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Pressure-dependent Knight shift in Na and Cs metal

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We present an experimental and theoretical study of the pressure dependence of the Knight shift of ^{23}Na and ^{133}Cs in sodium and cesium metal, respectively. The sodium shift has been measured, employing the diamond-anvil cell technique, up to about 8 GPa, and our previous discovery of a shift minimum around 1.5 GPa has been confirmed. The temperature dependence of the shift results solely from thermal expansion. The cesium shift, at 295 K, increases by 74% between normal pressure and 2.1 GPa. The theoretical studies of the sodium shift are based on a self-consistent band structure calculation with the scalar-relativistic linear muffin tin orbital method and the local density approximation. Using an appropriate description of the volume dependence of the hyperfine field, our calculations lead to a correct prediction of the Knight shift minimum. Differences between spin-restricted and exchange-enhanced calculations are discussed.

I. INTRODUCTION

The Knight shift, which is the displacement of the nuclear magnetic resonance (NMR) frequency in a metal due to the average static magnetic field produced by the conduction electrons, provides valuable insight into the electronic structure of metals. In particular, it allows the study of energy band structure and of electron wave functions. The Knight shift K is defined as

$$K=\left.\frac{\nu_m-\nu_r}{\nu_r}\right|_{B_0=\text{const}}, \tag{1.1}$$

where ν_m and ν_r are the NMR frequencies measured in the metal and in a nonmetallic reference compound, respectively, both determined in the same external magnetic field B_0.

If the magnetic field produced by conduction electrons arises from the contact interaction of unpaired electrons found in the vicinity of the Fermi energy, the shift may be written as

$$K=\frac{8\pi}{3}\chi P_F, \tag{1.2}$$

where χ is the atomic Pauli susceptibility and P_F the density of states at the Fermi energy. While the Knight shift usually depends only slightly on temperature, pressure-dependent shift measurements are of great importance since the volume dependence of K reveals the interplay of the trends of the volume dependence of the electronic structure parameters χ and P_F.

Such experiments were pioneered by Benedek and Kushida,[1] who determined the pressure dependence of alkali metal Knight shifts; more accurate remeasurements of the lithium and sodium shifts were performed by Kushida and Murphy.[2] All these experiments were done in the pressure range below 1 GPa using conventional techniques. By employing the diamond–anvil cell (DAC) technique we have previously extended the pressure range to about 8 GPa (Refs. 3,4) and have detected an unusual volume dependence of the sodium shift.

In this paper we present experimental data for sodium, in particular the pressure dependence as a function of temperature, and Knight shift measurements in cesium metal at pressures above 1 GPa.[5] Furthermore, we will present a detailed theoretical study of the volume dependence of the sodium Knight shift based on a self-consistent band structure calculation, with the scalar-relativistic linear muffin tin orbital method and the local density approximation. Finally, we will address the question why all previous theoretical examinations of this problem established a stronger volume dependence of K than found experimentally[6,7] and did not reproduce the minimum or found it at too low volume ratios.

The paper is organized as follows. The next section describes the experimental technique, followed by the presentation of the experimental results in Sec. III. In Sec. IV we sketch the calculations for sodium and present the numerical results and their discussion.

II. EXPERIMENTAL TECHNIQUE

All pressure experiments were performed in a home-built DAC in which diamonds are pressed together by a lever mechanism allowing pressures up to 10 GPa. The DAC operates in a cryostat, which fits into a 4.7 T superconducting magnet that is part of an NMR pulse spectrometer.

The present apparatus is an improved version of our earlier device[4] which was designed for solid state NMR studies.[3] The improvements are in the gaskets, the optical system for pressure measurement, and, in particular, the temperature variation. The NMR radio-frequency field generated by a special saddle coil is parallel to the gasket surface and dips into the sample hole of 0.7 mm diameter which is drilled into gaskets of 0.15–0.20 mm thickness. The anvil flats are 1.1 mm^2.

Since the magnetism of rhenium gaskets used in our earlier studies[3] caused a considerable broadening of the NMR signals, we switched to beryllium-copper alloy Berylco gaskets in which pressures up to at least 7 GPa can be generated.

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The pressure measurement is performed *in situ* by the ruby fluorescence method (e.g., Ref. 8) employing a small ruby chip placed in the sample hole. For all temperatures, we first determined, at ambient pressure, the wavelength of the fluorescence line with respect to its ambient temperature value. These data are in good agreement with the results of McCumber and Sturge.[9] To determine the pressure we assumed the pressure-induced wavelength shift to be independent of temperature.[10,11] The linear change with a slope of 0.365 nm/GPa allows pressure measurements with a precision of about ± 0.06 GPa.

The temperature variation is done by drawing nitrogen gas through the cryostat which contains the DAC. A particular temperature, in the range 180 – 366 K, could be maintained with a precision of about ± 0.2 K, which was sufficient for the present studies.

The Na and Cs samples (99.95% purity) consist of spheres (diameter up to about 30 μm) immersed in mineral oil which serves as pressure medium and prevents corrosion. The sample masses are about 30 and 100 μg for Na and Cs, respectively.

The NMR signals were obtained using a standard pulse spectrometer. The ^{23}Na spectra (resonance frequency 52.9 MHz in 4.7 T) were determined by accumulating about 10^5 free induction decay (FID) signals following a $\pi/2$ pulse and a subsequent Fourier transform. In the case of ^{133}Cs (resonance frequency 26.6 MHz), strong ringing signals[12] concealed the FID completely for pressures above 0.6 GPa. Therefore, we used a modified phase cycling pulse sequence[5] to record the spin echo after a fixed time of 100 μs. The spectra were obtained by Fourier transformation of about 10^6 accumulated spin echo signals.

We have recorded so-called *magnitude spectra* which are the square root of the sum of the squared real and imaginary parts of the Fourier transform of the complex FID. Linewidths quoted throughout this paper refer to the ‘‘full width at half height’’ of these spectra. The use of Berylco gaskets reduced the Na linewidth at ambient pressure and temperature to about 350 Hz, which is still larger than the linewidth due to magnetic inhomogeneities of the cryostat.

To get the Knight shift $K(p)$ at a particular pressure p, we measure the NMR frequency at this pressure, $\nu_m(p)$, and at ambient pressure, $\nu_m(0)$. With the frequency shift $\Delta\nu(p)$ defined as

$$\Delta\nu(p)=\nu_m(p)-\nu_m(0) \tag{2.1}$$

and Eq. (1.1) we obtain the following expression for the Knight shift at pressure p:

$$K(p)=K_0+\frac{\Delta\nu(p)}{\nu_m(0)}(1+K_0), \tag{2.2}$$

where K_0 is the Knight shift at ambient pressure.

For the discussion of the experimental data, it is useful to express the relative Knight shift $K(p)/K_0$ as a function of the relative volume $V(p)/V_0$, where $V(p)$ and V_0 are the sample volumes at pressure p and ambient pressure, respectively. We used the results of Boehler[13] and of Ho and Ruoff[14] to calculate, for a given temperature T, the pressure-volume isotherm for Na. For Cs, we used the experimental equation of state given by Anderson *et al.*[15] to transform pressure into volume.

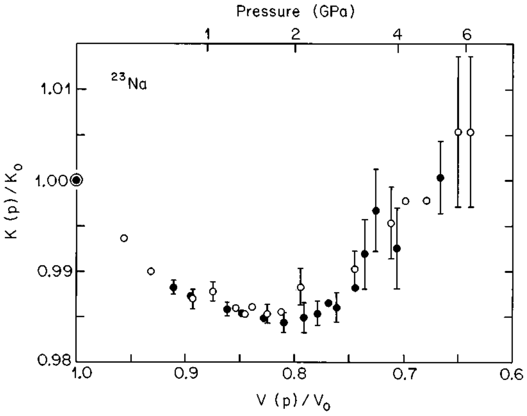

FIG. 1. The relative ^{23}Na Knight shift at 295 K as a function of relative volume $V(p)/V_0$ and pressure: ●, this work; ○, Ref. 3.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Sodium

The ^{23}Na Knight shift at ambient pressure and temperature (295 K) which we measured in the DAC is $K_0(295\text{ K}) = 0.1136(5)\%$ with respect to ^{23}Na in NaOH which was placed beside the probe hole. Our result is in excellent agreement with the literature value 0.113(1)%.[16]

In Fig. 1, we compare the volume dependence of the new relative shift data taken at 295 K with our previous results.[3] The increase of the error bars with rising pressure is due to the pressure-induced line broadening, which reduces the accuracy of $\Delta\nu(p)$. From ambient pressure up to about 2 GPa $[V(p)/V_0\approx 0.81]$ the NMR line is relatively narrow because of the translational diffusion of the Na ions. Between 2 and 4.5 GPa the linewidth increases steeply by a factor of about 20, because the diffusion is progressively hindered by pressure.[3] Above 4.5 GPa the linewidth stays nearly constant because the diffusion is suppressed to such an amount that the lattice is ‘‘rigid’’as defined by NMR.[3]

We note two important facts with respect to our previous study:[3] (i) The new ambient temperature data agree with the old measurements performed with a rhenium gasket, and hence the gasket material does not influence the NMR frequency; (ii) the presence of a Knight shift minimum is reconfirmed.

We will now turn to the temperature dependence of both the value of the Knight shift at ambient pressure, $K_0(T)$, and of the Knight shift minimum value. First, we noticed, in agreement with data from the literature,[16] a slight linear increase of K_0 with temperature with a slope $\partial K_0/\partial T=[1.23(15)\times 10^{-5}]\%/\text{K}$. This temperature dependence can be explained by the thermal expansion of the lattice, which causes a narrowing of the electronic bands and hence an enhancement of the density of states at the Fermi level. This in turn increases the electron spin susceptibility and therefore the Knight shift.

Next, we will discuss in some detail the significance of the temperature dependence of the Knight shift minimum.

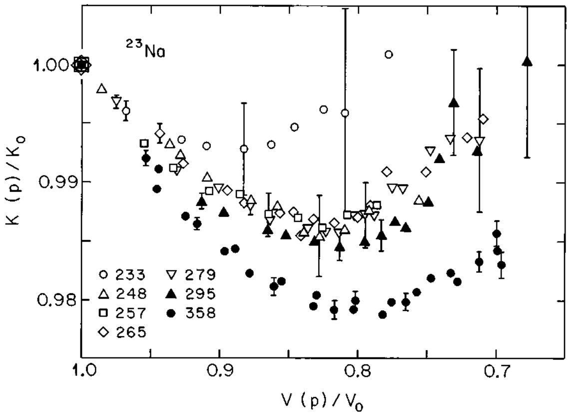

FIG. 2. The relative ^{23}Na Knight shift as a function of the relative volume $V(p)/V_0$ at various temperatures.

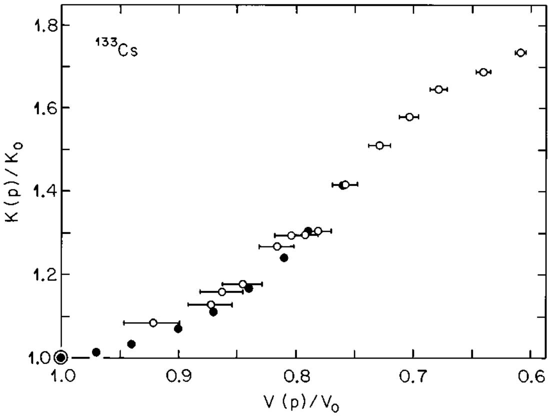

FIG. 4. The relative ^{133}Cs Knight shift as a function of the relative volume: ○, this work; ●, Ref.1.

The minimum appears at all temperatures (see Fig. 2), and the depth of the minimum seems to decrease with decreasing temperature. Unfortunately, the transition to the rigid lattice regime moves towards lower pressure if the temperature is reduced.[5] Therefore, the error bars around the minimum become larger with decreasing temperature. For the 358 K data, whose errors are relatively small up to 4.5 GPa, the relative shift value at the minimum is clearly smaller than the 295 K value; in addition, the minimum appears at a smaller relative volume.

What is the origin of the temperature dependence of the Knight shift minimum value? It is unlikely that it is caused by a thermal rearrangements of the density of states since these vary smoothly near the Fermi energy.[7] Instead, we suggest that the temperature dependence of the lattice constant accounts for the effect. Figure 3 shows the absolute Knight shift $K(p)$ as a function of the lattice constant d for 295 and 358 K. We have determined $d(p,T)$ as follows. The ambient pressure value at 295 K, $d_0=4.2906$ Å,[17] together with the coefficient of linear thermal expansion[17] provides the ambient pressure value for a particular temperature, $d_0(T)$. Using our calculated p-V isotherm for this temperature (see above), the relation

$$\left(\frac{d(p,T)}{d_0(T)}\right)^3=\frac{V(p,T)}{V_0(T)} \tag{3.1}$$

yields the pressure- and temperature-dependent cubic lattice constant $d(p,T)$.

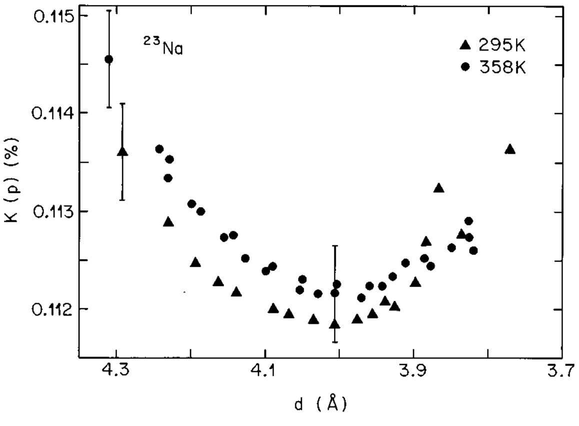

FIG. 3. The absolute ^{23}Na Knight shift as a function of the lattice constant d at two temperatures.

Figure 3 shows how both $K(p)$ curves are parallel to each other from low pressures up to the shift minimum which occurs, within the experimental accuracy, at the same lattice constant. The vertical displacement of both curves is about $(5\times10^{-4})\%$ which is the same as the experimental error of $K_0(T)$. Since $K_0(T)$ fixes the vertical position of the $K(p)$ curve for a given temperature [see Eq. (2.2)], the error of $K_0(T)$ causes a systematic displacement of the whole curve. Thus, both $K(p)$ curves can be made to coincide (at least up to the minimum) if one varies $K_0(T)$ within the error bars. This procedure can also be applied to the $K(p)$ curves at other temperatures since all Knight shift minima fall into the interval $(0.1118\pm0.0005)\%$. Thus, the minimum value of $K(p)$ is constant, as a function of temperature. The experimental data for $K(d)$ are also consistent with a temperature-independent position of the minimum. In other words, the temperature dependence of $K(p,T)$ results solely from the thermal changes in the lattice constant. On the high-pressure side of the minimum the large errors do not allow us to draw reliable conclusions.

B. Cesium

We have measured, at 295 K, the pressure dependence of the ^{133}Cs Knight shift in the bcc phase up to 2.1 GPa, corresponding to a volume reduction of about 40%.[15] These measurements were more difficult than those with sodium, because cesium metal is extremely reactive, thus complicating the sample preparation, and because the NMR sensitivity of ^{133}Cs is only half that of ^{23}Na. In addition, the measurements become increasingly time consuming at high pressure since the Cs signals get very weak due to line broadening and perhaps due to increased spin-lattice relaxation times.

The determination of the ambient pressure Knight shift value carried out in our DAC, using CsF as reference yields $K_0=1.489(5)\%$ which agrees very well with the literature value $K_0=1.49(1)\%$.[16] Figure 4 displays the relative Knight shift $K(p)/K_0$ as a function of the relative volume. We have included the results of Benedek and Kushida[1] who determined the Knight shift up to 0.8 GPa.

The relative Knight shift increases by 74% when reducing the volume to $0.6V_0$. To our knowledge, this is the strongest pressure-induced change in a Knight shift observed so far. Comparing this enormous pressure dependence with the small change of about 2% in Na, it is obvious that the experimental data for Cs will serve as a challenging test for theories concerned with many-electron problem in metals.

IV. THEORY

Our theoretical studies of the sodium Knight shift are based on a self-consistent band structure calculation with the scalar-relativistic linear muffin tin orbital (LMTO) method and the local density approximation (LDA). Since it is inconsistent to use the Fermi contact term in the scalar-relativistic case,[18,19] the contact term was replaced by the corresponding relativistic expression. Starting with a relativistic formulation has the additional advantage of putting the present investigations on an equal footing with future calculations of heavier alkali metals, where a relativistic treatment of local quantities such as the Knight shift is indispensable. Consequently, we use Dirac wave functions based on the self-consistent scalar-relativistic crystal potential.

A. Method of calculation

There are several electronic-nuclear interactions which contribute to the Knight shift: (i) the Fermi contact term of s states, which has in our case to be replaced by its relativistic counterpart, (ii) the core polarization by conduction electrons, (iii) the spin dipolar interaction, and (iv) the interaction with the orbital motion of the conduction electrons. The dipolar interaction vanishes in crystals with cubic symmetry and yields an anisotropic shift in systems with lower symmetry. The core polarization amounts to 2% estimated from the polarization hyperfine field of Carter *et al.*[16] and from our calculated density of states (DOS). Finally, the orbital contribution, as estimated by second-order perturbation, is three orders of magnitude smaller than the measured Knight shift. Thus, we are left with contribution (i).

The Dirac equation describing the motion of an electron in the presence of a crystal potential and a nuclear magnetic dipolar field yields the hyperfine interaction in a straightforward manner:

$$H_{\mathrm{HF}}=\frac{ec(\boldsymbol{\alpha}\times\mathbf{r})\boldsymbol{\mu}_N}{r^3}, \tag{4.1}$$

where $\boldsymbol{\alpha}$ is the 4×4 velocity matrix, c the velocity of light, and $\boldsymbol{\mu}_N$ the magnetic moment of the nucleus. Then, the spin contribution to the Knight shift becomes, using first order perturbation theory,

$$K=-\frac{\Sigma_k\langle\psi_k|H_{\mathrm{HF}}|\psi_k\rangle f(\varepsilon_k)}{\boldsymbol{\mu}_N\mathbf{B}_0}. \tag{4.2}$$

Since ψ_k represents a relativistic Bloch state of the spin-polarized electron system, the numerator is proportional to the external field $\mathbf{B}_0$ and one obtains for K (Ref. 19,20)

$$K=-\frac{8\pi}{3}\mu_B^2 n_s\frac{4m_0c}{\hbar}\int_0^{r_{\mathrm{WS}}}f_{-1}(r)g_{-1}(r)Y_{00}^2dr. \tag{4.3}$$

where $g_{-1}(r)$ and $f_{-1}(r)$ are the radial parts of the major and minor components, respectively, of the s state spinor at the Fermi energy E_F, n_s is the density of s states at E_F, m_0 is the electron mass, and Y_{00} is the spherical harmonic of zero order. The radial integrals are restricted to the Wigner-Seitz sphere with radius r_{WS}.

Using the abbreviations

$$P_F=-\frac{4m_0c}{\hbar}\int_0^{r_{\mathrm{WS}}}f_{-1}(r)g_{-1}(r)Y_{00}^2dr, \tag{4.4}$$

$$\chi=\mu_B^2n_s, \tag{4.5}$$

Eq. (4.3) turns into Eq. (1.2). Passing to the nonrelativistic limit, one can show that P_F is the density of Fermi electrons at the nuclear position $\rho(0)|_{E_F}$. Thus the hyperfine coupling constant

$$H_F=\frac{8\pi}{3}\mu_BP_F \tag{4.6}$$

is the relativistic counterpart of the Fermi contact hyperfine interaction.

The band structure calculations are carried out with the self-consistent LMTO method, which was developed by Andersen[21] and discussed in detail by Skriver.[22] This LMTO version contains mass-velocity and Darwin corrections up to any order. In a first step, we perform *spin-restricted* calculations, where the magnetization is given by the net spin produced by the external magnetic field only, and the susceptibility is determined by the DOS at E_F. In a second step, we take into account the *exchange enhancement* from the spin-polarized calculations of Leiberich *et al.*[7] The enhancement occurs because the net spin gives rise to exchange potentials which are different for ''spin up'' and ''spin down'' electrons, thus encouraging further polarization of the electrons. The enhanced susceptibility due to s states, χ, is related to the unenhanced susceptibility χ_0 via the relation[16]

$$\chi=\frac{\chi_0}{1-\alpha}. \tag{4.7}$$

α is the Stoner enhancement factor which is equal to the product of the exchange-correlation integral[23] and the density of s states.

We start the calculations with a crystal potential that is derived from renormalized atomic charge densities, which follow from Dirac-Fock-Slater calculations[24] for the Na ground state configuration. In the band structure calculations, the exchange and correlation (XC) potential of von Barth and Hedin[25] is used. The structure constants appearing in the LMTO formalism involve lattice sums which are extended over about 30 atomic shells in the direct as well as in the reciprocal space, so that the numerical error is lower than 0.1%. To construct the new potential we use, in each iteration, the band structure data at 55 **k** points in the irreducible part of the Brillouin zone; for the final two iterations 819 points are considered. The partial DOS is obtained by the tetrahedron method.[26,27] The self-consistent procedure is continued until the largest relative change of the valence charge density on the radial mesh is less than 10^{-3}. Once self-consistency has been achieved, the Dirac equation is integrated using a basis set that includes s, p, and d states and the crystal potential at the Fermi energy. At all steps, the

TABLE I. Theoretical results of the ^{23}Na Knight shift calculation for various values of the relative volume $V(p)/V_0$. n_s, n = partial and total DOS [states/Ry atom]; H_F = hyperfine field [kOe]; χ/χ_0 = susceptibility enhancement (Ref. 7; K_{n_s} = Knight shift in effective one-particle approximation; K_χ = enhanced Knight shift; K_{expt} = experimental value; all Knight shifts in %.

$V(p)/V_0$	1	0.9	0.85	0.75	0.65
$n_s(p)$	2.1831	1.9948	1.9018	1.7190	1.5391
$n(p)$	6.1292	5.7740	5.5921	5.2163	4.8211
$H_F(p)$	826.2	897.6	937.6	1042.6	1186.5
χ/χ_0	1.53 [a]	1.516	1.509	1.494	1.48 [a]
$K_{n_s}(p)$	0.07674	0.07602	0.07586	0.07626	0.07769
$K_\chi(p)$	0.1174	0.1152	0.1145	0.1139	0.1150
$K_{\mathrm{expt}}(p)$	0.1136	0.1121	0.1119	0.1125	0.1142

[a] Ref. 7.

complete LMTO formalism including the combined muffin tin corrections to the atomic sphere approximation is applied.

B. Numerical results

The numerical results for the hyperfine field, the DOS, and the Knight shift at normal pressure were obtained with the theoretical equilibrium lattice constant of $7.6767a_0$, where a_0 is the Bohr radius. This value, which corresponds to the XC potential used throughout, was calculated with the Barth-Hedin XC potential entering the pressure relation of Nieminen and Hodges.[22,28] It is satisfying that our lattice constant agrees within 0.3% with the calculations of Moruzzi *et al.*[29]

Table I shows the theoretical results. First, we consider the normal pressure data and start with the hyperfine field H_F. Carter *et al.*[16] cite an *atomic* hyperfine field of 390 kOe. In the renormalized atom picture of Hodges *et al.*,[30] the s density in metals is about twice the atomic value. Hence, theoretical H_F values in metals turn out to be about twice the atomic data[31] which is in accordance with our theoretical value. It is important to note that H_F depends only weakly on the position of the Fermi energy but very sensitively on volume effects. This is due to the s character of the corresponding states, whereas for d states the situation is just vice versa.

Next, we note that the total DOS at normal pressure agrees with Janak's value of 6.2 states/Ry atom.[23] To test the accuracy of the electronic structure data, we calculated the "spin-lattice relaxation rate per unit temperature" $(T_1T)^{-1}$. The rate is less enhanced by electron-electron interactions than the Knight shift because the Lindhard function, which is the linear response function of the dynamic susceptibility in the case of a spherical Fermi surface, decreases monotonically with the scattering momentum. The theoretical rate, including p and d states, is $(T_1T)^{-1} = 0.16$ (s K)$^{-1}$, which is only 20% lower than the experimental rate.[16]

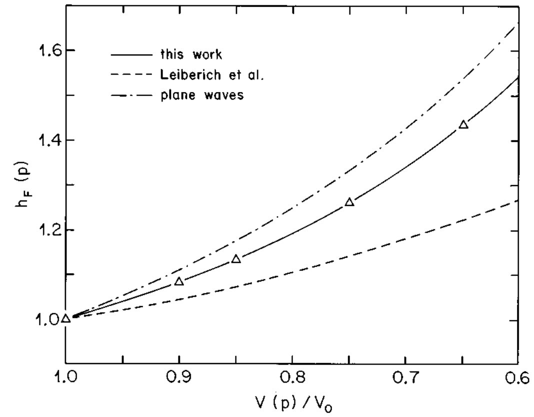

FIG. 5. Reduced hyperfine field $h_F(p)$ versus relative volume $V(p)/V_0$. Solid line and △, this work; dashed line, Leiberich *et al.* (Ref. 7); dash-dotted line, plane-wave method.

Now we will deal with the volume dependence of the quantities entering the Knight shift, namely, the DOS and the hyperfine coupling. We found that the total DOS, divided by its value at normal pressure, increases linearly with increasing $V(p)/V_0$ with a slope of 0.6, which agrees with the experimental susceptibility value.[32] Thus, the relative change of the susceptibility is very well described by the LDA calculations. However, its magnitude is underestimated by using the effective one-particle theory, which yields a Knight shift denoted by K_{n_s} about 30% lower than the experimental value. Therefore, in a next step, we included the "exchange enhancement," which is known to be large for alkali metals according to Stoner-like theories[23] and spin-polarized calculations.[7] In calculating the exchange-enhanced Knight shift K_χ, we have taken linearly interpolated χ/χ_0 ratios (see Table I) from spin-polarized calculations.[7] The K_χ value at normal pressure (Table I) is in fairly good agreement with our experimental result.

Coming now to the hyperfine field we note a pronounced contrast between our result and all previous calculations. The calculated reduced hyperfine field, $h_F(p) = H_F(p)/H_{F0}$, where H_{F0} is the hyperfine coupling constant at normal pressure, varies much more strongly than the data of Leiberich *et al.*[7] as shown in Fig. 5. Wilk and Vosko[6] found an even weaker volume dependence. For comparison, Fig. 5 also contains the plane-wave result which is given by the reciprocal volume ratio. Obviously, our hyperfine field values are closer to the plane-wave curve than those of Leiberich *et al.*[7]

Combining these theoretical results yields the volume dependence of the Knight shift. Figure 6 summarizes, together with the experimental data, the various theoretical results. The dotted line represents the results of our spin-restricted calculations. Taking into account the exchange enhancement, as discussed above, leads to the final result expressed by the solid line.

C. Discussion

All previous theoretical examinations of the sodium Knight shift established a stronger volume dependence[6,7] than the experiment, and did not reproduce the minimum or found it at too low volume ratios. So far, the discrepancies have been attributed to (nonlocal) exchange and correlation effects[6] in the susceptibility. On the other hand, the volume dependence of the theoretical χ is much closer to the experiment than the theoretical Knight shift, as shown in the foregoing subsection. Therefore, we will discuss now whether an

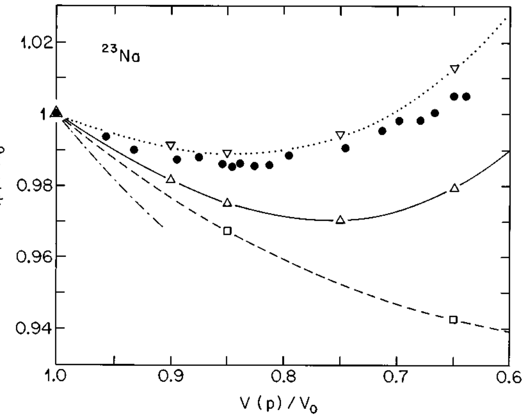

FIG. 6. Calculated relative Knight shift $K(p)/K_0$ of ^{23}Na in sodium metal as a function of the relative volume $V(p)/V_0$. Solid line and △, this work (using enhanced susceptibility); dotted line and ▽, this work (without enhancement); dashed line and □, Ref. 7; dash-dotted line, Ref. 6; ●, experimental data (this work).

inadequate description of either the susceptibility or the hyperfine field is mainly responsible for the deviations from experiment.

For doing so, we have to compare the theoretical exchange enhancement of the susceptibility $\chi/\chi_0 = 1.53$ with an estimated experimental value. The estimate can be done with the help of the Korringa relation

$$T_1 T K^2 C_0 = S_K^{-1} \tag{4.8}$$

and

$$C_0 = \frac{4\pi k_B}{\hbar}\left(\frac{\gamma_n}{\gamma_e}\right)^2, \tag{4.9}$$

where γ_n and γ_e are the nuclear and electronic gyromagnetic ratios, respectively, and S_K is called the ''Korringa enhancement factor'' which takes into account many-particle effects; S_K is equal to 1 for noninteracting electrons. (In fact, it is S_K^{-1} which describes the enhancement.) The Korringa relation, with S_K close to 1, is known to be valid in alkali metals due to the fact that both K and T_1T are dominated by s states. The p states in Na, according to our calculations, contribute only 2% to the total spin-lattice relaxation rate.

The parameter S_K is a function of the Stoner enhancement factor α. The exchange enhancements of both the Knight shift and the relaxation rate contribute to the value of $S_K(\alpha)^{-1}$. The enhancement of K is given by a factor $(1-\alpha)^{-1}$ [see Eq. (4.7)], resulting in a factor $(1-\alpha)^{-2}$ in $S_K(\alpha)^{-1}$. The enhancement of the relaxation rate is given by a squared expression[33] containing α, the Lindhard function, and an effective electron-electron potential. The results in Fig. 2 of Ref. 34 suggest that, for realistic effective interaction potentials[35,36] in alkali metals, this squared expression behaves approximately like $(1-\alpha)$. We therefore write the Korringa relation as

$$T_1 T K^2 C_0 = \frac{1}{1-\alpha}. \tag{4.10}$$

Using the experimental values for T_1T (Ref. 16) and K (from this work), Eq. (4.10) yields a static susceptibility enhancement χ/χ_0 of 1.58 which is in accordance with the theoretical value of 1.53.

We now pass over to the volume dependence of the hyperfine field. The reason for the steeper upturn of the hyperfine field we have calculated, as compared to the result of Ref. 7, is that we used the theoretical equilibrium lattice constant and employed a relativistic theory. The difference between the hyperfine field values of this work and of Ref. 7 can be expressed in the following way. For plane waves, we have the relation $h_F(p)[V(p)/V_0]=1$. As mentioned above, the hyperfine field of s states reflects very strongly their plane-wave character. Thus, it is reasonable, as has been done by Leiberich *et al.*,[7] to take into account deviations of the calculated s states from the plane-wave results by a linear correction of the plane-wave relation

$$h_F(p)\frac{V(p)}{V_0} = 1 - c_h \frac{V_0 - V(p)}{V_0}. \tag{4.11}$$

The solid line in Fig. 5 represents a fit of Eq. (4.11) to the calculated $h_F(p)$ values with $c_h = 0.185$, whereas the dashed line due to Leiberich *et al.* corresponds to $c_h = 0.60$. The volume dependence of our h_F result then yields the K minimum at the volume ratio found experimentally. Weaker volume dependences result in a minimum at higher pressures.[7]

Finally, when comparing absolute values of the calculated relative Knight shift (see Fig. 6) we note that our spin-restricted calculations (dotted line) come closer to the experimental values than the calculations which take into account exchange enhancement (solid line). This is a puzzling result since, as explained above, the exchange enhancement should not be neglected in these calculations. It should be noted that the results of the spin-polarized calculations (dashed line in Fig. 6) would agree with those of our spin-restricted calculations (dotted line), if the exchange enhancement were independent of the electron density. Thus, the above-mentioned puzzle probably arises because the exchange enhancement used in the spin-polarized calculations depends too strongly on the electron density. In any case, the main reason for the differences between theory and experiment does not lie in nonlocal exchange and correlation corrections for the susceptibility, but in an inappropriate description of the hyperfine field.

V. SUMMARY

We have presented an experimental and theoretical study of the pressure dependence of the Knight shift of ^{23}Na and ^{133}Cs in sodium and cesium metal, respectively. For sodium, we have measured the shift up to about 8 GPa and confirmed our earlier experimental data, in particular the shift minimum around 1.5 GPa. We have also shown that the temperature dependence of the shift, at a fixed pressure, results solely from the thermal changes in the lattice constant.

For cesium, the Knight shift at 295 K has been measured beyond 0.8 GPa. Between normal pressure and 2.1 GPa, the Knight shift increases by 74%, which seems to be the strongest pressure-induced change in a Knight shift observed so far.

Our theoretical studies of the sodium Knight shift are based on a self-consistent band structure calculation, with the scalar-relativistic linear muffin tin orbital method and the local density approximation. The relativistic counterpart of the Fermi contact hyperfine interaction has been considered. We have performed spin-restricted and exchange-enhanced calculations; in the latter case the enhancement is taken from spin-polarized calculations.

Our results provide a more appropriate description of the experimental data, in particular of the Knight shift minimum, than earlier calculations could do. The improvement is mainly caused by using the *calculated* lattice constant which ensures a consistent treatment of all electronic structure data. This procedure affects, for the most part, the volume dependence of the hyperfine field.

The spin-restricted calculations result in data which are in better agreement with experiment than those of the exchange-enhanced calculations. The reason for this deviation is probably that, in the spin-polarized calculations, the exchange enhancement depends too strongly on the electron density.

In conclusion, correct calculations of the hyperfine field's volume dependence will make future investigations of the pressure-dependent Knight shifts, for instance in cesium, a valuable tool to deliver reliable information on the dependence of the exchange enhancement on the electron density.

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