Measurement of the Knight Shift of the Positive-Muon-Spin Rotation Frequency in the Alkali and Alkaline-Earth Series and in Copper

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By means of a stroboscopic positive-muon–spin rotation technique, the Knight shift of the local field at positive muons in Na, K, Rb, Cs and Be, Mg, Ca, Sr, Ba and in Cu has been measured to a high precision. The results are discussed in relation to recent theoretical calculations on the local electronic structure of hydrogen in metals.

Information on the local electronic structure of dilute hydrogen in metals is basic to a deeper understanding of many of its properties, such as its site of localization and the induced lattice relaxation, its diffusion, its solubility, its chemical bonding, and its interaction with defects.[1] Despite the importance of such information, only very little is known about the local electronic structure of hydrogen in metals, and consequently of its residual interaction with the lattice environment. For instance, one is sometimes still debating whether hydrogen is in the protonic, anionic, or neutral state in the host lattice.

Significant information on the electronic structure is in principle obtainable from Knight-shift measurements of the local magnetic field at a hydrogen impurity. The Knight-shift constant K is usually given by the expression

$$K = \tfrac{8}{3}\pi \chi_s \rho_s(r_\mu), \tag{1}$$

where $\rho_s(r_\mu)$ is the spin density enhancement at the impurity and χ_s is the conduction-electron spin susceptibility. In conventional Knight-shift theory the spin-density enhancement is simply related to the charge density at the impurity averaged over the Fermi surface,

$$\rho_s(0) = \langle |\psi(r_\mu)|^2 \rangle_F / \bar{n}_0 \tag{2}$$

($\bar{n}_0$ = average conduction-electron density). More recent calculations show that this equality does not necessarily hold true (see below).

The actual values for $\rho_s(r_\mu)$ and/or for $\langle |\psi(r_\mu)|^2 \rangle_F$ depend on the structure of the electron cloud around the proton, screening its positive charge, and are therefore to be derived directly from the established electronic structure in a particular lattice environment. Unfortunately NMR investigations of the Knight shift of protons in metals (α phase) are only available in a few cases such as for Pd,[2] V, Nb, and Ta,[3] where because of the complicated electronic structure of the host metals, any interpretation of measured Knight shifts meets with considerable theoretical difficulties. Indeed, as far as we know, none of the experimental Knight-shift values has found an adequate theoretical explanation.

No Knight-shift data are available for protons in simple metals like Cu or the alkalis, whereas a number of theoretical papers have dealt with the screening and the electronic structure of hydrogen in such metals.[4] To fill this gap in the experimental information we have performed Knight-shift measurements of the local field at positive muons in the alkali and alkaline-earth metals Na, K, Rb, Cs and Be, Mg, Ca, Sr, Ba, and in Cu, at room temperature by means of the positive-muon–spin rotation technique.[5] Some of these metals have already been studied by Hutchinson *et al.*[6] in an earlier μ^+ magnetic moment experiment, where no special consideration was given to sample purity and shape.

The positive muon is used as a proton substitute. Within the limits of the Born-Oppenheimer approximation the electronic structure at positive muons or at protons should be identical (muon mass $\simeq \frac{1}{9}$ proton mass). All experimental evidence points also to the fact that muons and protons occupy the same interstitial lattice sites.

The Knight-shift constant K_μ is obtained from a careful measurement of the magnetic field at the implanted muon, B_μ, and the external field B_{ext}:

$$B_\mu = [1 + (\tfrac{4}{3}\pi - N)\chi_t + K_\mu] B_{\text{ext}}. \tag{3}$$

N is the demagnetization factor and χ_t is the total magnetic susceptibility of the target material. In order to avoid problems arising from the de-

magnetization factor N, spherical targets were used in most cases ($N = \frac{4}{3}\pi$).

The present experiment has been performed at the superconducting muon channel of the Swiss Institute for Nuclear Research (SIN), with an experimental apparatus previously used for a new precision measurement of the magnetic moment of the positive muon,[7] employing a stroboscopic technique[5] (for details concerning the apparatus and the data analysis, see Ref. 7). The applied field was $B_{ext} \simeq 0.75$ T, measured by NMR to a precision of ±1 ppm.

The results for K_μ are listed in Table I together with relevant information on sample properties. The errors quoted are mainly determined by the statistical errors, but contributions of the error in B_{ext} (±1 ppm) of the background (±1 ppm), and of the demagnetization field (±1 ppm, if applicable) are also included.

Comparison of the present results with the older ones by Hutchinson *et al.*[6] (Table I, column 6) shows good agreement for Na, K, and Cu, and no agreement for Mg and Ca. In particular, the old value of $K_\mu = 400$ ppm for Ca points to a possible contamination with magnetic impurities. Included in the table is also an unpublished value for the Knight shift in Al.[8,9]

For further discussion all results are plotted in Fig. 1(a) as a function of the conduction-electron concentration expressed by the density parameter $r_s = (\frac{3}{4}\pi n^{-1})^{1/3} a_B^{-1}$ (n = electron density; a_B = Bohr radius).

Most remarkable are the large negative shift obtained for Be and the somewhat smaller negative ones for Li and Sr. One has the impression that K_μ tends to be small or negative for the metals with high electron density, which are also those that cannot be termed really simple, i.e., free-electron-gas like. For Cu and the alkalis Na, K, Rb, and Cs, which are closer to a free-electron-gas picture, K_μ seems to follow a more systematic dependence on r_s (indicated by the dashed line).

To reveal other possible correlations Fig. 1(b) shows a plot of K_μ versus the Knight shift of the host nuclei and Fig. 1(c) shows K_μ versus the experimentally known or estimated electron spin susceptibilities χ_p of the host metals. The negative K_μ in Be and Li corresponds to a negative, albeit extremely small Knight shift at the Be nuclei (−10 ppm)[13] and a rather small positive one at the Li nuclei (+250 ppm)[14] respectively. The idea behind the plot 1(c) is that χ_p may be a better parameter than r_s to characterize the electronic properties of the host metal. Interestingly all data, except for Be, seem to follow roughly a linear dependence on χ_p with a negative slope (indicated by the dashed line).

TABLE I. Properties of target materials and collection of results.

Target (r_s)	Purity (%)	Disposition	Shape	Knight shift[b] (ppm)	Knight shift[c] (ppm)
Li (3.25)	?	?	?	...	−9.5±19[d]
Na (3.93	> 99.95	solid	thick disk	76.5±5.0	55±11[d]
K (4.86)	> 99.95	solid	thick disk	63.2±4.5	64±11[d]
Rb (5.20)	99.9	solid[a]	sphere[a]	66.1±4.3	
Cs (5.64)	99.99	solid[a]	sphere[a]	34.9±4.4	
Be (1.88)	> 99	powder	sphere	−48.4±5.3	
Mg (2.65)	> 99.8	powder	sphere	20.6±6.5	63±11[d]
Ca (3.27)	99.5	grains	sphere	21.2±6.2	400±15[d]
Sr (3.56)	> 99	solid	sphere	−18.4±6.8	
Ba (3.69)	99.5	solid	sphere	29.6±5.0	
Cu (2.67)	99.999	solid	sphere	57.6±4.0	55±11[d] 58±6[e]
Al (2.07)	?	solid	thin sheets	...	15±15[e]

[a] Sealed off under high vacuum.
[b] The present work.
[c] Earlier work; corrected for target demagnetization field and diamagnetic shielding of protons of the reference NMR probe (Ref. 9).
[d] Ref. 6.
[e] Ref. 8.

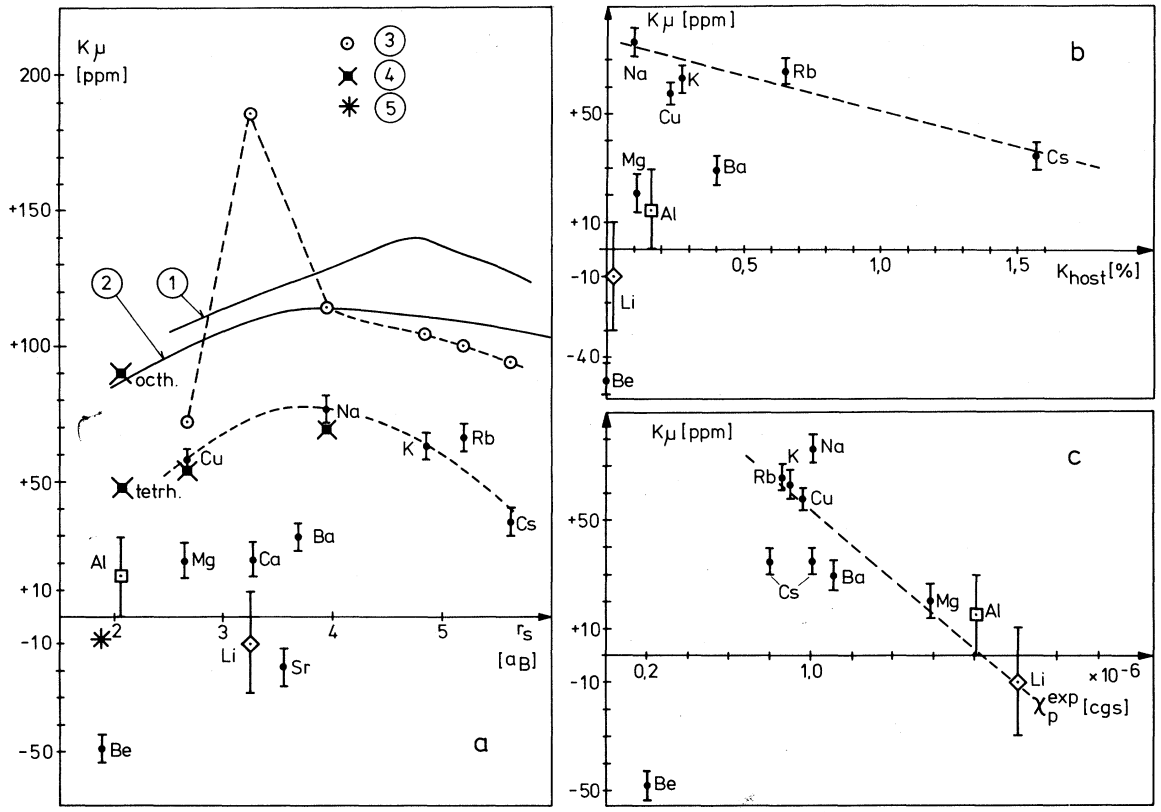

FIG. 1. Measured Knight shift K_μ vs (a) the electron density parameter r_s, (b) the host Knight shift K_{host}, and (c) the electron spin susceptibility χ_p^{exp} of the host material. Theoretical predictions in (a), labeled 1–5, are from Refs. 4, 10, 10, 11, 12, respectively. Dashed lines are intended to guide the eye only.

Next we compare the experimental results to theoretical predictions, also plotted in Fig. 1(a). The curves labeled 1,[4] 2,[10] and 3 [12] represent nonlinear-response calculations in the jellium-model approach, adopting the spin-density-functional formalism. These calculations lead essentially to identical results for $\rho_s(r_\mu)$. The differences in the plotted prediction 1–3 are due to different input data for χ_p, 1 and 2 being calculated using theoretical χ_p values and 3 using experimental values. The calculations also show that $\rho_s(r_\mu) < \langle|\psi(r_\mu)|^2\rangle_F$ for $r_s > 1.9$. The difference is traced back to the occurrence of bound states for $r_s > 1.9$ and magnetic-field–induced wave-function distortions.[10] It is thus not allowed to calculate K_μ using $\langle|\psi(r_\mu)|^2\rangle_F$. Corresponding older predictions are therefore not included in the comparison.

It is obvious that the jellium-model predictions do not reproduce the measured data, although it appears as if at least the general trend of K_μ for the "simple" metals Cu, Na, K, Rb, and Cs parallels the predictions.

Far better agreement with the data is obtained in a calculation by Nieminen and Manninen[11] (labeled 4) for muons in Na, Cu, and Al. It incorporates the effect of the discrete ions surrounding the impurity into a jellium model. It allows one to predict $\rho_s(r_\mu)$ at particular lattice sites; different site assignments lead particularly in Al to different values for K_μ. The prediction for the tetrahedral interstitial position is closest to the experimental value, which is in agreement with recent experimental evidence for a tetrahedral site occupation in Al.[15]

None of the calculations is able, however, to predict a negative Knight shift for the metals investigated. Since the muon does not possess an electron core in the conventional sense, negative contributions to the Knight shift from core polarization will also be absent, in contrast to the situation for the Knight shift at Be nuclei,[16] where such a contribution was found to be very important.

A recent first-principles calculation by Keller and Schenck[12] on the electronic structure of μ^+ in Be metal, using the cluster multiple-scattering technique,[17] suggests that diamagnetic shielding analogous to a chemical shift in molecules may simulate a negative total Knight shift. Such an effect is to be expected if bound states or certain bonding states do exist.[12,18] The calculated total shift of -8 ppm is still far away from the measured value, but has at least the right sign. The cluster bonding states could induce a local-geometry distortion and, furthermore, be polarized by the conduction electrons and contribute an extra negative term in analogy to the classical core-polarization mechanism. This might account for the difference between the calculated and measured value. The possibility that one is observing shifts other than only the direct Knight shift is, of course, most exciting as it would provide a different and sensitive source of information on the electronic structure of hydrogen in metals.

Finally we consider the influence of diffusion and trapping on the present results, obtained at room temperature. Since the time of localization at some preferred lattice site is long compared to the jump time in this temperature range, one expects to observe the Knight shift typical for that site, independent of the jump rate. Trapping in the vicinity of interstitial impurities, which is found to be important at low temperatures, seems to place the muon into the same interstitial sites as self-trapping does, or where hydrogen is found.[16,19,20] It is, therefore, concluded that the present results are largely unaffected by diffusion and trapping.

In conclusion, the present data fill an important gap in experimental information on the electronic properties of "hydrogen" in metals using the positive muon as a proton substitute. Comparison with theory indicates that refinements in the calculations are necessary. The observation of a negative field shift in some instances suggests strongly the presence of bound states or well-localized bonding states between the impurity and its host neighbors. The occurrence of a paramagnetic atomic hydrogen state is, however, definitely ruled out in the metals investigated in this study.

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