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Temperature-dependent Knight shift in cadmium

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The temperature-dependent Knight shift in cadmium has been investigated using our recent results for the temperature-dependent spin susceptibility. Our calculation of the spin susceptibility includes the effect of lattice potential which includes the effect of electron-electron interaction via an effective one-particle approximation and spin-orbit interaction. Thermal effects of lattice expansion and electron-phonon interactions have been included in our calculation in a pseudopotential formalism. Our results for the temperature-dependent Knight shift show improvement on the earlier theoretical results and agree well with the experimental results.

I. INTRODUCTION

The NMR properties of cadmium present some interesting behavior in the variation of the spin susceptibility and Knight shift with temperature. The Knight shift in cadmium has been measured by a number of experiments.[1–5] The band structure and Fermi surface of cadmium have been well studied. However, no theoretical result existed from which the temperature-dependent spin susceptibility of cadmium could be calculated. Kasowski and Falicov[6,7] have proposed an explanation of the peculiar behavior of the temperature dependence of the Knight shift in cadmium, based on the influence of the electron-phonon interaction on the pseudopotential and through this on the wave function. Jena *et al.*[8] have investigated the core-polarization contribution to the isotropic Knight shift K_{iso} of cadmium. Gupta, Kumar, and Ramchandani[9] have calculated the isotropic Knight shift of Cd using the band structure of Cd calculated by the nonrelativistic APW (augmented plane wave) method.

In the calculations of Kasowski[7] and Jena *et al.*[8] one of the factors to which the discrepancy between theoretical and experimental values has been attributed is the electron-electron interaction. This electron-electron interaction enhances the spin susceptibility, the enhancement being primarily a function of the electron density. This enhancement is empirically found to be 1.55 and 1.894 by Kasowski and Jena *et al.*, respectively, by fitting the calculated K_{iso} value at $T = 0$ °K with the experimental data. Jena *et al.* have observed that the core-polarization (CP) effect is dominated by the S part of the conduction-electron wave function and is positive. The CP gives a contribution which is 10% of the direct spin contribution to K_{iso}. However, in all the above calculations of Knight shift they have used the spin susceptibility χ_s calculated using the density of states at the Fermi surface, $N(\epsilon_F)$, from band-structure calculations. Thus the calculation of the temperature-dependent susceptibility required the knowledge of band structures at various temperatures. This makes the procedure extremely tedious and complicated. Secondly, many-body corrections to χ_s were included[7,8] in the above-mentioned calculations by means of a temperature-independent enhancement factor, determined empirically for $T = 0$ °K. In all the above calculations of spin susceptibility the effects of spin-orbit interaction have been neglected. Mahanti and Das[10] have pointed out that the exchange core polarization, the exchange enhancement of the χ_s due to the electron-electron interaction, and the relativistic corrections to the spin density at the nucleus are quite important factors and should be taken into account to get accurate theoretical values of the Knight shift for alkali metals.

The purpose of this paper is to present the results of our investigation on the effects of thermal expansion and lattice vibration on the Knight shift of cadmium. We report here on the temperature-dependent Knight shift using the values of the temperature-dependent spin susceptibility obtained from our recent calculation (Ref. 14). Our calculation of the Knight shift is more reliable in the sense that we have used the values of χ_s calculated from our general expression[11–14] for the spin susceptibility. This calculation of the spin susceptibility includes the effect of the lattice potential, which includes the effect of the electron-electron interaction via an effective one-particle approximation and spin-orbit interaction. The effects of the thermal expansion and electron-phonon interaction are included, as in Ref. 14, to obtain the temperature-dependent χ_s.

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TABLE I. Temperature-dependent isotropic Knight shift in Cd.

T (°K)	$\Omega_0\langle\langle\lvert\bar{\phi}_k\rvert^2\rangle_p\rangle_F$	$\langle\chi_s\rangle_p$ (10^{-6} cgs vol. units)	K_{iso} (present calc.)
0	0.74	0.9202	0.38%
298	0.81	1.039	0.47%
462	0.86	0.9706	0.467%

II. CALCULATION OF THE TEMPERATURE-DEPENDENT KNIGHT SHIFT

We now calculate the temperature-dependent Knight shift using our results for the temperature-dependent spin susceptibility and the averaged spin density at the nuclear site at various temperatures, as calculated by Kasowski.[7] The direct contribution to the isotropic Knight shift is given by[7]

$$K_{\mathrm{iso}}=\frac{\Delta H}{H}=\frac{8\pi}{3}\langle\chi_s\rangle_p\,\Omega_0 C^2\langle\langle\lvert\bar{\phi}_k(\vec{R}_j)\rvert^2\rangle_p\rangle_F\,, \tag{1}$$

where $\langle\chi_s\rangle_p$ is the phonon ensemble average of the effective spin susceptibility calculated from our result.[11–14]

$$C^2\langle\langle\lvert\bar{\phi}_k(\vec{R}_j)\rvert^2\rangle_p\rangle_F$$

is the ensemble-averaged spin density at the nuclear site $\vec{R}_j$ of conduction electrons at the Fermi surface. Ω_0 is the volume of the entire crystal over which the conduction-electron wave function is normalized. $\langle\ \rangle_p$ refers to the phonon ensemble average and the $\langle\ \rangle_F$ refers to the Fermi-surface average. $\bar{\phi}_k(\vec{R}_j)$ is the ensemble-averaged pseudo wave function. The anisotropic Knight shift is given by[7]

$$K_{\mathrm{an}}=3\langle\chi_s\rangle_p\,\Omega_0\langle\langle\langle\bar{\psi}_k\rvert(3\cos^2\alpha-1)/r^3\lvert\bar{\psi}_k\rangle\rangle_p\rangle_F\,, \tag{2}$$

where $\bar{\psi}_k$ is defined by

$$\bar{\psi}_k=\bar{\phi}_k-\sum_{t,j}\Theta_t(\vec{r}-\vec{R}_j)\,\langle\Theta_t(\vec{r}-\vec{R}_j)\vert\bar{\phi}_k\rangle\,. \tag{3}$$

TABLE III. Comparison of our K_{iso} with earlier results.

T (°K)	K_{iso} (earlier theory)	K_{iso} (expt.)	K_{iso} (present calc.)
0	0.23%[a] 0.1848%[c] 0.305%[e]	0.33%[b] 0.34%[d]	0.38%
298	0.27%[a]	0.40%[b] 0.40%[f]	0.47%
462	0.30%[a]	0.48%[d] 0.48%[f] 0.47%[g]	0.467%

[a] Reference 7.
[b] Reference 4.
[c] Reference 8.
[d] Reference 3.
[e] Reference 9.
[f] Reference 5.
[g] Reference 2.

Here $\Theta_t(\vec{r}-\vec{R}_j)$ is the core function centered at the site $\vec{R}_j$, t refers to the quantum numbers n, l, m and α is the angle between the applied field and the radius vector $\vec{r}$ from the nuclear site to the electron. One can write

$$\langle\langle\langle\bar{\psi}_k\rvert\frac{(3\cos^2\alpha-1)}{r^3}\lvert\bar{\psi}_k\rangle\rangle_p\rangle_F=A_p+A_{sd} \tag{4}$$

and

$$K_{\mathrm{an}}=3\langle\chi_s\rangle_p\,\Omega_0(A_p+A_{sd})\,. \tag{5}$$

In Table I we tabulate our results for the temperature-dependent isotropic Knight shift and in Table II we tabulate our results for the temperature-dependent anisotropic Knight shift. In this calculation we use the values of $\langle\langle\lvert\bar{\phi}_k(\vec{R}_j)\rvert^2\rangle_p\rangle_F, A_p, A_{sd}$ as tabulated by Kasowski.[7] The value of C^2 is taken to be 669. In Table III we compare our results of K_{iso} with the other theoretical and experimental results. In Table IV we compare our results of K_{an} with other theoretical and experimental results.

TABLE II. Temperature-dependent anisotropic Knight shift in Cd.

T (°K)	$\Omega_0 A_p(T)$	$\Omega_0 A_{sd}(T)$	$\langle\chi_s\rangle_p$	K_{an} (present calc.)
0	−44	21	0.9202	−0.0064%
298	99	24	1.039	0.038%
462	104	22	0.9706	0.036%

TABLE IV. Comparison of our K_{an} with earlier results.

T (°K)	K_{an} (earlier theory)	K_{an} (expt.)	K_{an} (precent calc.)
0	−0.004[a]	−0.01[b,c]	−0.0064
298	0.022[a]	0.044[b] 0.047[d]	0.038
462	0.024[a]	0.051[b] 0.049[d]	0.036

[a] Reference 7.
[b] Reference 3.
[c] Reference 4.
[d] Reference 2.

III. DISCUSSION

We note that our theoretical results show an improvement over the earlier theoretical results in their comparison with the experimental results. In the calculation of the temperature-dependent Knight shift the two quantities involved are: (i) the temperature-dependent spin susceptibility and (ii) the ensemble-averaged spin density $\langle|\psi(\vec{R}_j)|^2\rangle$ of conduction electrons at the nuclear site. The accuracy of the theoretical results therefore depends on the accuracy of the calculation of these two quantities. In our calculation of the spin susceptibility we have included the effect of the lattice potential which includes the effect of the electron-electron interaction via an effective one-particle approximation and spin-orbit interaction. Because of the difficulties associated with the simultaneous treatment of the lattice potential and the correlation effect among Bloch electrons the latter effect has not been included in our calculation of χ_s. However, we note from recent calculations[15] that the exchange-correlation enhancement of χ_s for cadmium is quite small (~18%) compared to the enhancement of 71–125% in the case of alkali metals. Furthermore, this result for the enhancement factor[15] does not include the effect of spin-orbit interaction the inclusion of which is expected to decrease the enhancement factor owing to the diamagnetic contribution of the spin-orbit interaction.[13,14] The results for $\langle|\psi(\vec{R}_j)|^2\rangle$ in our calculation have been taken from an earlier calculation which uses the atomic core functions of Herman and Skillman (HS). Owing to the nature of the Slater approximation the HS atomic functions differ substantially from the Hartree-Fock atomic functions. It has been shown[10] that $\langle|\psi(\vec{R}_j)|^2\rangle$ obtained from the HS atomic functions is about 10% higher than the one calculated using the Hartree-Fock core functions of Mann.[10] Thus, with use of the Hartree-Fock atomic core functions for the evaluation of $\langle|\psi(\vec{R}_j)|^2\rangle$, we may expect an about 10% decrease in our present calculated value of the Knight shift.

The above considerations, together with the uncertainties in the experimental results, may provide an explanation for the discrepancy between the experimental and our theoretical results. In conclusion, we wish to mention that our calculated values of K_{iso} and K_{an} for Cd are not likely to change significantly if one incorporates simultaneously the change in χ_s due to exchange enhancement and the change in $\langle|\psi(\vec{R}_j)|^2\rangle$ arising from the use of the Hartree-Fock function in place of the HS functions.

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