of these two factors seems to make the CP contribution from the $3s$ core the largest. In the case of the CP contribution to K_s from the p part of the conduction-electron wave function ($K_s^{CP,p}$), there is, however, a much more drastic variation from core to core, both in magnitude and in sign. While the core contributions to $K_s^{CP,p}$ are individually smaller than that for $K_s^{CP,s}$, the combination of opposing contributions from the various core states makes $K_s^{CP,p}$ about a factor of 8 smaller than $K_s^{CP,s}$. The contributions from the higher l components of the conduction-electron wave functions, as evidenced from the d contribution to K_s^{CP} ($K_s^{CP,d}$) in Table I, are negligible. Combining the CP contributions to K_s from the s, p, and d parts of the conduction-electron wave functions, one has the total CP contribution to Knight shift,

$$K_s^{CP} = 0.0175\%. \tag{20}$$

It is interesting to compare the small, but positive, contribution to K_s in cadmium with the substantial positive value in magnesium[1] and substantial negative value in beryllium.[8] In the last mentioned case, $K_s^{CP,p}$ has the actual decisive effect in cancelling a substantial part of the contribution whereas in the case of magnesium, it substantially helps the agreement of K_s with experiment. This variation in $K_s^{CP,p}$ over the three metals reinforces the conclusion that one cannot in general predict either the sign or the magnitude of $K_s^{CP,p}$ without actual calculations as in the case of atoms.[26,27]

It is also interesting to note that $K_s^{CP,s}$ in cadmium is about a factor of 2 larger than that in magnesium,[1] but is actually a smaller fraction of total Knight shift. This is well understood, since the monster in cadmium has strong s character, unlike that in magnesium, thus resulting in a much larger direct Knight shift in cadmium. The small $K_s^{CP,p}$ obtained from our calculation has an important implication for the temperature dependence of the Knight shift in solid cadmium. The observed anomalous temperature variation in solid cadmium has recently been explained[10] by an increase in the s character of the wave function with increasing temperature. Had $K_s^{CP,p}$ been substantial and especially had a negative sign, the change in p character would have been an important factor for the temperature dependence of K_s. Our results in Table I indicate that this is not the case in cadmium. However, in the case of beryllium[8] where the above stated condition on $K_s^{CP,p}$ does apply, the change in the p character is expected to be an important contributor for the temperature dependence of K_s (about 30% increase from 4.2°K to room temperature[2]).

[26] N. C. Dutta, C. Matsubara, R. T. Pu, and T. P. Das, Phys. Rev. **177**, 33 (1968).

[27] N. Bessis, H. Lefebvre-Brion, C. M. Moser, A. J. Freeman, R. K. Nesbet, and R. E. Watson, Phys. Rev. **135**, A588 (1964).

To compare the theoretical value of the Knight shift at 0°K,

$$K_s = 0.1848\%, \tag{21}$$

with experiment, the experimental Knight-shift curves for variation of K_s with room temperature was extrapolated to 0°K, leading to the experimental value of 0.35%. Thus, for theory and experiment to agree, one needs an empirical enhancement factor

$$\eta_s = 1.894. \tag{22}$$

This enhancement factor may be the result of a combination of enhancement effects associated with χ_p and additional mechanisms[1] contributing to K_s. Kasowski and Falicov[10] in their recent calculation obtained a value of 1.55 for the empirical enhancement factor. The apparent disagreement between our value and theirs may be due to a combination of two reasons. First, they have neglected the core-polarization contribution to spin density. Secondly, they have utilized the atomic core wave functions due to Herman and Skillman[28] which were obtained using the Slater approximation[29] for exchange. In our calculation, we have utilized the Hartree-Fock core functions obtained by Mann.[19] Due to the approximate nature of the Slater approximation, the Herman and Skillman functions can differ substantially from the Hartree-Fock functions. In particular, using $k_F = 0.747 a_0^{-1}$, the value of O^2 in Eq. (7) for Herman-Skillman core wave functions[28] comes out as 585.9, compared to the value of 534.9 one gets using Mann's Hartree-Fock wave functions[19] for core states.

We would like next to analyze the effects of core polarization on the relaxation rate and Korringa constant. The appropriate expression[11,30,31] for the relaxation rate is given by

$$\left(\frac{1}{T_1T}\right)_{\text{tot}} = \left(\frac{1}{T_1T}\right)^{d+\text{CP},s} + \frac{1}{3}\left(\frac{1}{T_1T}\right)^{\text{CP},p} + \frac{1}{5}\left(\frac{1}{T_1T}\right)^{\text{CP},d}, \tag{23}$$

where

$$\left(\frac{1}{T_1T}\right)^{d} = A[\langle|\psi_{\mathbf{k}_F}(\mathbf{R}_j)|^2\rangle_{\text{av}}{}^{d}]^2, \tag{24}$$

$$\left(\frac{1}{T_1T}\right)^{d+\text{CP},s} = A[\langle|\psi_{\mathbf{k}_F}(\mathbf{R}_j)|^2\rangle_{\text{av}}{}^{d} + \langle|\psi_{\mathbf{k}_F}(\mathbf{R}_j)|^2\rangle_{\text{av}}{}^{\text{CP},s}]^2, \tag{25}$$

and

$$\left(\frac{1}{T_1T}\right)^{\text{CP},l} = A[\langle|\psi_{\mathbf{k}_F}(\mathbf{R}_j)|^2\rangle_{\text{av}}{}^{\text{CP},l}]^2, \quad l>0 \tag{26}$$

with

$$A = \frac{16}{9}\pi^3\hbar^3\gamma_e{}^2\gamma_n{}^2 k_B g^2(\epsilon_F) V^2. \tag{27}$$

In Eq. (27), γ_e and γ_n are, respectively, the electron and nuclear gyromagnetic ratios, $g(\epsilon_F)$ is the band density of states per conduction electron at the Fermi surface, and k_B is the usual Boltzmann constant.

Using Eqs. (24) and (25), our calculated direct and CP spin densities, and the density of states from the band calculation, the relaxation rate at 0°K is calculated as

$$\left(\frac{1}{T_1T}\right)_{\text{tot}} = 0.5756 \text{ (deg sec)}^{-1}. \tag{28}$$

The direct spin density alone gives for $(T_1T)^{-1}$, the value 0.4789 (deg sec)$^{-1}$ while the inclusion of s-type CP spin density increases it to the value in Eq. (28). The p-type CP contribution to spin density being relatively small (Table I) affects the relaxation rate in the fifth significant figure and can be neglected. We find the experimental value of $(T_1T)^{-1}$ at 0°K through the quoted Korringa ratio,[5] R defined by the relation

$$R = (K_s{}^2T_1T)_{\text{expt}}/(K_s{}^2T_1T)_{\text{ideal}} \tag{29}$$

with

$$(K_s{}^2T_1T)_{\text{ideal}} = \frac{\hbar}{4\pi k_B}(\gamma_e/\gamma_n)^2. \tag{30}$$

The experimental Korringa ratio is found to be independent of temperature[5] and is given by

$$R^{\text{expt}} = 1.1765. \tag{31}$$

On combining this experimental value (0.35%) of K_s at 0°K, the experimental value for the relaxation rate at 0°K is deduced to be

$$(1/T_1T)_{\text{expt}} = 1.7860. \tag{32}$$

A comparison of the relaxation rate in Eqs. (28) and (32) indicates that an empirical enhancement factor

$$\eta_M = 3.103 \tag{33}$$

is required to match experiment. For the Korringa ratio, our theoretical results for K_s and T_1T in Eqs. (21) and (28) lead to

$$R_{\text{CP}}{}^{\text{theor}} = 1.018. \tag{34}$$

The small departure (1.8%) of R^{theor} from unity is a result of the influence of the weak p-type CP effect on Knight shift. The explanation for the difference between $R_{\text{CP}}{}^{\text{theor}}$ and R^{expt} has thus to be sought elsewhere.[32]

[28] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965).
[29] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[30] S. D. Mahanti, and T. P. Das (unpublished); S. D. Mahanti, Ph.D. thesis, University of California, Riverside, California (unpublished).
[31] A. Narath and H. T. Weaver, Phys. Rev. **175**, 373 (1968).

[32] While an actual calculation is necessary to arrive at a definite conclusion, one does not expect the CP effect in the liquid to be of any greater importance than in the solid. Thus, the experimentally observed departure (Ref. 5) of R from unity has to be sought elsewhere, perhaps through exchange enhancement effects discussed subsequently for the solid phase.

Any mechanism such as the orbital effect[33,34] or the conduction-conduction exchange[1,35] process, which involves different effects on $(T_1T)^{-1}$ from s and non-s components of the wave function can lead to a departure of R^{theor} from unity and can explain a part or all of the difference between theory and experiment. However, the fairly large values of η_s and η_M in Eqs. (22) and (33) suggest that exchange-enhancement effects on the susceptibility might be responsible. If, in fact, exchange-enhancement effects were totally responsible for η_s and η_M the Korringa ratio R^{theor} would be given by

$$R^{\text{theor}}=R_{\text{CP}}{}^{\text{theor}}(\eta_S{}^2/\eta_M). \tag{35}$$

It is interesting to compare η_S and η_M with the predictions of current-exchange-enhancement theories due to Silverstein[36] and Moriya.[37]

Silverstein's expression[36] for the exchange enhanced susceptibility χ_s is

$$\chi_s=\chi_s{}^*/[1+(m/m^*-1)\chi_s{}^*/\chi_s{}^{\text{free}}], \tag{36}$$

where χ_f is the free-electron Pauli susceptibility and χ is the exchange-enhanced susceptibility in the free-electron approximation appropriate to the density of conduction electrons in the metal under study. Using the value of $\chi=1.35\times10^{-6}$ cgs vol units obtained from Silverstein's curve for the density appropriate for cadmium and $m^*/m=0.54$ from density of states from band calculations,[25] Eq. (36) yields

$$\chi_s=0.63\times10^{-6}\text{ cgs vol units}. \tag{37}$$

The enhancement factor $\eta_S=\chi_s/\chi^{\text{band}}$ is thus given by

$$\eta_S{}^{\text{theor}}=1.17 \tag{38}$$

which compares rather poorly with the empirical ratio in Eq. (22).

For the exchange enhancement of $(T_1T)^{-1}$, we have utilized Moriya's theory[37] where one carries out an evaluation of $\chi(\mathbf{q})$ using a δ-function approximation for the screened exchange potential between the electrons. While this is an approximation, it is a reasonable one for semiquantitative purposes in view of the short range of the screened exchange between electrons in a metal. Making a similar effective-mass approximation as in Silverstein's[36] expression to include band effects, the modified[30] Moriya expression is

$$(1/T_1T)_{\text{Moriya}}=(1/T_1T)_{\text{tot}}\eta_M{}^{\text{theor}}, \tag{39}$$

where

$$\eta_M{}^{\text{theor}}=\langle[1-\zeta^*F(q)]\rangle_{\text{av}} \tag{40}$$

with

$$\zeta^*=(m^*/m)(1-\chi_f/\chi). \tag{41}$$

In Eq. (41), χ_f and χ have the same meaning as in Eq. (36). The function $F(q)$ is the linear dielectric function which, for a spherical Fermi surface, is given by

$$F(q)=\tfrac{1}{2}\left[1+\frac{4k_f{}^2-q^2}{4k_fq}\log\left|\frac{2k_f+q}{2k_f-q}\right|\right], \tag{42}$$

where q ranges over 0 to $2k_f$ for a spherical Fermi surface and the average in Eq. (40) is carried out over this range of q. Substituting for m^* and for χ_f and χ from Silverstein's curve, we found $\zeta^*=0.14$ for cadmium and

$$\eta_M{}^{\text{theor}}=1.27, \tag{43}$$

which is again rather small compared to the empirical exchange enhancement factor η_M in Eq. (33).

It is intriguing that the value of $\eta_S{}^2/\eta_M$ from Silverstein[37] and Moriya's[38] theory is about 1.08 which is not very different from the experimental value of R in Eq. (31). However, not much weight can be attached to this observation in view of the strong departures of the empirical enhancement factors from those predicted by current-exchange-enhancement theories. Thus, the question regarding the origin of these empirical enhancement parameters is unresolved, and may require either the estimation of contributions from other mechanisms for the Knight shift or an improved treatment of exchange-enhancement effects for Bloch electrons. The need for the latter is crystallized by a comparison with similar empirical enhancement factors for K_s of 0.31 and 2.69 in the related metals beryllium[8] and magnesium.[1] The former, actually a deenhancement, is derived from a spin-resonance measurement[6] of χ_p, and the latter comes from an analysis of Knight-shift data[3] in magnesium similar to that used here.

ACKNOWLEDGMENTS

We are thankful to Professor D. L. Ikenberry for supplying us with the MP functions for cadmium, and to Dr. E. M. Dickson for a copy of his Ph.D. thesis and for many stimulating discussions.

[33] Y. Obata, J. Phys. Soc. Japan **18**, 1020 (1963).
[34] R. Kubo, J. Phys. Soc. Japan **17**, 975 (1962); R. Kubo and Y. Obata, *ibid.* **11**, 547 (1956).
[35] S. H. Vosko and R. A. Moore, Bull. Am. Phys. Soc. **12**, 314 (1967).
[36] S. D. Silverstein, Phys. Rev. **130**, 912 (1963).
[37] T. Moriya, J. Phys. Soc. Japan **18**, 516 (1963).
[38] Y. Yafet and V. Jacarrino, Phys. Rev. **133**, A1630 (1964).