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Temperature dependence of knight shift of liquid alkali metals (Li, Na and K)

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ABSTRACT

In the present paper we have studied the temperature dependence of knight shift of simple liquid metals through the Harrison's first principle (HFP) pseudopotential technique. The structure factor needed for liquid metals has been taken from experimental measurements [X-ray and neutron diffraction]. The results have been compared with experimental data and theoretical values of other authors. Reasonable agreement has been obtained.   © 2010 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

The frequency of nuclear magnetic resonance (NMR) associated with a metallic state is generally higher than the corresponding frequency for non-metallic state. Such a shift of the NMR frequency is known as the knight shift. This arises due to the hyperfine contact interaction between the nucleus and the surrounding conduction electrons. The knight shift K is defined as the ratio of the frequency shift to the frequency at which the NMR is observed for the metallic state. The hyperfine interaction between conduction electron and nuclear moment in metals provides a rich array of properties that can be studied through nuclear magnetic technique[5,6]. Although the experimental technique of the measurement of knight shift had been developed much earlier, its theoretical development had been in a state of infancy and has been developed much later. The previous theoretical work[2,7,8,12-14] on the magnetic prop-

erties of metals substantiates the view that like electrical resistivity, the nearly free electron approximation is also valid for the theoretical treatment of various magnetic properties viz, knight shift, magnetic susceptibility, Hall coefficient etc. The study of the plethora of literature on pseudopotential theory and specially Harrison's first principle (HFP) technique brings out the fact that this property has not been studied through this technique except by Singh[11] who has applied it to some multivalent liquid metals. We propose to proceed on this line for the investigation of the knight shift of alkali metals for which the experimental data is available. It is interesting to note that the previous authors[3,4,10] have observed that even in the simple metals, the orbital effect of the electrons also contributes.

FORMALISM

We shall now present the concise theory within the

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framework of pseudopotential technique. The knight shift[9] may be written as,

$$K = \left(\frac{8\pi}{3}\right)\chi_P P_F \Omega \tag{1}$$

Here χ_p is the spin paramagnetic susceptibility of conduction electron per unit volume, Ω is the volume of the crystal and P_F the average electron density at the site of the nucleus from the conduction electrons with energy E_F.

This electron density is represented by an average of the form,

$$P_F = \left\langle N^{-1} \sum_j \left|\psi_{k_F}(R_i)\right|^2 \right\rangle \tag{2}$$

where, R_i is the position vector of the ith ions, N is the total number of ions and ψ_{kF} are the electron wave functions. In OPW approximation the wave function is expressed in terms of the pseudo wave function $\phi_k(R)$ and $\psi_\alpha(R)$.

The core wave function is written as,

$$\psi_k(R) = C_k\left[\phi_k(R) - \sum_\alpha (\psi_\alpha, \phi_k)\psi_\alpha(R)\right] \tag{3}$$

here, C_k is the normalization factor, Since the psedopotential is very weak in nature. We can expand ϕ_k according to the first order perturbation theory,

$$\phi_k = \phi_k^0 + \phi_k' \tag{4}$$

where,

$$\phi_k^0 = \Omega^{-1}\exp(ik.R) \tag{5}$$

$$\phi_k' = \frac{\Omega}{8\pi^3}\int \frac{dq\,a(q)w(k,q)}{E_k - E_{k+q}} \phi_{k+q}^0 \tag{6}$$

Using the above analogy we can express the electron density as,

$$P_F = P_F^0 + P_F' \tag{7}$$

Similarly the knight shift may also be written as,

$$K = K_0 + K_1 \tag{8}$$

The variation of $\phi_{kF}(R)$ in the core region is small thus the equation (2), (3) and (6) may be used to obtain

$$\frac{P_F'}{P_F^0} = 2\,Re\left\langle N-1\sum_i \frac{\phi_{kF}'(R)}{\phi_{kF}^0(R)}\right\rangle = \frac{2\Omega}{8\pi^3}P\int \frac{w(k,q)a(q)}{E_k - E_{k+q}}d^3q \tag{9}$$

where P is the Cauchy principal value. Assuming the form factor w (k, q) and structure factor a (q) to be spherically symmetric we get,

$$\frac{K_1}{K_0} = \frac{P_F'}{P_F^0} = -\frac{3Z}{4E_F k_F^2}$$

$$\int_0^\alpha a(q)w(k,q)q\ln\left|\frac{q+2k_F}{q-2k_F}\right|dq \tag{10}$$

where E_F is the fermi energy and k_F is the fermi wave vector.

The temperature coefficient of knight shift is represented by

$$\alpha_k = \frac{R_T - R_{T_M}}{R_T(R_T - R_{T_M})} \tag{11}$$

where, T is the desired temperature and T_M is the melting point of the metals.

COMPUTATION AND RESULT

The computation of knight shift has been done through equation (10). The result has been given in TABLE 1 to TABLE 3 for Li, Na and K respectively. The temperature dependence of knight shift of Li, Na and K has been shown in figure 1 to figure 3 respectively with two sets of eigenvalues and the estimated experimental curve have also been given for comparison.

Observations

Lithium

From TABLE 1 it is observed that with C- eigenvalues the form factor using $\alpha = \alpha_{vt}$ and $\beta = 1$ gives the closest agreement with the experimental data i.e. 0.035 against 0.026 at 170°C and 0.044 against 0.028 at 250°C. However, with the C- eigenvalues $\alpha = \alpha_{vt}$ and $\beta = 5/8$ also gives reasonable agreement.

Sodium

For Sodium from TABLE 2 it is observed that the C- eigenvalues with $\alpha = \alpha_{vt}$ and $\beta = 1$ gives K = 0.144 against $K_{exp.} = 0.116$ at 105°C and K = 0.159 against $K_{exp} = 0.121$ at 200°C.

Potassium

For Potassium from TABLE 3 it is observed that the C- eigenvalues with $\alpha = \alpha_{vt}$ and $\beta = 1$ gives K = 0.315 and with $\alpha = \alpha_{vt}$ and $\beta = 5/8$ it gives K = 0.315 against $K_{exp.} = 0.265$, at 70°C and K = 0.321 against

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TABLE 1

| Metal | α
β
ϵ_{nl} | $K_0 = 0.05$ | | | | $K_{exp.}$ | Temp.
(^{0}C) |
		α_{vt} 1	α_{vt} 5/8	2/3 1	2/3 5/8		
Li	H	0.059	0.058	0.058	0.158	0.026	170
	C	0.035	0.035	0.035	0.036		
	H	0.065	0.065	0.064	0.064	0.028*	250
	C	0.044	0.045	0.045	0.045		

TABLE 2

| Metal | α
β
ϵ_{nl} | $K_0 = 0.140$ | | | | $K_{exp.}$ | Temp.
(^{0}C) |
		α_{vt} 1	α_{vt} 5/8	2/3 1	2/3 5/8		
Na	H	0.158	0.158	0.156	0.157	0.116	105
	C	0.144	0.144	0.145	0.145		
	H	0.159	0.159	0.158	0.156	0.121*	200
	C	0.159	0.158	0.158	0.159		

TABLE 3

| Metal | α
β
ϵ_{nl} | $K_0 = 0.320$ | | | | $K_{exp.}$ | Temp.
(^{0}C) |
		α_{vt} 1	α_{vt} 5/8	2/3 1	2/3 5/8		
K	H	0.328	0.333	0.316	0.313	0.265	70
	C	0.315	0.315	0.321	0.321		
	H	0.339	0.339	0.338	0.337	0.278*	105
	C	0.3	0.3	0.3	0.3		

$K_{exp} = 0.278$ at 105°C.

Figure 1 : Temperature dependence of knight shift of Li
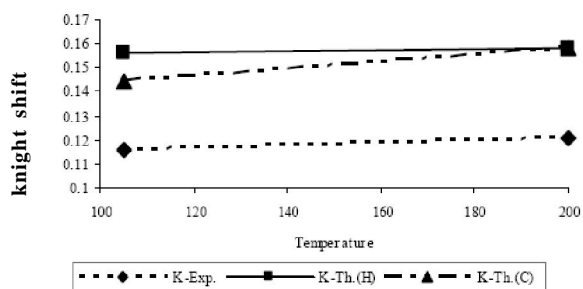
Figure 2 : Temperature dependence of knight shift of Na
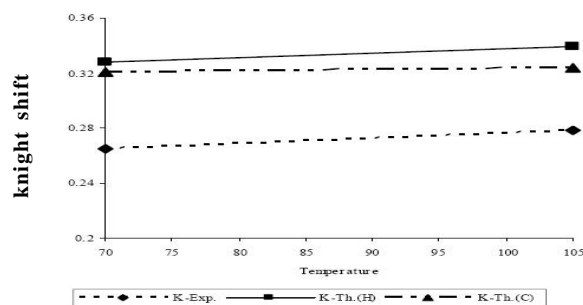
Figure 3 : Temperature dependence of knight shift of K

For Lithium, we observe that the temperature dependence of knight shift with C-eigenvalues is closer to the experimental curve with slight difference in the slope. However, the curve for H- eigenvalues has almost the same slope as that of the experimental curve. Thus in general reasonable qualitative agreement has been obtained.

For Sodium, temperature dependence of knight shift with H-eigenvalues has almost the same slope as that of the experimental curve. But the slope of the curve using C-eigenvalues is slightly different from that of experimental curve. In this case also qualitative agreement has been obtained.

For Potassium, the temperature dependence curve with H and C- eigenvalues are very close to each other and agreement with the experimental curve is quite reasonable.

Thus we observe that inspite of various approximations involved in the theoretical framework reasonable qualitative agreement has been obtained for the al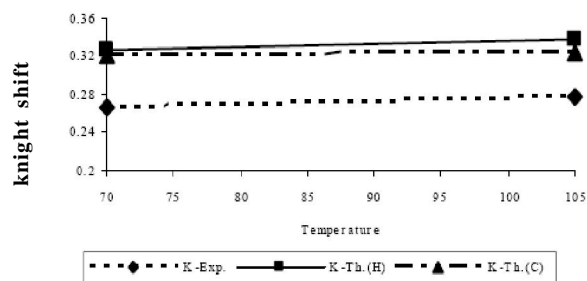kali metals. The formula may be refined for further improvement on the lines of Beer [1972], for future studies. From the above mentioned facts it is apparent that the knight shift and its temperature dependence have been reasonably predicted on the basis of the HFP technique in conjunction with Pake's formalism.

It is to be mentioned that the Ziman's formalism for the electrical resistivity involves the square of the form factor within its integrand hence, it depends only on the magnitude of the form factor. In contrast, the Pake's formalism for the knight shift involves the form factor linearly within its integrand. Hence it depends both on the magnitude and the sign of the form factor.

CONCLUSION

From the above mentioned facts it may be concluded that the HFP technique can be successfully used for the computation of the knight shift of liquid metals provided suitable input parameters are used. However,

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as various approximations are involved within the framework exact reproduction of the experimental data is neither expected nor desired.

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