Volume dependence of the Knight shift in lithium

Toshimoto Kushida and J. C. Murphy

Research Staff, Ford Motor Company, Dearborn, Michigan 48121

(Received 1 August 1979)

This work is to confirm a significant discrepancy between the calculated volume dependence of $\langle|\psi(0)|^2\rangle$ in Li metal and the corresponding quantity deduced from experimental results using a simple equation for the Knight shift, $K = (8\pi/3)\chi_P\Omega\langle|\psi(0)|^2\rangle$. Here $\langle|\psi(0)|^2\rangle \equiv P_F$ is the amplitude of the conduction-electron wave function averaged over the Fermi surface. χ_P and Ω are the Pauli susceptibility and the atomic volume, respectively. The experimental determination of $\langle|\psi(0)|^2\rangle$ was obtained from an old measurement of K [G. B. Benedek and T. Kushida, J. Phys. Chem. Solids $\underline{5}$, 241 (1958)] and a recent measurement for χ_P [Toshimoto Kushida, J. C. Murphy, and M. Hanabusa, Phys. Rev. B $\underline{13}$, 5136 (1976)]. Both quantities K and χ_P were measured as a function of volume. It was felt important to repeat the old Knight-shift experiment, since the experiment requires an accurate resonance-frequency measurement ($\simeq$ one part in 10^7), which was marginal 20 years ago, and a resolution of the discrepancy is essential to the understanding of the electronic structure of a simple metal. The present measurement is one order of magnitude more accurate and indicates a small systematic error in the previous data. The conclusion is, however, essentially unchanged; an electron polarization enhancement seen by the Li nucleus in Li metal is almost independent of the volume change, contrary to an intuitive model which predicts $d\ln P_F/d\ln V = -1$. Recent calculations show that the core-polarization effect P_F^{cp} is important for Li and that P_F^{cp} has a *large volume dependence*. The Knight-shift equation should be modified to $K = (8\pi/3)\chi_P\Omega(P_F + P_F^{cp})$. The volume dependence of P_F is almost canceled by that of the P_F^{cp}.

INTRODUCTION

The pressure-dependence measurements of both Knight shift[1] K and Pauli-spin susceptibility[2] χ_P in Li metal have revealed a significant discrepancy between the calculated volume dependence of $\langle|\psi(0)|^2\rangle$ and the corresponding value derived from the experimental values by using the elementary Knight-shift equation

$$K = \tfrac{8}{3}\pi\chi_P\Omega\langle|\psi(0)|^2\rangle . \tag{1}$$

Here Ω is the atomic volume and $\langle|\psi(0)|^2\rangle$ is the amplitude of the conduction-electron wave function at the nucleus, averaged over the Fermi surface. The wave function is normalized over the unit cell. The direct measurements of both χ_P and K as a function of volume[1,2] enabled us for the first time to obtain $\langle|\psi(0)|^2\rangle \equiv P_F$ as a function of volume.

A simple model predicts that a uniform squeezing of the Wigner-Seitz cell would increase P_F roughly[3] as $\Delta P_F/P_F \simeq -\Delta V/V$. In this model the wave functions are compressed with little distortion as the cell size is reduced. More detailed models take into account some reduction in P_F due to the distortion of the wave functions (mixing more p functions, for instance) caused by the squeezing of the cell. This is indeed the case for Na metal. A 10% decrease in volume for Na metal is accompanied by approximately a 6% increase in P_F (Ref. 4). Many theories[4] agree with this result for Na. In the case of Li, however, all the calculations for $\langle|\psi(0)|^2\rangle$, which predict essentially the same results as for Na, failed to describe the ob-

served results: The experimental value of P_F derived from Eq. (1) is essentially unchanged as the volume is decreased.

The most extensive calculations have been carried out by Perdew, Nickerson, Vosko, and Moore[5] using three independent methods: the spherical cell, the APW, and the OPW-pseudopotential method. Their OPW calculations include over 100 OPW functions. Although these three independent calculations agree with one another, they do not describe the experimental behavior of P_F defined by Eq. (1).

Possible inadequacies of Eq. (1) are discussed in Ref. 2 and the references therein. A core-polarization effect, sometimes called an indirect Knight shift, is known to be important for transition metals and ferromagnets.[6] The possibility of a core-polarization effect for simple metals has also been discussed.[6] Equation (1) can be rewritten as

$$K = \tfrac{8}{3}\pi\chi_P\Omega(P_F + P_F^{cp}), \tag{2}$$

in order to include the core-polarization effect. Here the contribution from the core polarization is expressed by P_F^{cp}.

Mahanti[7] has estimated the effect of the core polarization. His result is closer to the experimental result. Although P_F^{cp} is smaller than P_F, the volume dependence of P_F^{cp} is stronger than that of P_F and opposite in sign. The recent detailed calculations by Wilk and Vosko[8] have confirmed this model. P_F^{cp} is as much as 25% of the total Fermi contact term $(P_F + P_F^{cp})$ for Li; P_F^{cp} is

only 2.5% for Na. The strong volume dependence of P_F^{cp} makes $P_F + P_F^{cp}$ virtually volume independent.

The observed Knight-shift change in Li is very small. It is necessary to measure the resonance frequency with great accuracy (one part in 10^7) and to keep the strength of the magnetic field constant with the same accuracy during the pressure measurement. Such accuracy was marginal 20 years ago, and some doubt has been cast upon the reliability of the old measurement. Since an experimental check of the wave-function amplitude in the simplest metal is very important for metal physics in general, it was decided to repeat this experiment.

EXPERIMENTAL RESULTS AND DISCUSSION

Detailed experimental procedures have been described elsewhere.[9] The magnetic field was stabilized using an Na metal NMR line.[9] The Na NMR frequency, which was stabilized against a crystal oscillator, was continuously monitored with a frequency counter. The frequency of the NMR spectrometer for the Li sample was also continuously monitored with another counter. The ^{7}Li resonance frequency was measured at 86°C in order to take advantage of a motional narrowing of the resonance line.[10] The resonance frequency ν was measured at atmospheric pressure first. ν at pressure P was measured next. Then the atmospheric pressure value was measured again. These procedures were repeated several times to get the pressure shift of ν at a given pressure P.[11]

The observed pressure shift in the ^{7}Li resonance frequency is shown in Fig. 1. It is noted that the resonance frequency increases with pressure, as opposed to a decrease in the old measurement.[1] The magnitude of the error flags is smaller by one order of magnitude than that of the previous measurement. The volume dependence of the
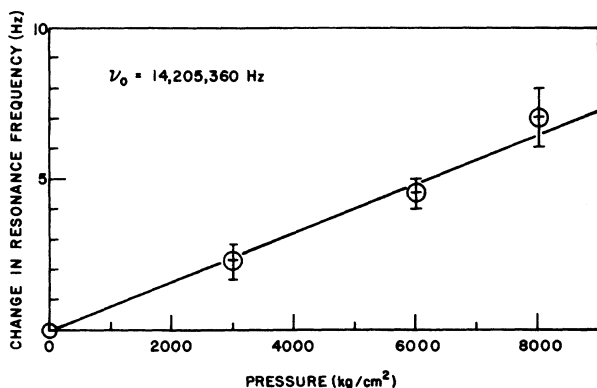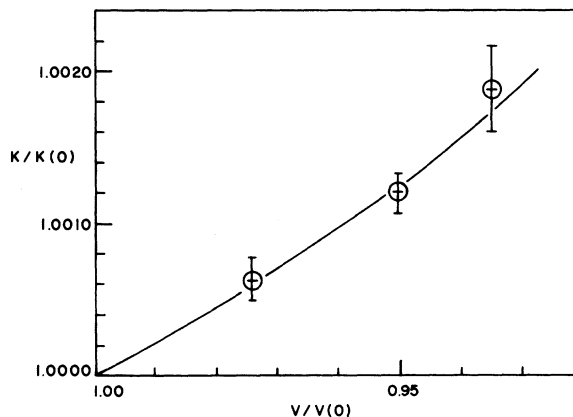

FIG. 2. The volume dependence of the Knight shift K of Li metal. Both K and V are normalized to their atmospheric values, respectively.

Knight shift is shown in Fig. 2, where Bridgman's compressibility data at 75°C is used.[12] The Knight-shift value used is[13]

$$K(0) = 0.026(2)\%.$$

The volume dependence of the total Fermi contact term, $P_F + P_F^{cp} \equiv P_F^T$, is shown in Fig. 3 in conjunction with theoretical predictions, where the volume

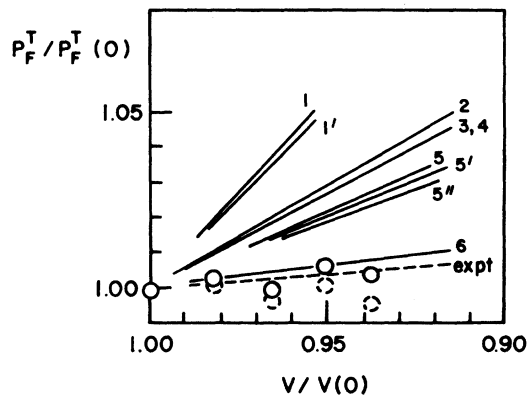FIG. 3. The volume dependence of P_F^T for Li. $P_F^T = P_F + P_F^{cp}$. Both P_F^T and V are normalized to their atmospheric values, respectively. The full and the dotted circles are derived from the present and the old (Ref. 1) data, respectively. 1, Holland, Ref. 3; 1', Heighway and Seymour, Ref. 92 in I; 2, Asano and Yamashita, Ref. 9 in I; 3, Micah, Stocks, and Young, Ref. 63 in I; 4, Moore and Vosko, Ref. 90 in I; 5, Perdew, Nickerson, Vosko, and Moore, spherical cell model, Ref. 14; 5', Perdew, Nickerson, Vosko, and Moore, APW, Ref. 14; 5″, Perdew, Nickerson, Vosko, and Moore, all OPW's Ref. 14; 6, Mahanti, Ref. 7. All the calculations except number 6 do not include the volume dependence of P_F^{cp}. The recent detailed calculation by Wilk and Vosko, Ref. 8, which includes the effect of P_F^{cp} but is not shown in this figure, is in essential agreement with the experimental values.

FIG. 1. The pressure shift of ^{7}Li NMR frequency in Li metal.

dependence of χ_P was taken from Ref. 2. The present results $\bigcirc$ indicate that the $P_F + P_F^{cp}$ value slightly *increases* with a decrease of volume. It is noted that the present data are closest to Mahanti's estimate (6 in the figure) which includes the core-polarization effect.[7]

It is concluded that the present more accurate measurement of the Knight shift as a function of hydrostatic pressure indicates that P_F^T, which is the total electron-spin polarization enhancement seen by the nucleus, is almost independent of volume for Li metal as opposed to the results for other alkali metals.[1,2] The volume dependence of P_F^{cp} can be deduced from the relation

$$d\ln P_F^T/d\ln V = (P_F/P_F^T)d\ln P_F/d\ln V$$
$$+ (P_F^{cp}/P_F^T)d\ln P_F^{cp}/d\ln V, \qquad (3)$$

by using the present experimental value, $d\ln P_F^T/d\ln V = -0.08 \pm 0.04$, and the calculated values, P_F^{cp}/P_F^T, P_F/P_F^T, and $d\ln P_F/d\ln V$ as

$$d\ln P_F^{cp}/d\ln V = 0.9. \qquad (4)$$

The calculated values used are[8]

$$P_F^{cp}/P_F^T = 0.25,$$

$$P_F/P_F^T = 0.75,$$

where a small contribution (2.5%) from the valence electron polarization below the Fermi surface is neglected, and[14] $d\ln P_F/d\ln V = -0.4$. It is noted again that the core-electron polarization P_F^{cp} has a large volume dependence, as opposed to a naive model where the core electronic distribution is rigid and not affected by the lattice deformation. The magnitude of $d\ln P_F^{cp}/d\ln V$ is *larger* than the typical volume dependence of the *conduction-electron* polarization,[15] and its sign is opposite.

The physical model of the core polarization is understood as follows: The core-wave function $\phi_{1s}^0(\vec{r})$ is perturbed by the exchange interaction with conduction electrons as[16,17]

$$\phi_{1s}^\uparrow(\vec{r}) = \phi_{1s}^0(\vec{r}) + \sum_{n \neq 1s} \phi_n^0(\vec{r})\frac{\langle n\uparrow|A|1s\uparrow\rangle}{\epsilon_{1s} - \epsilon_n}$$
$$+ \sum_{\vec{k}'} \psi_{\vec{k}'}^0(\vec{r})\frac{\langle \vec{k}'\uparrow|A|1s\uparrow\rangle}{\epsilon_{1s} - \epsilon_{\vec{k}'}}, \qquad (5)$$

where

$$\langle n\uparrow|A|1s\uparrow\rangle = -\sum_{\vec{k}\uparrow}\int \phi_n^{0*}(\vec{r}_1)\psi_{\vec{k}}^{0*}(\vec{r}_2)(e^2/r_{12})$$
$$\times \psi_{\vec{k}}^0(\vec{r}_1)\phi_{1s}^0(\vec{r}_2)d\tau_1 d\tau_2 \qquad (6)$$

and

$$\langle \vec{k}'\uparrow|A|1s\uparrow\rangle = -\sum_{\vec{k}\uparrow}\int \psi_{\vec{k}'}^{0*}(\vec{r}_1)\psi_{\vec{k}}^{0*}(\vec{r}_2)(e^2/r_{12})$$
$$\times \psi_{\vec{k}}^0(\vec{r}_1)\phi_{1s}^0(\vec{r}_2)d\tau_1 d\tau_2. \qquad (7)$$

Here $\phi_{1s}^\uparrow(\vec{r})$ is the up-spin core wave function perturbed by the exchange interactions. The second and third terms in Eq. (5) are the admixture of the nth excited core wave functions, $\phi_n^0(\vec{r})$'s, and that of the conduction-electron wave functions, $\psi_{\vec{k}}^0(\vec{r})$'s, respectively. Equations (6) and (7) are the exchange integrals. ϵ_{1s} and ϵ_n's are the ground and the excited-state energies of the core electron, respectively. Similar equations describe perturbed down-spin core wave function, $\phi_{1s}^\downarrow(\vec{r})$.

The same procedure used to derive Eq. (1) (Ref. 18) leads to the expression of P_F^{cp} as

$$P_F^{cp} = \sum_{n \neq 1s} \phi_{1s}^{0*}(0)\phi_n^0(0)\frac{J(n,1s)}{\epsilon_{1s} - \epsilon_n}$$
$$+ \sum_{\vec{k}'} \phi_{1s}^{0*}(0)\psi_{\vec{k}}^0(0)\frac{J(\vec{k}',1s)}{\epsilon_{1s} - \epsilon_{\vec{k}}} + \text{c.c.} \qquad (8)$$

Here $J(n,1s)$ and $J(\vec{k}',1s)$ are the exchange integrals in Eqs. (6) and (7), respectively, averaged over the Fermi surface,

$$J(n,1s) = \left\langle \int \phi_n^{0*}(\vec{r}_1)\psi_{\vec{k}_F}^{0*}(\vec{r}_2)(e^2/r_{12})\psi_{\vec{k}_F}^0(\vec{r}_1)\phi_{1s}^0(\vec{r}_2) \right.$$
$$\left. \times d\tau_1 d\tau_2 \right\rangle_{\text{av}} \qquad (9)$$

and

$$J(\vec{k}',1s) = \left\langle \int \psi_{\vec{k}'}^{0*}(\vec{r}_1)\psi_{\vec{k}_F}^{0*}(\vec{r}_2)(e^2/r_{12})\psi_{\vec{k}_F}^0(\vec{r}_1)\phi_{1s}^0(\vec{r}_2) \right.$$
$$\left. \times d\tau_1 d\tau_2 \right\rangle_{\text{av}}. \qquad (10)$$

From Eq. (8), P_F^{cp} can be understood as an exchange distortion of the core charge at the nucleus caused by an average conduction electron at the Fermi surface. The contribution from the balanced conduction electrons below the Fermi surface vanishes when the summation $\sum_{k\uparrow} - \sum_{k\downarrow}$ is carried out. The effect of the unbalanced electrons near the Fermi surface caused by the external field H is replaced by the product of the number of the unbalanced electrons, $\chi_P\Omega H/\mu_B$, and the average exchange integrals at the Fermi surface, Eqs. (9) and (10), in deriving Eq. (8). Here μ_B is the Bohr magneton.

It is noticed from Eqs. (2) and (8) that the exchange *distortion* of the core charge at the nucleus P_F^{cp} plays the same role as the conduction-electron *charge* at the nucleus, P_F. The experimentally deduced volume dependence in P_F^{cp} is caused by the volume change in the exchange integrals, $J(n,1s)$ and $J(\vec{k}',1s)$. It is not necessarily surprising that the overlap integrals $J(n,1s)$ and/or $J(\vec{k}',1s)$ are sharply dependent on the volume. The large value of $d\ln P_F^{cp}/d\ln V$, Eq. (4), implies that a fractional change in the exchange *distortion* is large. The fractional change in the core *charge* itself (at the nucleus) is, however, quite small, since the ex-

change distortion is a small fraction of the core-charge distribution.

CONCLUSION

The pressure-dependence measurement of the Knight shift in Li metal, in conjunction with the recent measurement of the Pauli susceptibility as a function of the volume of this metal, has re-

vealed a strong volume dependence of the core polarization.

[1] G. B. Benedek and Toshimoto Kushida, J. Phys. Chem. Solids 5, 241 (1958).

[2] Toshimoto Kushida, J. C. Murphy, and M. Hanabusa, Phys. Rev. B 13, 5136 (1976); 15, 1231 (E) (1977). This literature (referred to hereafter as I) includes extensive references and associated discussion.

[3] B. W. Holland, Phys. Status Solidi 28, 121 (1968). See also Ref. 91 in I.

[4] Figure 5 in I.

[5] J. P. Perdew, S. B. Nickerson, S. H. Vosko, and R. A. Moore, Can. J. Phys. 53, 648 (1975).

[6] See I for references.

[7] S. D. Mahanti, Solid State Commun. 15, 779 (1974).

[8] L. Wilk and S. H. Vosko, Bull. Am. Phys. Soc. 24, 490 (1979).

[9] For instance, Toshimoto Kushida and J. C. Murphy, Phys. Rev. B 3, 1574 (1971).

[10] H. S. Gutowsky and B. R. McGarvey, J. Chem. Phys. 20, 1472 (1952).

[11] The alternating measurements at atmospheric pressure and P were necessary, since a slight difference in the magnetic field strength at the Na probe and at the Li sample might change during a few hours of runs. The degree of the homogeneity of the magnet might change, presumably due to the temperature change of the pole pieces of the magnet. The constancy of the magnetic field at the position of the field-control probe (the Na-NMR probe) does not necessarily guarantee the constancy of the field at the Li sample. Indeed, it was noticed that the difference between the magnetic field at the Li sample and at the Na probe, ΔH, changed by

several mG during the run. The ΔH change was, however, slow, monotonic, and almost linear except for the first 30 min. The effect of the slow drift of the magnetic field at the Li sample due to this origin was eliminated by averaging the observed pressure shift in the Li NMR frequency $\Delta \nu$ over the successive runs; $\Delta \nu$ produced by the pressure increase from the atmospheric value to P and $\Delta \nu$ caused by the successive pressure decrease to one atmosphere. The distance between the Li and the Na probe was approximately 10 cm in 12-in. pole caps.

[12] P. W. Bridgman, The Physics of High Pressure (Bell, London, 1952), p. 160.

[13] NMR Properties of Pure Metals, NBS, Washington, D. C., Alloy Data Center, compiled by G. C. Carter (1/5-K-4/9/74). This value is recommended as an average extending over the range of reliable data. Other representative values are also listed in this literature.

[14] Reference 5, here the result of APW method is used.

[15] See the result for Na, Fig. 5 in I.

[16] S. D. Mahanti, L. Tterlikkis, and T. P. Das, in Proceedings of the International Symposium on Electron and Nuclear Magnetic Resonance, Melbourne, 1969, edited by C. K. Coogan et al. (Plenum, New York, 1970), p. 105.

[17] Toshinosuke Muto and Syoiti Kobayasi, J. Phys. Soc. Jpn. 19, 1837 (1964).

[18] C. P. Slichter, Principles of Magnetic Resonance (Harper and Row, New York, 1963), p. 89 ff.