

The Knight shift and diffusion in solid lithium and sodium at pressures up to 8 GPa studied by NMR

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 7911

(<http://iopscience.iop.org/0953-8984/2/39/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 06:54

Please note that [terms and conditions apply](#).

The Knight shift and diffusion in solid lithium and sodium at pressures up to 8 GPa studied by NMR

R Bertani, M Mali, J Roos and D Brinkmann

Physik-Institut, Universität Zürich, Schönberggasse 9, 8001 Zürich, Switzerland

Received 6 February 1990, in final form 15 May 1990

Abstract. We have measured the pressure dependence of the Knight shift and the linewidth of the nuclear magnetic resonance (NMR) signals of ${}^7\text{Li}$ (up to 8 GPa) and ${}^{23}\text{Na}$ (up to 6 GPa) in metallic lithium and sodium, respectively, at room temperature using a diamond anvil cell (DAC). It is concluded that diffusion is hindered by pressure; the diffusion coefficients and the activation volumes are estimated. In Li, diffusion increases at the BCC-FCC phase transition. The Li Knight shift increases with rising pressure up to the phase transition, where a marked reduction is observed which might be due to a drastic decrease of the s character of the conduction electron wave function. The Na shift decreases up to about 1.7 GPa and then increases. The Knight shift data are compared with theories that exist for pressures up to 1 GPa. By extrapolating existing values for the Pauli susceptibility, the pressure dependence of the spin density at the nuclear site is estimated.

1. Introduction

Nuclear magnetic resonance (NMR) is a well established method for studying properties of metals on the atomic scale (e.g. Winter 1971). A classical example is the Knight shift: the displacement of the NMR frequency observed in a metal with respect to the frequency measured in a non-metallic reference compound. Since the shift arises from the interaction between nuclear magnetic moments and conduction electrons, it is possible to probe local magnetic properties of the metal. The experimental results may be used to test the validity and accuracy of theoretical approaches to the many-electron problem we face in metals. A second quite different example is the study of atomic jump processes in self-diffusion (Mehrer 1978) either by measuring various relaxation times (e.g. Wolf 1977, 1978) or by directly determining the diffusion coefficient of the metal ions by the pulsed field gradient technique (e.g. Mali *et al* 1988).

The overwhelming number of NMR investigations in metals is performed at ambient pressure. This is regrettable since pressure as well as temperature is one of the most important thermodynamic variables in solid state physics and high-pressure studies can provide a wealth of additional information. These experiments were pioneered by Benedek and Kushida (1958) who were the first to measure the pressure dependence of alkali metal Knight shifts; more accurate remeasurements of the Li and Na shifts were performed by Kushida and Murphy (1980). All these experiments were done in the pressure range below 1 GPa using conventional techniques.

Extension of the NMR experiments to higher pressures is hampered by the fact that the pressure can no longer be generated by simply compressing the fluid in the NMR

probe head by means of a pressure generator (e.g. Huber *et al* 1984). Instead one has to resort to other methods such as the diamond-anvil cell (DAC) technique which became, in the 1970s, the most powerful tool for high-pressure research in solid state physics (e.g. Jayaraman 1983, Minomura 1985, Jayaraman 1986). We have recently built a DAC for solid state NMR studies (Bertani *et al* 1990) and have investigated the room temperature NMR of Li and Na in metallic samples at pressures above 1 GPa. The only other DAC device for solid state NMR studies we are aware of has been built by Conradi *et al* (1987).

In this paper we report the first measurements of both the Knight shift and the linewidth of the ${}^7\text{Li}$ and ${}^{23}\text{Na}$ NMR signals at pressures up to 8 and 6 GPa, respectively. In section 2 we will briefly describe the experimental technique. In section 3 we will present and discuss the linewidth data. It will be shown how self-diffusion can be hindered by pressure and how diffusion changes at the BCC-FCC phase transition in Li. From the linewidth data we will estimate the Li and Na diffusion coefficients. The Knight shift data including the abrupt change at the BCC-FCC phase transition, will be presented in section 4. They will be looked at in the light of recent theoretical studies which take into account core-polarization contributions to the contact interaction. The data will be used to estimate electron spin densities at the nuclear sites.

2. Experimental technique

All pressure experiments were performed at room temperature using an NMR pulse spectrometer with a 4.7 T superconducting magnet. Details of the DAC are described elsewhere (Bertani *et al* 1990). We use anvil flats of 1 mm^2 and rhenium gaskets. The radio frequency field of a special saddle coil parallel to the gasket surface dips into the sample hole of 0.7 mm diameter and 0.15 mm thickness. The Li and Na samples (99.9% purity) consist of spheres (diameter 10 to 30 μm) in mineral oil serving as pressure medium and preventing corrosion.

The pressure is measured by the ruby fluorescence method (e.g. Jayaraman 1983). A tiny chip of ruby (Cr^{3+} -doped Al_2O_3) placed in the mineral oil adjacent to the NMR sample is excited by an argon laser. The shift of the emission lines with pressure is used as pressure calibration with a precision of about ± 0.1 GPa. The absence of any broadening of the fluorescence lines proves that the pressure is hydrostatic. Pressures can be measured and can be increased without removing the DAC from the magnet.

The NMR signals (so-called power spectrum) were determined by Fourier transformation of $\approx 10^5$ accumulated free induction decay signals. These signals are broadened due to magnetism present in the DAC (especially in the rhenium gasket) and the cryostat. At room temperature and ambient pressure the full width of the power spectrum at half height, $\delta\nu$, is 2100 and 950 Hz for ${}^7\text{Li}$ and ${}^{23}\text{Na}$, respectively, while the intrinsic linewidths are probably below 160 and 60 Hz, respectively (Gutowsky and McGarvey 1952).

The Knight shift K of an NMR line is defined as

$$K = (\nu_m - \nu_r)/\nu_r \quad (1)$$

where ν_m and ν_r are the NMR frequencies measured in the metal and in a non-metallic reference compound, respectively, with the external magnetic field kept constant.

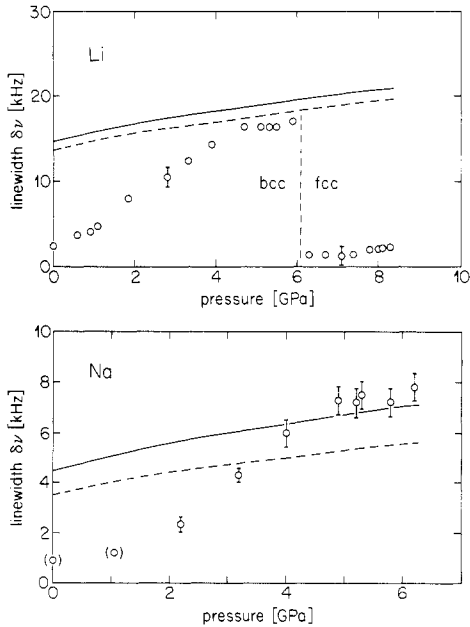


Figure 1. Pressure dependence of the linewidth $\delta\nu$ (full width at half height) of the NMR power spectrum of ${}^7\text{Li}$ and ${}^{23}\text{Na}$ at room temperature. The vertical dashed line separates the BCC and FCC phase of Li. The solid and broken curves are plots of equations (10) and (9), respectively. The low pressure Na data are falsified by magnetic inhomogeneities.

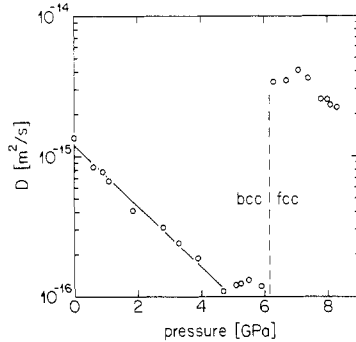


Figure 2. Pressure dependence of the ${}^7\text{Li}$ self-diffusion coefficient at room temperature. The BCC-FCC phase transition is indicated by the vertical broken line. The full line in the BCC phase is an exponential fit to the data.

When determining the Knight shift $K(p)$ for a particular pressure p , every measurement of the NMR frequency $\nu_m(p)$ was preceded by a determination of the frequency $\nu_m(0)$ at normal pressure. Defining a frequency shift $\Delta\nu$ by

$$\Delta\nu = \nu_m(p) - \nu_m(0) \quad (2)$$

equation (1) yields the following expression for the Knight shift at pressure p :

$$K(p) = K(0) + [\Delta\nu(p)/\nu_m(0)][1 + K(0)] \quad (3)$$

For the Knight shift $K(0)$ at normal pressure we have used the literature values 0.026(2)% for Li and 0.113(1)% for Na (Carter *et al* 1977). A determination of $K(0)$ for Na carried out in our DAC using NaCl as a reference agrees with the literature value.

3. Linewidth: results and discussion

3.1. Results and origin of linewidth

The pressure dependence of the linewidth $\delta\nu$ (full width at half height) of the NMR power spectrum of ${}^7\text{Li}$ and ${}^{23}\text{Na}$ is plotted in figure 1. Up to about 1 GPa the values are strongly falsified by the magnetic inhomogeneities mentioned in section 2. In both metals the linewidth increases with pressure up to about 5 GPa and then

becomes nearly constant at a value of 17 and 7.5 kHz for Li and Na, respectively. The BCC-FCC phase transition in Li at 6.3 GPa is accompanied by a drastic drop of the linewidth to 1.5 kHz. If the external contribution to the linewidth (due to magnetic inhomogeneities) does not change with pressure, this result implies that the intrinsic linewidth in the FCC phase just above the transition is much smaller than the width at normal pressure in the BCC phase. Further increase of the pressure in the FCC phase increases $\delta\nu$ only slightly.

What are the mechanisms responsible for the linewidth we observe? In perfect Li and Na crystals no electric field gradients (EFG) and no anisotropic Knight shifts are present at the nuclear sites because of cubic symmetry. However, the cubic symmetry can be disturbed by non-hydrostatic pressure that may create strain. Given the width of the ruby fluorescence lines we estimate the maximum pressure gradient across the crystallographic unit cell of Li or Na to be only about 3 kPa. Using experimental pressure-volume isotherms (Swenson 1966, Grover *et al* 1969, Vaidya *et al* 1971, Olinger and Shaner 1983) the resulting change of the length of the unit cell is only 0.1 ppm. Therefore any strain-related EFG is completely negligible. This conclusion is supported by the fact that no so-called spin-echo signal could be detected at any pressure, since spin-echoes require the presence of static broadening effects such as, for instance, the above-mentioned EFGs.

On the same grounds we can rule out a contribution from anisotropic Knight shift and, finally, pressure-induced dislocations. Dislocations would cause large quadrupolar broadening. However, the linewidths we observe never exceed the dipolar width (see next section). We thus exclude the presence of a high density of dislocations. Since NMR measures bulk properties a small amount of dislocations could escape detection. We therefore conclude that the origin of the linewidth is dipolar spin-spin interaction of the nuclear moments and the coupling of the nuclear spins with conduction electrons although the latter contribution is small (Gutowsky and McGarvey 1952).

3.2. Pressure inhibited motional narrowing

It is well known (Gutowsky and McGarvey 1952) that the linewidth is considerably narrowed by translational diffusion of the metal ions if the local field at the nuclear sites fluctuates at a rate $1/\tau$ which is larger than the rigid lattice linewidth. It is common practice to correlate the narrowed linewidth $\delta\nu$ of the resonance line (the power spectrum in our case) with the rigid lattice linewidth $\delta\nu_{\text{RL}}$ which is the linewidth in the absence of any line narrowing process, by the relation (Abragam 1961)

$$\delta\nu^2 = \delta\nu_{\text{RL}}^2 (2/\pi) \tan^{-1}(2\pi \alpha \delta\nu \tau) \quad (4)$$

where the numerical factor α is of the order unity.

We have remeasured the temperature dependence of $\delta\nu$ for Li and Na at normal pressure outside the high-pressure device. The rigid lattice linewidths $\delta\nu_{\text{RL}}$ determined at low temperatures are 14.7 kHz for Li and 4.5 kHz for Na. Line narrowing sets in at about 240 K for Li and at 180 K for Na; it is complete at about 320 K for Li and 220 K for Na. The narrowed linewidth data agree with the 'zero pressure' data of figure 1 if the effect of the magnetic inhomogeneities mentioned above is taken into account. The increase of $\delta\nu$ with rising pressure thus suggests a decrease in motional narrowing, in other words translational diffusion is hindered by pressure.

How does the hindrance of diffusion depend on pressure? To answer the question one must know the rigid lattice linewidth as a function of pressure p , $\delta\nu_{\text{RL}}(p)$. One

way to obtain this quantity is to proceed from the second moment of the resonance line defined as (Abragam 1961)

$$\langle \Delta\nu^2 \rangle = \int_{-\infty}^{+\infty} (\nu - \nu_0)^2 f(\nu) d\nu \quad (5)$$

where $f(\nu)$ is the normalized lineshape function having a maximum at ν_0 . The poor signal-to-noise ratio of the Li and Na signals neither allows a reliable experimental determination of the second moment nor a statement whether $f(\nu)$ is Gaussian or Lorentzian. We assume $f(\nu)$ to be Gaussian in order to evaluate equation (5) exactly. This yields the following relation for the full width of the power spectrum at pressure p in a rigid lattice:

$$\delta\nu_{\text{RL}}^{(\text{G})}(p) = 2 \times 1.69 \sqrt{2 \ln 2} \sqrt{\langle \Delta\nu_{\text{RL}}^2 \rangle} \quad (6)$$

where the index (G) reminds us that this expression is valid for a Gaussian only. The rigid lattice second moment for a polycrystalline cubic sample is given by (Lösche 1957)

$$\langle \Delta\nu_{\text{RL}}^2 \rangle = (1/12\pi^2) C_1 \gamma^4 \hbar^2 I(I+1)/d(p)^6 \quad (7)$$

where $C_1 = 52.281$ and $C_1 = 208.14$ for a BCC and a FCC lattice, respectively; γ is the gyromagnetic ratio of the nuclear spin I ($I = 3/2$ for both Li and Na). $d(p)$ is the cubic lattice constant at pressure p which is related to the lattice constant at ambient pressure, $d(0)$, by

$$d^3(p) V(0) = d^3(0) V(p) \quad (8)$$

where $V(p)$ is the sample volume. Combining equations (6), (7) and (8) finally yields

$$\delta\nu_{\text{RL}}^{(\text{G})}(p) = C_2 \gamma^2 \hbar [V(0)/V(p)] d^{-3}(0). \quad (9)$$

The coefficient C_2 is 5.121 and 10.22 for BCC and FCC lattices, respectively, and spin $3/2$ nuclei. The factor $V(0)/V(p)$ may be calculated from room temperature pressure-volume isotherms (Swenson 1966, Grover *et al* 1969, Vaidya *et al* 1971, Olinger and Shaner 1983). A plot of equation (9) is given by the broken lines in figure 1.

An alternative to determine $\delta\nu_{\text{RL}}(p)$ without the assumption of a Gaussian lineshape is a 'scaling' of the low temperature linewidth. Using the ambient pressure rigid lattice linewidth measured at low temperatures (see above) and taking into account the volume dependence of the lattice constant by the factor $V(0)/V(p)$, we obtain the expression:

$$\delta\nu_{\text{RL}}(p) = \delta\nu_{\text{RL}}(0)[V(0)/V(p)]. \quad (10)$$

Equation (10) is plotted as a solid curve in figure 1.

We note that the rigid lattice linewidths for a Gaussian lineshape (equation (9)) are always slightly smaller than the linewidths $\delta\nu_{\text{RL}}(p)$ as given by equation (10). For Li in the BCC structure the experimental values do not quite approach the rigid lattice 'limit' at high pressures: $\delta\nu$ stays about 3 kHz below $\delta\nu_{\text{RL}}$ given by equation (10). On the other side, for Na the experimental linewidth data approach the theoretical limit predicted by equation (10). We thus conclude that in Na at about 5 GPa

diffusion is hindered to such an extent that it does not narrow the NMR line any more. The line itself is non-Gaussian since its width at high pressure is larger than the value given by equation (9) for a Gaussian. In Li, however, at pressures just below the phase transition, diffusion is less hindered: the phase transition occurs before the lattice has become completely rigid as defined by NMR. The change of the rigid lattice second moment and hence the linewidth $\delta\nu_{\text{RL}}^{(\text{G})}$ at the BCC-FCC phase transition is negligible (broken line in figure 1(a)) because the change in volume is only 0.25% (Olinger and Shaner 1983) which compensates the change of the factor C_1 in equation (7). Experimentally, however, the linewidth is considerably narrowed by the phase transition; this suggests strong diffusion in the high-pressure phase.

3.3. Calculation of diffusion coefficient

Having interpreted the pressure induced line-broadening as the result of hindered diffusion we can estimate the self-diffusion coefficient D for isotropic diffusion if we identify τ of equation (4) as the mean residence time of a jumping metal ion. Then D is given by the modified Einstein equation

$$D = f\langle r^2 \rangle / 6\tau \quad (11)$$

where $\langle r^2 \rangle$ is the mean square jump distance and f is the spatial correlation factor. For diffusion via monovacancies we have $f = 8/11$ (Seeger and Mehrer 1970).

The numerical evaluation of D goes as follows. Equation (10) provides the volume-dependent rigid lattice linewidths $\delta\nu_{\text{RL}}(p)$ for Na and the BCC phase of Li; for the Li FCC phase we use the extrapolated values of the BCC phase (see figure 1). These values together with the actually measured linewidths $\delta\nu(p)$ are inserted into equation (4). This equation then is solved for τ , which is inserted into equation (11). For $\langle r^2 \rangle$ we take the pressure dependent nearest neighbour distance in a BCC or FCC lattice calculated from compressibility data (Grover *et al* 1969). The results for the Li diffusion coefficient are plotted in figure 2.

The Li diffusion coefficient decreases exponentially with rising pressure up to about 4.2 GPa and then remains constant up to the BCC-FCC phase transition. The transition enhances the diffusion coefficient by a factor of about 15. Further increase of pressure seems to lower the diffusion constant again.

The reliability of this estimate can be checked by comparing the diffusion coefficient at ambient pressure with a value determined directly. We have previously measured the ^6Li and ^7Li diffusion coefficients between 350 and 454 K at normal pressure by the NMR pulsed field gradient technique (Mali *et al* 1988). D obeys an Arrhenius law with an average activation energy of 0.561 ± 0.002 eV. Extrapolating those data to 300 K yields for ^7Li the value $6 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$, which is in reasonable agreement with the present value $1.2 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$, keeping in mind the relatively crude evaluation method. The last value is also in fair agreement with the tracer diffusion coefficient $8 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ (average for ^6Li and ^7Li) measured by mass spectroscopy (Lodding *et al* 1970).

From the pressure variation of the diffusion coefficient one can calculate the activation volume ΔV_{a} associated with each atomic jump process according to

$$\Delta V_{\text{a}} = -kT \partial \ln D / \partial p \quad (12)$$

For pressures up to 4 GPa we obtain an activation volume of about $2.1 \times 10^{-30} \text{ m}^3$ ($1.3 \text{ cm}^3 \text{ mol}^{-1}$), which is only 10% of the Li atomic volume at ambient pressure.

This is a relatively small value, which seems to exclude a divacancy jump mechanism (Mehrer 1978). However, whether a monovacancy or an interstitialcy (e.g. Mundy 1971) mechanism causes diffusion cannot be decided on the basis of the present data.

The two facts (i) that the BCC-FCC phase transition occurs before the lattice has become rigid (as defined by NMR), and (ii) the enhancement of the diffusion coefficient at the phase transition seem to reflect the nature of this transition. Stager and Drickamer (1963) studying the effect of pressure on the resistance of some alkali metals, were the first to detect the phase transition in Li. At 296 K, they observed that the resistance rises to a maximum value at 7 GPa and then drops abruptly. At 77 K the drop in resistance was found to be smeared out. This effect was attributed to a possible first order, diffusion-controlled phase transition. Olinger and Shaner (1983) showed by x-ray diffraction that the transition consists of a BCC-FCC transformation taking place at 6.9 GPa and 296 K. Our results seem to support the suggestion of the diffusion-controlled transition.

For Na the only reliable diffusion coefficients are those at 3.2 and 4.0 GPa for the following reasons. At pressures below 3.2 GPa the measured linewidth $\delta\nu(p)$ is too large because of the magnetic inhomogeneities, hence τ comes out too large and therefore D would be too small. At pressures above 5 GPa $\delta\nu_{\text{RL}}(p)$ agrees with the experimental value $\delta\nu(p)$ within the error bars (compare figure 1), hence the calculated τ values are highly uncertain. At 3.2 GPa we obtain a diffusion coefficient of $1.1 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$.

Mundy (1971) has measured the pressure dependence of the ^{22}Na diffusion coefficient up to 1 GPa by the radio-tracer method. His $\ln D-p$ plot exhibits a curvature typical for materials where several diffusion processes are operative. Mundy's value for 1 GPa is $2 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. Mundy could determine three activation volumes: 70, 70 and 30% in the order of increasing pressure. If we assume the curvature to continue to higher pressures, our value for D at 3.2 GPa is in reasonable agreement with the extrapolation. Application of equation (12) to the values of the diffusion coefficients at 1 and 3.2 GPa (Mundy's and our value, respectively) yields an average value $8 \times 10^{-30} \text{ m}^3$ for ΔV_a . This is 20% of the Na atomic volume at ambient pressure and seems to point to a decrease of the activation volume with increasing pressure.

4. Knight shift: results and discussion

4.1. Results

Figure 3 shows the pressure dependence of $\Delta\nu$ which is the shift of the NMR frequency $\nu_m(p)$ at pressure p with respect to the frequency at ambient pressure. For Na we have included the results of Benedek and Kushida (1958). The error bars get larger with rising pressure because of the increasing linewidth.

For Li, $\Delta\nu$ is roughly proportional to pressure up to the phase transition. This result agrees qualitatively with that of Kushida and Murphy (1980) but disagrees with the old data of Benedek and Kushida (1958) who obtained a negative slope for the $\Delta\nu-p$ curve. At the BCC-FCC phase transition the frequency shift becomes negative and stays about constant in the FCC phase. For Na, our data agree with those of Benedek and Kushida (1958), who measured up to about 1 GPa. Around 1.5 GPa the shift is about constant and then increases with rising pressure.

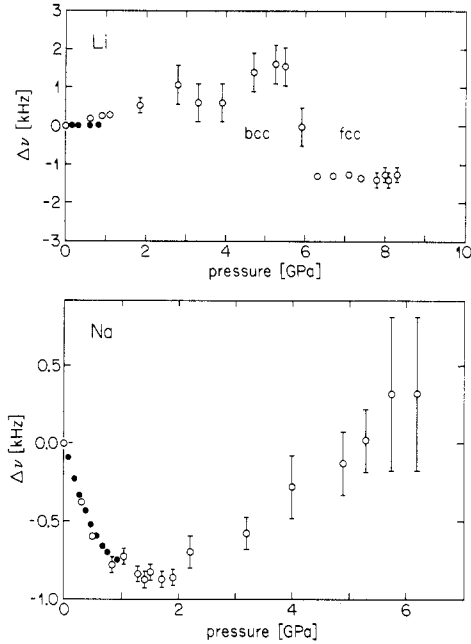


Figure 3. Pressure dependence of the shift of the NMR frequency of ${}^7\text{Li}$ in Li (above) and ${}^{23}\text{Na}$ in Na (below) with respect to the corresponding frequency at ambient pressure. The full circles denote the results of Kushida and Murphy (1980) for Li and of Benedek and Kushida (1958) for Na.

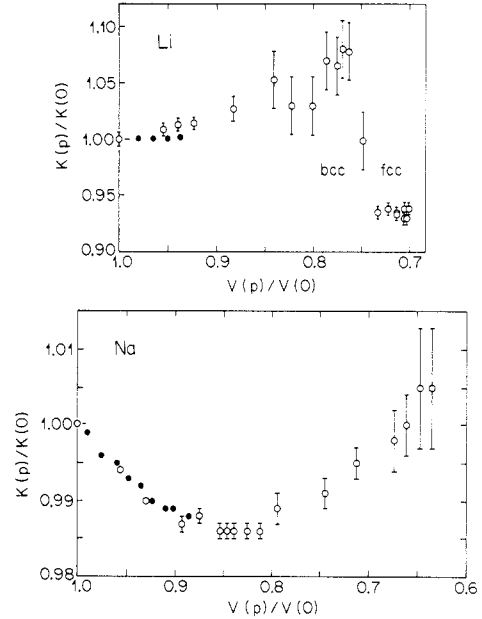


Figure 4. The relative Knight shift (see equation (3)) of ${}^7\text{Li}$ in Li (above) and ${}^{23}\text{Na}$ in Na (below) as a function of the relative volume $V(p)/V(0)$ of the unit cell at pressure p with $V(0)$ being the volume at ambient pressure.

For further discussions it is useful to convert the resonance shift data into relative Knight shifts $K(p)/K(0)$ according to equation (3). In figure 4 these results are plotted as a function of the relative volume $V(p)/V(0)$.

To our knowledge, detailed theoretical treatments of the volume dependence of the Knight shift have only been published by Wilk and Vosko (1981) and only for volume changes smaller than 10%. We therefore compare these theoretical values with our data in figure 5. For lithium we have also included the experimental data of Kushida and Murphy (1979), who measured the shift at 89 °C where the Li signal is very narrow and hence the error bars very small (they are smaller than the symbols used). Their data are smaller than ours, at least for relative volumes $V(p)/V(0)$ smaller than about 0.95%. The origin of this discrepancy is not known.

4.2. Volume dependence of Knight shift

We briefly summarize some theoretical results pertinent to the volume dependence of the Knight shift. Earlier interpretations of experimental Knight shift data took into account only contributions of the hyperfine Hamiltonian of Fermi surface valence electrons (cf. Winter 1971). A contribution which is usually dominating the others (as in Li and Na) comes from the Fermi contact term and can be written as

$$K_d = (8\pi/3)\chi_P\Omega_c P_F \quad (13)$$

where χ_P is the electron spin susceptibility (per unit volume), and P_F is the square of the valence electron wave function (evaluated at the nucleus) averaged over the Fermi

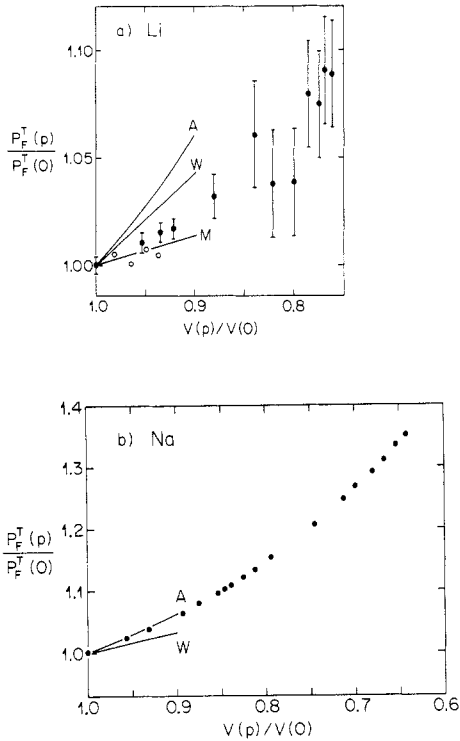


Figure 5. Volume dependence of the relative Knight shift of ${}^7\text{Li}$ in Li (above) and ${}^{23}\text{Na}$ in Na (below). Full circles: this work; open circles: data of Kushida and Murphy (1980); full and open triangles: theoretical values of Wilk and Vosko (1981) according to equation (13) and (14), respectively.

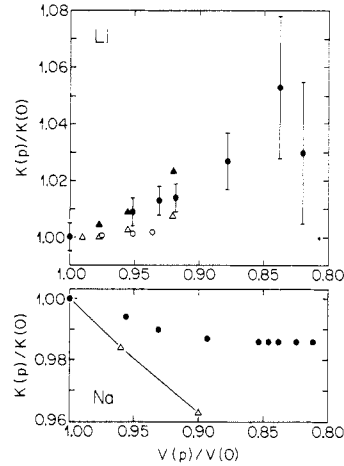


Figure 6. Comparison of experimental data (circles) for the volume dependence of the relative spin density (given by equation (17)) at the nucleus of ${}^7\text{Li}$ in Li (figure 6(a)) and ${}^{23}\text{Na}$ in Na (figure 6(b)) with theoretical values (full curves). Full circles: this work; open circles: data of Kushida and Murphy (1980); M: Mahanti (1974); W: Wilk and Vosko (1981); A: Asano and Yamashita (1973).

surface and normalized over the volume Ω_c of the Wigner-Seitz cell. (The meaning of the index d standing for direct will become apparent shortly.) A second term due to the spin-dipole interaction vanishes in Li and Na because of the cubic site symmetry. A third term arising from orbital motion is expected to be small in Li and Na.

Later on it became apparent that the exchange core-polarization contribution to the contact term can play an important role. Among the first to perform detailed calculations were Mahanti and Das (1971). Later Manninen and Jena (1980) calculated the pressure dependence of the Knight shift in Li and Na using the model of a single ion embedded in an electron gas (jellium model). A drawback of these calculations is that band structure effects which may become important (especially in Li) are not taken into account.

A more recent treatment of the volume dependence of the Knight shift taking into account polarization and band structure effects was performed by Wilk and Vosko (1981). These authors write, for alkali metals, the total contribution of the Fermi contact interaction to the Knight shift as

$$K_s = (8\pi/3)(m(0)/B) \quad (14)$$

where $m(0)$ is the value at the nucleus of $m(\mathbf{r})$, the component of the total electron spin magnetic moment density along the direction of the external magnetic field B . K_s comprises contributions from all electrons (core and valence) that have a non-vanishing probability of being found at the nucleus in contrast to the direct term K_d (equation (13)) which is only due to valence electrons at the Fermi surface. Wilk and Vosko (1981) have performed self-consistent spin-polarized calculations of $m(\mathbf{r})$ within the framework of the spin density functional formalism. Especially in Li, the volume dependence of $m(\mathbf{r})$ is strongly affected by the volume dependence of the core contribution.

The theoretical values given in figure 5 were calculated from first principles (Wilk and Vosko 1981). For K_d , this involved a separate calculation of χ_P and P_F . We note that the Li K_s values come into near agreement with the experimental data of Kushida and Murphy (1979) except for the larger volume changes. For $V(p)/V(0) \geq 0.90$ our data are intermediate between the K_s and K_d curves, while for much larger volume changes it is conceivable that our results favour an extrapolation of the K_s curve. It is obvious that for the high pressure range we need both more precise experimental data and an extension of the theoretical calculations.

For Na the Wilk and Vosko results deviate appreciably from the experimental data of both Benedek and Kushida (1958) and this work which both are in agreement. Wilk and Vosko (1981) attributed this discrepancy to unknown non-local corrections to the exchange-correlation energy functional.

4.3. Volume dependence of spin density

As just mentioned, a direct comparison of theoretical and experimental Knight shifts is not possible. Nevertheless, we can draw from our data some conclusions concerning the volume dependence of the electron spin density at the nucleus. For the following discussion we use the expression for the Knight shift given by Mahanti and Das (1971):

$$K_s = (8\pi/3)\chi_P^A P_F^T \quad (15)$$

with

$$P_F^T = P_F + \sum_l P_{F,l}^{cp} \quad (16)$$

Here, $\chi_P^A = \chi_P \Omega_c$ is the atomic susceptibility. P_F has the same meaning as in equation (13). The terms $P_{F,l}^{cp}$ define additional effective densities at the nucleus arising from the exchange core polarization effect and associated with the l th angular component of the conduction electrons at the Fermi surface.

If the pressure (volume) dependence of the electron spin susceptibility χ_P is known, equation (15) together with the experimental Knight shift data gives directly the pressure dependence of the spin density at the nucleus:

$$\frac{P_F^T(p)}{P_F^T(0)} = \frac{K_s(p) \chi_P^A(0)}{K_s(0) \chi_P^A(p)} \quad (17)$$

For Li and Na, $\chi_P^A(p)$ has been measured up to 0.8 GPa (Kushida *et al* 1976) corresponding to a relative volume $V(p)/V(0)$ of about 0.90. We have extrapolated these values to the smallest volumes we have attained in the following way. In a jellium

model which is appropriate for Na, the Pauli susceptibility χ_P is enhanced with respect to the free electron gas value, χ_F . Kushida *et al* (1976) have shown that in the volume range they studied, the ratio χ_P/χ_F depends only weakly on the Wigner–Seitz radius. This amounts to a change of χ_P/χ_F by about 2% for the pressure range we have used. For Na we therefore assume χ_P^A to be proportional to $V(p)^{2/3}$ in the whole pressure range. In the case of Li the free electron gas approximation cannot be used. However, χ_P^A depends only very weakly on $V(p)$. We therefore have made a linear extrapolation up to the phase transition.

In figure 6 we have plotted equation (17) together with the data of Kushida and Murphy (1980) and some theoretical results. As one would expect, for both Li and Na pressure increases the spin density at the nucleus. The increase of the Li Knight shift with rising pressure is mainly due to this increase of $P_F^T(p)/P_F^T(0)$. The peculiar behaviour of the Na Knight shift is the result of the different pressure behaviour of the atomic susceptibility (decrease with rising pressure) and $P_F^T(p)/P_F^T(0)$ (increase with pressure). At a pressure where the different tendencies cancel, the slope of the $K_s(p)/K_s(0)$ curve must change its sign; this happens around $V(p)/V(0) = 0.84$.

We now turn to the theoretical data of figure 6. As to Li, we note that Asano and Yamashita (1973), who calculated the spin density by means of the Korringa–Kohn–Rostoker (KKR) method taking into account the conduction electron contribution only, obtain a curve which is too steep compared to the experimental data. Wilk and Vosko (1981) who included exchange effects and considered the crystal structure, get a better agreement with experiment. Finally, Mahanti (1974) estimated the volume dependence of the spin density by analyzing the influence of the s and p character of the conduction electron wave function on core polarization. He concluded that the p character has to increase on account of the s character with rising pressure. Though Mahanti's estimation, which is in good agreement with the experiments, is valid only for small volume changes it is tempting to suppose that the decrease of the s character continues up to higher pressures and one might speculate that it even undergoes a drastic reduction at the phase transition. This would be in agreement with the observed drop of the Knight shift.

Since the Knight shift is a product of both the spin density and the Pauli susceptibility one must also consider a possible change of the latter quantity at the BCC–FCC phase transition. Unfortunately there is no experimental or theoretical work about this problem. We believe that the theory of Wilk *et al.* (1979) about the pressure dependence of χ_P at lower pressures which takes account of band structure effects and which is in excellent agreement with the experiments of Kushida *et al.* (1976), could yield the χ_P contribution to the Knight shift reduction at the phase transition.

Figure 6(b) shows our Na Knight shift results together with theoretical data of Asano and Yamashita (1973) and Wilk and Vosko (1981). In this case the latter data lie below the experimental results in contrast to the case of Li. We believe that the agreement of the Asano–Yamashita data with experiment is fortuitous since these calculations depend very sensitively on the crystal potential used.

5. Conclusions

We have measured at room temperature the linewidth and the Knight shift of the ^7Li and ^{23}Na NMR signals at pressures up to 8 and 6 GPa, respectively. From the linewidth data we have concluded that increasing pressure progressively hinders diffusion. In

Li, the hindrance is weaker and the BCC-FCC phase transition seems to be diffusion-controlled; diffusion in the high-pressure FCC phase is larger than in the low-pressure BCC phase. The Li and Na diffusion coefficients have been calculated and a rough estimate of the activation volumes has been made.

The Knight shift data at pressures up to 1 GPa agree quantitatively with earlier data of Benedek and Kushida (1958) for Na. For Li there is qualitative agreement with results of Kushida and Murphy (1980) showing that the shift definitely increases with rising pressure. The increase continues up to the BCC-FCC phase transition where the shift jumps to values below the ambient pressure value of the BCC phase. The Na Knight shift decreases up to about 1.7 GPa and then steadily increases up to the highest pressure (6.2 GPa). This behaviour is explained in terms of different pressure dependences of the atomic susceptibility and the spin density at the nuclear site.

The Knight shift data have been compared with various theoretical predictions that take into account core polarization effects. For Li, the large errors of the present data at high pressure do not yet make it possible to distinguish between extrapolations of various models which exist only for a volume decrease of 10%. For Na, there is striking disagreement with theory.

By extrapolating experimental values for the Pauli susceptibility (Kushida *et al* 1976) we have estimated the pressure dependence of the spin density at the nuclear site. For Li these estimates support considerations of Mahanti (1974) who took into account the influence of the s and p character of the conduction electron wave function on core polarization. Based on these results one may speculate that the drastic reduction of the Knight shift at the phase transition arises, as well as from a possible change of the Pauli susceptibility from a pronounced change of the wave function character.

Our results clearly indicate the need for both improved and more precise experiments which are in progress in our laboratory and an extension of present Knight shift theories to higher pressures.

Acknowledgments

The partial support of our work by the Schweizerischer Nationalfonds is gratefully acknowledged.

References

- Abraham A 1961 *Principles of Nuclear Magnetism* (Oxford: Clarendon)
Asano S and Yamashita J 1973 *J. Phys. Soc. Japan* **34** 1223
Benedek G B and Kushida T 1958 *J. Phys. Chem. Solids* **5** 241
Bertani R, Mali M, Roos J and Brinkmann D 1990 to be published
Carter G C, Bennet L H and Kahan D J 1977 *Metallic Shifts in NMR, Part I-IV, Progress in Materials Science* **20** (Oxford: Pergamon)
Conradi M S, Lee S H, Luszczynski K and Norberg R E 1987 *Rev. Sci. Instrum.* **58** 415
Forman R A, Piermarini G J, Barnett J D and Block S 1972 *Science* **176** 284
Grover R, Keeler R N, Rogers F J and Kennedy G C 1969 *J. Phys. Chem. Solids* **30** 2091
Gutowsky H S and McGarvey B R 1952 *J. Chem. Phys.* **20** 1472
Huber H, Mali M, Roos J and Brinkmann D 1984 *Rev. Sci. Instrum.* **55** 1325
Jayaraman A 1983 *Rev. Mod. Phys.* **55** 65
Jayaraman A 1986 *Rev. Sci. Instrum.* **57** 1013
Kushida T and Murphy J C 1980 *Phys. Rev. B* **21** 4247
Kushida T, Murphy J C and Hanabusa M 1976 *Phys. Rev. B* **13** 5136

- Lodding A, Mundy J N and Ott A 1970 *Phys. Status Solidi* **38** 559
Lösche 1957 *Kerninduktion* (Berlin: VEB Deutscher Verlag der Wissenschaften)
Mahanti S D 1974 *Solid State Commun.* **15** 779
Mahanti S D and Das T P 1971 *Phys. Rev. B* **3** 1599
Mali M, Roos J, Sonderegger M, Brinkmann D and Heitjans P 1988 *J. Phys. F: Met. Phys.* **18** 403
Manninen M and Jena P 1980 *J. Phys. F: Met. Phys.* **10** 1567
Mehrer H 1978 *J. Nucl. Mater.* **69 & 70** 38
Minomura S (ed) 1985 *Solid State Physics under Pressure: Recent Advance with Anvil Devices* (Tokyo: KTK Scientific)
Mundy J N 1971 *Phys. Rev. B* **3** 2431
Olinger B and Shaner J W 1983 *Science* **219** 1071
Seeger A and Mehrer H 1970 *Vacancies and Interstitials in Metals* ed A Seeger et al (Amsterdam: North-Holland) p 1
Stager R A and Drickamer H G 1963 *Phys. Rev.* **132** 124
Swenson C A 1966 *J. Phys. Chem. Solids* **27** 33
Vaidya S N, Getting I C and Kennedy G C *J. Phys. Chem. Solids* **32** 2545
Wilk L and Vosko S H 1981 *Can. J. Phys.* **59** 888
Winter J 1971 *Magnetic Resonance in Metals* (Oxford: Clarendon)
Wolf D 1977 *Phys. Rev. B* **15** 37
— 1978 *J. Appl. Phys.* **49** 2752