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Isotropic Knight shift of cadmium

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The isotropic knight shift of cadmium has been calculated using the band structure of cadmium calculated by Ramchandani. The calculated value of 0.305% agrees well with experimental values from 0.300% to 0.350%. The agreement between the experimental and calculated values of the isotropic Knight shift is considered to be good owing to the choice of a realistic potential which is based on Liberman's self-consistent calculation of atomic charge densities.

I. INTRODUCTION

The Knight shift of cadmium has been measured by a number of experiments.[1-4] The band structure[5,6] as well as Fermi surface of Cd have been well studied. This motivates one to calculate theoretically the Knight shift using the results of band-structure calculation and then to compare the same with the experimental value. The reported experimental values of the Knight shift of cadmium vary from 0.35% to 0.30% at 4.2 °K.

Starting with de Haas-van Alphen (dHvA) data Stark and Falicov[5] have constructed a nonlocal pseudopotential to calculate the band structure of cadmium. Ramchandani[6] calculated the band structure of cadmium by the nonrelativistic augmented-plane-wave (APW) method using a potential based on Liberman's[7] self-consistent Slater-Dirac charge densities. For the exchange part, Slater's free-electron approximation was used. Calculations of the Knight shift of Cd have been performed by Kasowski and Falicov[8] and Kasowski[9] using the band structure of Stark and Falicov.[5] Jena *et al.*[10] have calculated the Knight shift of cadmium using the conduction-electron wave functions in the orthogonalized-plane-wave (OPW) form where the coefficients for plane-wave sets were derived from the nonlocal pseudopotential of Stark and Falicov. The present attempt was to see how well the Knight shift, obtained by using a band structure calculated from first principles agrees with the experimental value.

In Sec. II the formulation of the theory is given, and Sec. III deals with the results and discussions.

II. THEORY

The isotropic Knight shift is considered to result only from the hyperfine contact interaction of the nuclear spin with the orbital angular momentum of the conduction electrons, and is expressed

$$K_{\rm iso} = \Delta H/H = \tfrac{8}{3}\pi \chi_P \langle | \Psi_{\vec{k}}(0) |^2 \rangle_{E_F} , \qquad (1)$$

where χ_P is the Pauli spin susceptibility and $\langle | \Psi_{\vec{k}}(0) |^2 \rangle_{E_F}$ is a measure of the electronic density of conduction electrons at the nuclear site averaged over all the allowed $\vec{k}$ points of the Fermi surface. Core polarization can also contribute to $K_{\rm iso}$ through the contact term. However, we have neglected the core polarization and orbital effects in the present calculation.

Starting from the APW band-structure results, Gupta and Kumar[11] calculated the isotropic Knight shift of lanthanum. The same procedure has been applied in the present case for calculating the isotropic Knight shift of cadmium.

For the evaluation of the spin susceptibility χ_P we have used the expression

$$\chi_P = \mu_B^2 N(E_F) \qquad (2)$$

for a noninteracting electron gas, where $N(E_F)$ is the density of states at the Fermi surface and μ_B is the Bohr magneton. $N(E_F)$ is obtained from the band-structure calculations for cadmium.[6] In calculating $K_{\rm iso}$ we also require the conduction-electron wave function $\Psi_{\vec{k}}(\vec{r})$ at the nucleus. We shall now discuss briefly the method which has been used for calculating these conduction-electron wave functions. First, we express $\Psi_{\vec{k}_0}(\vec{r})$ as a linear combination of APW functions in the following form:

$$\Psi_{\vec{k}_0}(\vec{r}) = \sum_n C_{\vec{k}_n} \Psi_{\vec{k}_n}(\vec{r}) , \qquad (3)$$

where

$$\vec{k}_n = \vec{K}_n + \vec{k}_0 ,$$

$\vec{k}_0$ being an allowed $\vec{k}$ vector in the first Brillouin zone (BZ), i.e., a reduced vector, and $\vec{K}_n$ is the reciprocal-lattice vector. The coefficients $C_{\vec{k}_n}$'s are obtained by solving the corresponding set of secular equations

$$\sum_n C_{\vec{k}_n} (\mathcal{H} - E)_{\vec{k}_n, \vec{k}_{n'}} = 0 \qquad (4)$$

for all $\vec{k}_{n'}$ values. The Hamiltonian $\mathcal{H}$ in the above equation is based on the muffin-tin potential. As regards the $\Psi_{\vec{k}_n}$'s, they are single APW functions and can be expressed as

$$\Psi_{\vec{k}_n}(\vec{r}) = \delta_1 e^{i\vec{k}_n \cdot \vec{r}_i} 4\pi \sum_{l=0}^{\infty}{}' \sum_{m=-l}^{l} i^l \times \left(Y^*_{lm}(\hat{k}_n) Y_{lm}(\hat{\rho}) j_l(k_n \sigma_i) \frac{R_l(E,\rho)}{R_l(E,\sigma_i)} \right) + \delta_2 e^{i\vec{k}_n \cdot \vec{r}} , \qquad (5)$$

where $\delta_1 = 0$, $\delta_2 = 1$ for the region outside APW spheres, and $\delta_1 = 1$, $\delta_2 = 0$ for the region inside an APW sphere. In Eq. (5) σ_i is the radius of the ith APW sphere, $\vec{r}_i$ is the position vector of the ith atom, and $\rho = |\vec{\rho}| = |\vec{r} - \vec{r}_i|$. $R_l(E,\rho)$ in the above equation is the radial solution of the Schrödinger equation

$$\left(\frac{\partial^2}{\partial \rho^2} + [E - V(\rho)] - \frac{l(l+1)}{\rho^2} \right) \rho R_l(E,\rho) = 0 , \qquad (6)$$

where $V(\rho)$ is the potential inside the APW sphere and is of spherically symmetric nature. The potential has been constructed following the procedure of Mattheiss, which has been discussed in detail by Loucks.[12] The central Coulomb potential V_0 has been determined from the charge densities of Liberman[7] by solution of Poisson's equation,

$$\nabla^2 V_0(r) = -8\pi \rho_0(r) , \qquad (7)$$

with $\rho_0(r)$ the electronic density given by the expression

$$\rho_0(r) = \sum |\psi_{nl}(r)|^2 ,$$

where the summation is only over the occupied orbitals. These electronic densities are taken from the relativistic calculation of Liberman.[7] The potential at an outside point is assumed to be of the form

$$V(r) = -2Z/r . \qquad (8)$$

Using such a potential the energy-band calculation for cadmium was performed by Ramchandani.[6] From these calculations we obtain the energy eigenvalues at various $\vec{k}$ points and also the value of the Fermi energy E_F. Making use of this information we have solved Eq. (4) at all the allowed $\vec{k}$ points of the first BZ distributed over the Fermi surface, and applied the normalization condition for $\Psi_{\vec{k}_0}(\vec{r})$, i.e.,

$$|\Psi_{\vec{k}_0}(\vec{r})|^2 = \sum_{n,n'} C^*_{\vec{k}_n} C_{\vec{k}_{n'}} \langle \Psi_{\vec{k}_n} | \Psi_{\vec{k}_{n'}} \rangle = 1 , \qquad (9)$$

to obtain the normalized coefficients $C_{\vec{k}_n}$. Once we know these coefficients, the conduction-electron density at the nucleus

$$|\Psi_{\vec{k}}(0)|^2 = \sum_n \sum_{n'} C^*_{\vec{k}_n} C_{\vec{k}_{n'}} j_0(k_n \sigma) j_0(k_{n'} \sigma) \left(\frac{R_0(E,\sigma)}{R_0(E,\sigma)} \right)^2 \qquad (10)$$

can be easily evaluated.

III. RESULTS AND DISCUSSION

The calculations were done on a CDC 3600 and BESM 6 computers. The conduction-electron density at the nucleus has been calculated and averaged over for the equivalent of 90 allowed $\vec{k}$ points which have energies 0.005 Ry on either side of the Fermi energy. Table I gives the experimental and calculated values of the isotropic Knight shift for cadmium.

In the previous calculations[9,10] one of the factors to which the discrepancy between theoretical and experimental values has been attributed is the electron-electron interaction. This interaction enhances the spin susceptibility χ_P, the enhancement being primarily a function of the electron density. This enhancement factor is empirically found to be 1.55 and 1.894 by Kasowski[9] and Jena *et al.*,[10] respectively, by fitting the calculated K_{iso} value at $T = 0$ °K with the experimental data; the experimental Knight-shift curves for K_{iso} at room temperature were extrapolated to 0 °K, which leads to the experimental value of 0.35%. Jena *et al.* considered the effect of core polarization in their calculation of K_{iso} from s, p, and d parts of the conduction-electron wave functions, and observed that the core-polarization effect is dominated by the s part of the conduction-electron wave function and it is positive. This gives a contribution which is 10% of the direct spin contribution to the Knight shift. Mahanti and Das[13] have pointed out that the exchange core polarization, the exchange enhancement of the susceptibility due to electron-electron interactions, and the relativistic corrections to the spin density at the nucleus are quite important factors and should be taken

TABLE I. Isotropic Knight shift of cadmium.

Experimental values at 4.2 °K :	
Schone[a]	0.300%
Borsa and Barnes[b]	0.350%
Sharma and Williams[c]	0.338%
Theoretical:	
Kasowski[d]	0.230%
Jena *et al.*[e]	0.1848%
Present calculations	0.305%

[a] See Ref. 1.
[b] See Ref. 2.
[c] See Ref. 3.
[d] See Ref. 9.
[e] See Ref. 10.

into account to get accurate theoretical values of the Knight shift for alkali metals.

In the present calculation we have solved the Schrödinger equation, using the potential obtained from the relativistic self-consistent atomic charge densities of Liberman. The exchange contribution to the muffin-tin potential is treated using Slater's exchange approximation. This introduces correlation effects only partially in the present calculation. Using the density of states from band calculations[6] [see Eq. (2)], we obtain the spin susceptibility value

$$\chi_P = 0.79 \times 10^{-6} \text{ cgs volume units,}$$

whereas Kasowski and Falicov[8] obtained for χ_P the value 0.54×10^{-6} cgs volume units at $T = 0$ °K and 0.60×10^{-6} cgs volume units at room temperature. This value of χ_P is also used by Jena *et al.*[10] For the direct spin density at the nucleus averaged over the Fermi surface we obtain 459.8, whereas Jena *et al.* obtained 369.9.

We would also like to mention here that the calculation of the density at the Fermi energy plays a very important role as this enters into the calculation of the isotropic Knight shift through the Pauli susceptibility χ_P. We have obtained the density of states to be 2.167 states/atom Ry. Our calculation slightly overestimates the density of states at the Fermi energy since it yields for the specific-heat constant γ the value 0.745 mJ/mole °K^2 compared to the experimental value 0.688 mJ/mole °K^2 reported by Phillips,[14] whereas usual the experimental value is expected to be somewhat higher owing to electron-phonon interaction. Assuming that the phonon enhancement[15] of γ is ~ 20%, our bare density of states has been overestimated by ~ 30%.

The present calculation is a nonrelativistic one, in which we have used the potential obtained on the basis of charge densities calculated relativistically (those of Liberman). This should presumably give a better value for the spin density at the nucleus compared to the one obtained by using a potential based on a nonrelativistic charge density. Moreover the χ_P calculated from the density of states using the results of band calculations is also larger than that obtained by Kasowski and Falicov[8] using the pseudopotential method. Therefore, we feel that the inclusion of the relativistic effect in the construction of the muffin-tin potential [Eq. (7)] improves the values of $\langle |\psi_{\vec{k}}(0)|^2 \rangle_{E_F}$ and hence gives a value of K_{iso} which is in good agreement with various experimental results.[1-4] However, if we take into account a 10% core-polarization correction[10] and reasonable estimates of the exchange enhancement of the Pauli susceptibility, then the agreement between theory and experiment is poor. A better value of the bare density of states will again restore the agreement between theory and experiment. It appears that the overestimation of the density of states is due to the inadequacy of the Slater approximation for the exchange potential. Though the Slater approximation is good enough for noble metals,[16] it overestimates the exchange part for other metals, since the electrons in them are not so free as in noble metals.

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