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Pseudopotential Calculation of Knight-Shift Temperature and Volume Dependence in Liquid and Solid Sodium[†]

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We have used a pseudopotential formalism to compute the electron density at a nuclear site in liquid and bcc solid sodium. The temperature dependence of the electron density at atmospheric pressure is found to account satisfactorily for the experimental observation that the sodium Knight shift increases with temperature. A decrease would be expected to accompany lattice expansion in a free-electron metal. In addition, the temperature dependence at constant volume and the pressure dependence of the electron density are computed and compared with published experimental data. Agreement between theory and experiment is rather better for the liquid state than for the solid, probably because of a less than satisfactory approximation to the high-temperature solid lattice structure.

INTRODUCTION

The Knight shift of a simple metal is given by[1]

$$K=\tfrac{8}{3}\pi\,\chi\,\Omega\,P_F\,, \tag{1}$$

where χ is the dimensionless-spin susceptibility, Ω is the volume, and the "penetration factor" P_F is the average probability density for Fermi-energy electrons at a nucleus. Interactions other than the above contact term are expected to contribute no more than roughly 10% to the Knight shift of light nonmagnetic metals and are neglected in this paper. For free electrons, ΩP_F is unity; the spin susceptibility and, consequently, the Knight shift are proportional to the inverse cube root of the volume. Both should increase under pressure, and since the explicit dependence on temperature is usually negligible compared with the implicit dependence through lattice expansion, both should decrease with rising temperature. For real metals the volume and temperature dependence of ΩP_F must be considered as well. For example, the Knight shift of sodium is found to increase with temperature and decrease under pressure,[2–4] exactly the opposite of free-electron behavior. Although the spin susceptibility of sodium has not been measured with sufficient accuracy to determine its temperature or volume dependence, it has been shown theoretically[5] that within a given phase the volume dependence of χ is essentially free-electron-like. The different volume and temperature dependences of K and χ are attributed to changes in ΩP_F.

There have been a number of previous calculations of the magnitude and volume dependence of the sodium-penetration factor at zero temperature.[6–12] No prior work on the temperature dependence for sodium has been done, but Halder[13] has recently considered the effect of temperature on polyvalent liquid-metal Knight shifts in a manner similar to our treatment and Kasowski[14] has reported an elegant calculation of the anomalous temperature dependence of the solid-cadmium Knight shift. We have used the pseudopotential method to calculate the penetration factor vs temperature for bcc solid sodium and liquid sodium at normal pressure and for liquid sodium at constant volume. In addition, the volume dependence for solid sodium at room temperature was found. In order to obtain the Knight shift from Eq. (1) we assume that χ has a free-electron volume dependence, has no explicit temperature dependence, and is normalized to the experimental value[15] of 1.13×10^{-6} at room temperature and pressure. Results are shown in Figs. 1 and 2.

THEORY AND RESULTS

It is relatively straightforward to find the perturbation of electron-wave functions by the pseudopotential.[16] One takes as zero-order states the orthogonalized-plane-wave (OPW) wave functions

$$\Psi_{\vec{k}}(\vec{r})=\frac{1}{(\alpha\Omega)^{1/2}}\Big[e^{i\vec{k}\cdot\vec{r}}-\sum_{j,n}A_j(\vec{k})\,e^{i\vec{k}\cdot\vec{R}_n}\,\varphi_j(\vec{r}-\vec{R}_n)\Big]\,, \tag{2}$$

where $\varphi_j(\vec{r}-\vec{R}_n)$ is the jth core state of the ion at $\vec{R}_n$,

$$A_j(\vec{k})=\int d^3r\,\varphi_j^*(\vec{r})\,e^{i\vec{k}\cdot\vec{r}}\,,$$

and

$$\alpha=1-\frac{1}{\Omega}\sum_{j,n}|A_j(\vec{k})|^2\,.$$

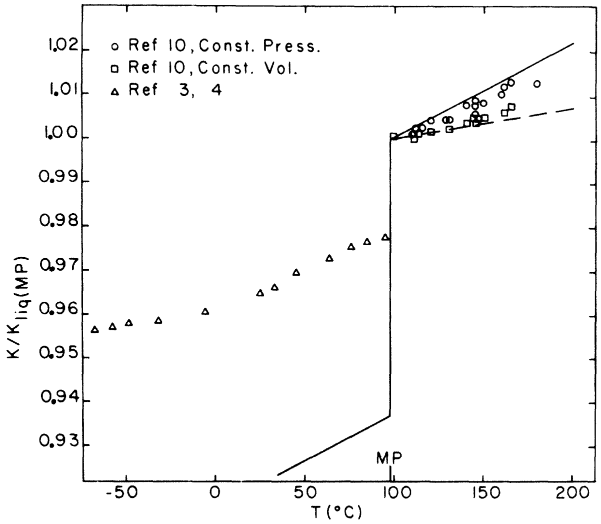

FIG. 1. Knight shift of Na vs temperature with K_{liq} normalized to unity at the melting point. The solid and dashed lines are the calculated Knight shift at atmospheric pressure and at (liquid melting point) constant volume, respectively.

The sum is over all core states and all N ions in volume Ω. By definition of the penetration factor

$$P_F=\frac{1}{N}\sum_n \langle\langle\,|\Psi_{\vec{k}}(\vec{R}_n)|^2\rangle\rangle\,, \tag{3}$$

where the brackets indicate both a thermodynamic average and averaging of $\vec{k}$ over the Fermi surface. To first order in the pseudopotential $U_{\vec{k}}(\vec{q})$ we find

$$\Omega P_F=\frac{1}{\alpha}\,\Big|1-\sum_j A_j(\vec{k})\varphi_j(0)\Big|^2(1+\Delta)\ , \tag{4}$$

with

$$\Delta=\left\langle\!\!\left\langle 2\sum_{\vec{q}}\frac{U_{\vec{k}}(\vec{q})a(q)}{E_{\vec{k}}-E_{\vec{k}+\vec{q}}}\ \frac{1-\sum_j A_j(\vec{k}+\vec{q})\varphi_j(0)}{1-\sum_j A_j(\vec{k})\varphi_j(0)}\right\rangle\!\!\right\rangle, \tag{5}$$

and $a(q)=\langle\langle(1/N)\,|\sum_n e^{i\vec{q}\cdot\vec{R}_n}|^2\rangle\rangle$ is the structure factor. The brackets in this case indicate thermodynamic and angular averaging. A similar expression was found by Watabe *et al.*[10]

The computed values of Δ, ΩP_F, and K are given in Table I along with $\partial K/\partial T$, the appropriate partial temperature derivative of the Knight shift. There are small effects due to volume dependence of normalization and OPW overlap integrals, but it is primarily the strong temperature and volume dependence of Δ which causes the departure of the Na Knight shift from free-electron behavior. Mathematically, the changes in Δ are caused by a temperature-dependent smearing and a volume-dependent shift of the structure factor with respect to the pseudopotential. The major contribution to the sum of Eq. (5) comes from the momentum range $2k_F < q < 4k_F$, which is the location of the first few points of the reciprocal lattice and the first peak of the liquid-structure factor. For meaningful results, it is necessary to use structure factors and a pseudopotential which are accurate in this range. Our choices for these quantities are discussed in detail below. Herman-Skillman[18] core states were used for this calculation, and the Na volume dependence on temperature was taken from crystallographic data[19,20] and the *Liquid Metals Handbook.*[21]

We have used Shaw's[22] optimized model potential parameters for $U_{\vec{k}}$ with a local-screening approximation for calculational simplicity. The local screening causes a slight deviation from the proper model potential near $q=0$ but causes negligible error in this case. One of the major difficulties encountered in pseudopotential calculations is the significant and frequently critical dependence of the calculated quantity on the choice of potential. In this case, for example, use of the local form factor rather than the full nonlocal pseudopotential resulted in values for Δ of order -0.5, a significant overestimate in magnitude. On the other hand, the qualitative form of the volume dependence is much less sensitive to details of the pseudopotential. The increase of Δ with volume is due primarily to a common qualitative feature of all pseudopotentials: that $U_{\vec{k}}$ is an increasing function of q just above $2k_F$ where the first significant peak of $a(q)$ occurs. It is clear from Eq. (5) that this portion of the sum must become more positive with increasing volume (shrinking reciprocal lattice). The influence of pseudopotential details on the explicit temperature dependence of Δ is more difficult to assess because we are uncertain of the precise temperature dependence of the structure factor. Qualitatively it is apparent, however, that the major changes are

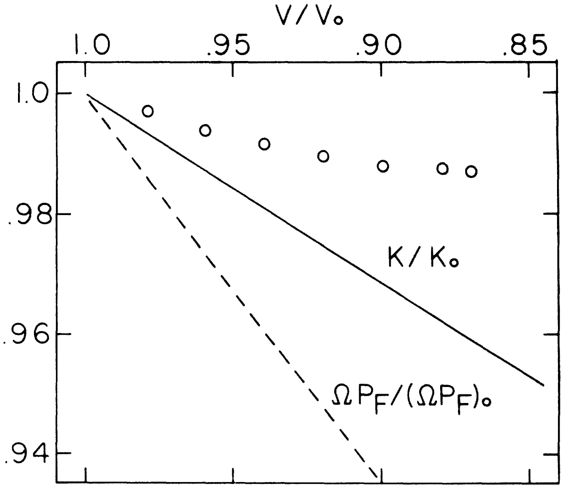

FIG. 2. Calculated Knight shift and penetration factor of Na vs volume at room temperature, normalized to unity at atmospheric pressure. Experimental points are Knight-shift data from Ref. 2.

TABLE I. Computed values of Δ, the relative first-order perturbation of the Knight shift, the resulting penetration factor, Knight shift, and temperature derivative of Knight shift.

Temperature (°C)	Δ	ΩP_F	K (%)	$\partial K/\partial T$ (°K^{-1})	K_{expt} (%)	$(\partial K/\partial T)_{\text{expt}}$ (°K^{-1})
			Liquid Na at atmospheric pressure			
100	−0.070	134.4	0.1255	0.27×10^{-6}	0.116[a]	0.21×10^{-6} [b]
160	−0.055	136.8	0.1270			
200	−0.044	138.6	0.1282			
240	−0.033	140.4	0.1294			
300	−0.019	142.6	0.1307			
			Liquid Na at constant (melting-point) volume			
100	−0.070	134.4	0.1255	0.10×10^{-6}	0.116[a]	0.13×10^{-6} [b]
160	−0.066	134.9	0.1260			
200	−0.063	135.4	0.1264			
240	−0.059	136.0	0.1270			
300	−0.054	136.7	0.1276			
			Solid Na at atmospheric pressure			
−73	−0.174	118.6	0.1129			
20	−0.150	122.2	0.1157	0.28×10^{-6}	0.112[a]	0.13×10^{-6} [a]
97	−0.133	125.0	0.1176		0.113[a]	
			Solid Na at 20 °C			
$V/V_0=1$	−0.150	122.2	0.1157		0.112[a]	
$V/V_0=0.95$	−0.173	118.2	0.1138			
$V/V_0=0.90$	−0.194	114.3	0.1121			

[a] Data from Ref. 17.
[b] Data from Ref. 10.

caused by temperature-dependent smearing of the structure factor near $q \gtrsim 2k_F$. We may speculate that only the qualitative feature of U_k discussed above is important and that the temperature dependence of Δ is similarly insensitive to details of the pseudopotential. We cannot even speculate about the effect of pseudopotential detail on the change of K on melting because of the quite different approximations used for $a(q)$ in the two phases. Since in any case the change in K across the melting transition is small, we expect only order of magnitude agreement.

For liquid alkali metals at atmospheric pressure, Ashcroft and Lekner[23] have shown that for $q < 4k_F$ the hard-sphere structure factor is an excellent approximation for $a(q)$. They pointed out that the hard-sphere structure factor depends only on k_F and a parameter σ, the sphere diameter, which they found for Na vs temperature by comparison with experiment. We used the hard-sphere structure factors for liquid Na with the Ashcroft-Lekner values of $\sigma(T)$ at both constant pressure and constant volume. Our implicit assumption of the volume independence of σ is consistent with Ashcroft and Langreth's[24] identification of the hard-sphere diameter as a cutoff on the negligibly volume-dependent ion-ion potential curve. On the other hand, we find that

$$\left(\frac{\partial a(0)}{\partial T}\bigg|_P\right)\bigg/\left(\frac{\partial a(0)}{\partial T}\bigg|_V\right) \cong 1.8\ ,$$

as contrasted to a value of 1.3 estimated by Endo[25] from compressibility data. Adjusting $\sigma(T)$ to bring the above ratio into agreement with Endo increases $(\partial K/\partial T)_V$ by roughly 40% and brings it into somewhat better agreement with experiment. The question as to the proper structure factor at constant volume has arisen before[26] and will probably not be settled satisfactorily until it is measured experimentally.

The solid-state structure factor is more difficult to approximate. Debye-Waller damping of the δ-function part of the structure factor and the troublesome continuous background which are usually ignored in band-structure calculations have quite a large effect on the magnitude and temperature dependence of K. Dropping multiple-phonon terms, the angular averaged structure factor can be written[27]

$$a(q) = Ve^{-2W}\left\langle \sum_G \delta(\vec{q}-\vec{G}) + \frac{q^2}{MV}\,\frac{\langle n_{\vec{p}}\rangle + \frac{1}{2}}{\omega_{\vec{p}}}\right\rangle\ , \tag{6}$$

where $\vec{p}$ is the reduced value of $\vec{q}$, V is the volume of the first Brillouin zone, $\vec{G}$ is a reciprocal lattice vector, and the Debye-Waller factor is given by

In principle, the above expression can be evaluated rather accurately using neutron scattering data, but the accuracy of the one-phonon approximation for the temperature and momentum range of interest does not justify the necessary work. Instead, we have used a simple Debye-like model taking $\omega_{\mathbf{k}} = sk$ for $k < K_0$ and equal to sK_0 for $k > K_0$. K_0 is one-half the first reciprocal lattice vector and s is the longitudinal sound velocity.[28]

CONCLUSIONS

For the liquid state, agreement between calculated and experimental values of $\partial K/\partial T$ is within the limits of confidence in the hard-sphere structure-factor parameters. For solid sodium, however, agreement is only qualitative for the slope of K with both temperature and volume. In addition, the change of K on melting is overestimated by a factor of 3. Although we cannot rule out the possibility that part of the disagreement is caused by an inadequate pseudopotential, the success of the liquid-state calculation for which a relatively accurate structure approximation was used suggests that the fault lies rather with our use of the one-phonon approximation for the solid-state structure. Integration of the high-temperature one-phonon structure factor reveals that as much as 25% of the ion density in the important momentum range just above $2k_F$ is lost by dropping higher-order terms. An attempt was made to assess the effect of this loss by using the unperturbed reciprocal lattice for $a(q)$. This approximation includes all ions but ignores explicit temperature dependence due to ion motion. Unfortunately, use of undamped δ functions results in a slow convergence for Eq. (5) and a significant dependence on the inaccurate large-q range of the pseudopotential. If the sum is arbitrarily cut off near $4k_F$, the slope of K with "temperature" (lattice expansion only) and volume and the change of K on melting are in better agreement with experiment than the one-phonon values for these quantities. It is not unlikely that a better description of the high-temperature solid-state structure would result in good agreement for all quantities.

Another possible source of error is our assumption of a phase-independent free-electron volume dependence for the spin susceptibility. At least part of the discrepancy between the experimental and calculated change of K on melting may be attributed to inadequancy of this assumption. It has been shown[29] that χ can change by a few percent at the low-temperature Martensitic transformation. The change of susceptibility on melting, which is probably of the same order, can also be calculated, but again accurate high-temperature structure-factor approximations are required for meaningful results.

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