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Temperature dependence of Knight shift for the metals Zn and Al

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Abstract

We have studied the variation of Knight Shift with temperature using pseudopotential technique for Zn and Al metals. Knight Shift occurs due to the hyperfine contact interaction between the nucleus and surrounding conduction electrons. The computed values of zinc is obtained using H-eigen values with $\alpha = \alpha vt$ and $\beta = 1$ gives K= 0.374 against Kexp = 0.337 at 419 ^{0}C and 0.391 against Kexp = 0.399 at 500 ^{0}C. For Aluminium with H-eigen values and $\beta = 1$ gives K= 0.199 whereas Kexp = 0.164 at 360 ^{0}C and K= 0.209 at 400 ^{0}C for Kexp = 0.184 have been found. The computed values and experimental values are in good agreement for both metals. It reveals that the Knight Shift increases with increasing temperatures for Zn and Al.

Keywords: Pseudopotential; Knight Shift; H-eigen Values

1. Introduction

It is observed that Nuclear Magnetic Resonance (NMR) associated with a metallic state is higher than the corresponding frequency for non-metallic state. This shift of the NMR frequency is known as the Knight Shift and this occurs due to the hyperfine contact interaction between the nucleus and the surrounding conduction electrons. The ratio of the frequency shift to the frequency at which the NMR is observed for the metallic state is known as Knight Shift (K). The hyperfine interaction between conduction electron and nuclear moment in metals provides a rich array of properties that can be studied through nuclear magnetic resonance technique (1-2). Although the experimental technique of the measurement of Knight Shift had been developed much earlier, its theoretical development was developed much later.

The previous theoretical work [3-4] on the magnetic properties 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 technique brings out the fact that this property has not been studied through this technique except by Singh [5] who has applied it to some multivalent liquid metals. We propose to proceed on this line for the investigation of the Knight shift of metals under investigation for which the experimental data is available. It is interesting to note that the previous authors (Seymour and Styles 1966, Heighway and Seymour 1971, Ford and Styles 1972) have observed that the orbital effect of the electrons also contributes even in the simple metals.

The experimentally measured Knight shift [2] for various metals shows insignificant change in it due to melting. Heine (1957) first obtained a simple expression for the Knight shift of metals in solid phase. But OPW method has only been used by Gerstner and Cutler (1969) for Ba and Singh (1988) for Mg, Al and Ga. Reasonable qualitative agreement has been obtained for the metals under investigation. Due to various approximations involved in the formalism of Knight shift and that of the form factor exact agreement is not expected. In the next sections we are presenting the formalism, result and significant observations.

2. Formalism

In this section of our study the precise theory within the framework of pseudopotential technique is presented. The Knight shift [7] 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_{k_F} 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,

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

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

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 $\phi_{k_F}(R)$ in the core region is small. Thus the equations (2), (3) and (6) may be used to obtain

$$\phi_k^{'} = \frac{2\Omega}{8\pi^3}P\int \frac{w(k,q)a(q)}{E_k - E_{k+q}}d^3q \tag{9}$$

$$\frac{P_F^{'}}{P_F^0} = 2\,\mathrm{Re}\left\langle N^{-1}\sum_l \phi_{k_F}^{'}(R)\middle|\phi_{k_F}^0(R)\right\rangle$$

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,

$$\frac{K_1}{K_0}=\frac{P_F^{'}}{P_F^{0}}=-\frac{3Z}{4E_F k_F^2}\int_0^{\alpha} a(q)w(k,q)q\ln\left|\frac{q+2k_F}{q-2k_F}\right|dq \qquad (10)$$

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

The temperature coefficient of Knight shift is represented by

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

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

3. Results and Discussion

By applying equation (10) we have calculated Knight Shift using two different eigen values (Herman-Skillman and Climenti eigen values). The results have been given in Table 1 and Table 2 for Zn and Al respectively. The H-eigenvalues with α = αvT and β =1 we get the values of K= 0.374 (Kexp = 0.337) at 419 ^{0}C and at 500 ^{0}C, K was found to be 0.391 (Kexp = 0.339) respectively. Similarly we have calculated Knight Shift using C-eigen values; the values of Knight shift are slightly different which are shown in Table 1. As the other computed values of Knight Shift opting α = 2/3 and β =1 & 5/8 do not lie in the vicinity of experimental value, hence they are discarded.

Table 1: Results for Zn

Metal	α β ϵnl	K = 0.540				Kexp.	Temp. (^{0}C)
		αvt 1	αvt 5/8	2/3 1	2/3 5/8		
Zn	H	0.374	0.601	0.399	0.398	0.337	419
	C	0.401	0.426	0.405	0.409		
	H	0.391	0.621	0.399	0.399	0.339*	500
	C	0.478	0.499	0.588	0.589		

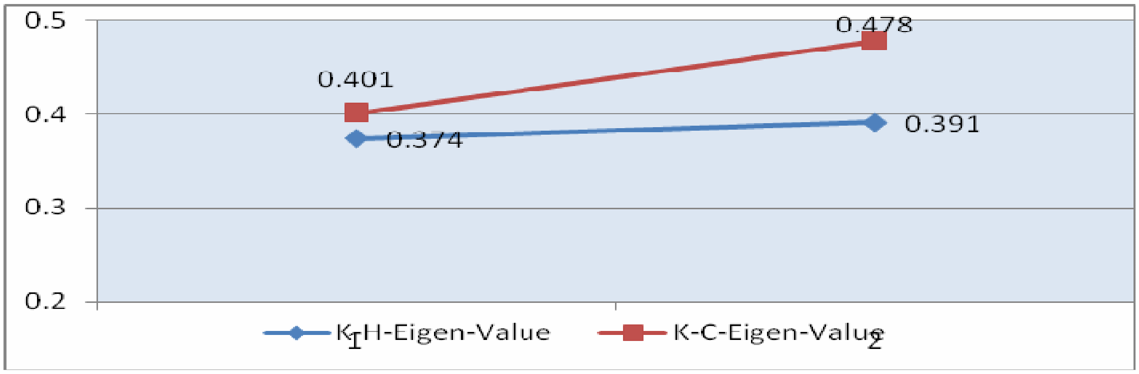

Fig. 1 : Temperature dependence of Knight shift of Zn

Table 2: Results for Al

Metal	α β єnl	K = 0.18				Kexp.	Temp. (^{0}C)
		αvt 1	αvt 5/8	2/3 1	2/3 5/8		
Al	H	0.199	0.126	0.119	0.139	0.164	360
	H	0.209	0.142	0.142	0.147	0.184	400

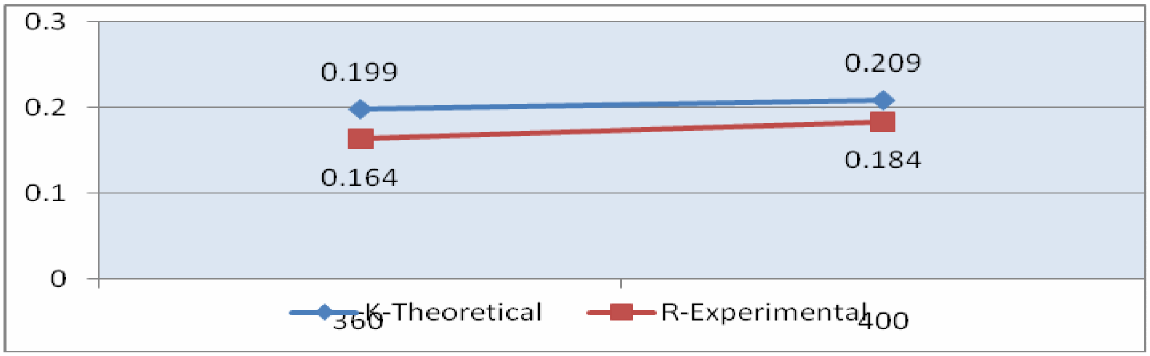

Fig. 2 : Temperature dependence of Knight shift of Al

We have calculated the Knight shift of aluminium at different temperatures by using H-eigen values. The calculated and experimental values of K are very close to each other. Since the C-eigen values are not available for Al, therefore it was not possible to calculate. The computed values for Knight shift come to be 0.126 and 0.142 for α =αvt and β = 5/8 at temperatures 360 ^{0}C and 400 ^{0}C respectively. At the same time the set of values obtained for α = 2/3 and β= 1 & 5/8 are 0.119 & 0.142 and 0.139 & 0.147 respectively. From the above mentioned table it is evident that the closest approach obtained from the computation is for α = αvt and β=1 . The value 0.199 and 0.209 also lie very close to experimental values 0.164 and 0.184 for two different opted temperatures 360 ^{0}C & 400 ^{0}C respectively. The temperature dependence of Knight shift of Zn and Al has been shown in Fig. 1 and Fig. 2 respectively with two sets of eigen values, and the estimated experimental curve have also been given for comparison.

4. Conclusion

For Zinc, temperature dependence of Knight shift with H-eigen values lies closer and has almost the same slope as that of the experimental curve. But the slope of the curve using C-eigen values is slightly different from that of experimental curve. In this case also qualitative agreement has been obtained. In case of Aluminium only H-eigen values are available and temperature dependence curve has almost the same slope as that of the experimental curve. It is evident to mention that the different values of K obtained by computation lie very close to experimental values and also the slope has similar inclination in both the cases viz. theoretical and experimental.

Thus we observe that in spite of various approximations involved in the theoretical framework reasonable qualitative agreement has been obtained for the metals under investigation. 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 Harrison's first principle 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. However, the electrical resistivity is very sensitive to the nature of the form factor especially in the region where the peak of the structure factor lies. Also it has a much larger magnitude. In contrast the Knight shift has a very small magnitude, hence the impact of the choice of various input parameters are not as much important as in the case of the electrical resistivity.

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