

Isotope Effect in the Nuclear Magnetic Resonance in Rubidium

W. E. BLUMBERG, J. EISINGER, AND M. P. KLEIN*

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received May 19, 1961)

By performing precise measurements of the nuclear magnetic resonance frequencies at constant field of the stable Rb isotopes in a metallic sample and in RbCl solution, we determined $\Delta = k^{85}/k^{87} - 1 = (0.38 \pm 0.03)\%$, where $k^{85,87}$ is the Knight shift of Rb^{85,87}. Δ is the hyperfine structure anomaly which will be equal to $\Delta(s_{\frac{1}{2}})$, determined from Rb(*5s* $S_{\frac{1}{2}}$) atomic beam experiments only if the hyperfine interaction responsible for the Knight shift arises from $s_{\frac{1}{2}}$ conduction electrons. The experimental results show that to high precision this is the case.

WHEN the nuclear magnetic resonance (NMR) frequency of nuclei in a metallic sample is compared with that of the same nuclei imbedded in an insulating diamagnetic substance, it is found that the nuclei in the metal usually "see" an effective magnetic field which exceeds the applied field. The fractional shift to higher fields is commonly called the Knight shift k , and is thought to have its origin in the paramagnetism of the unpaired conduction electrons. k is therefore a measure of the number of conduction electrons and the magnetic field they produce inside the nuclei under study. It can readily be shown that¹

$$k = a\chi M / 2g\mu_B, \quad (1)$$

where a is the hyperfine interaction between the nucleus and a conduction electron, g is the nuclear g factor, χ is the susceptibility of the conduction electrons, and M is the atomic mass. If a is isotropic, k will also be isotropic. It is generally assumed that a arises solely from $s_{\frac{1}{2}}$ electrons since the contact interaction for these will be particularly large.

Since $s_{\frac{1}{2}}$ electrons have a density maximum at the nucleus, their hyperfine interaction is sensitive to both the electron wavefunction inside the nucleus and the nuclear magnetization distribution,^{2,3} and one defines for two isotopes (e.g., Rb⁸⁵ and Rb⁸⁷) the so-called hyperfine structure anomaly

$$\Delta = (a^{85}/a^{87})(g^{87}/g^{85}) - 1. \quad (2)$$

Δ is of the order of a fraction of a percent for $s_{\frac{1}{2}}$ electrons. The sign and magnitude of Δ reflects differences in the nuclear structures of the two isotopes.

It can readily be seen from (1) and (2) that if the hyperfine interaction arises from $s_{\frac{1}{2}}$ electrons only,

$$\Delta(s_{\frac{1}{2}}) = (k^{85}/k^{87}) - 1. \quad (3)$$

Since $\Delta(s_{\frac{1}{2}})$ has been measured to considerable precision by atomic beam experiments on Rb atoms which are known to be in a pure (*5s*)² $S_{\frac{1}{2}}$ state, an experimental

verification of (3) would demonstrate unambiguously that the hyperfine interaction in the metal involves $s_{\frac{1}{2}}$ electrons only.

EXPERIMENTAL

Recalling the definition of k [Eq. (1)] and using it in Eq. (3), one can show that

$$\Delta(s_{\frac{1}{2}}) = (1/k)[(g_m^{85}/g_m^{87})(g^{85}/g^{87}) - 1], \quad (4)$$

where g_m refers to the effective nuclear g factor in the metal, g is the g factor in a diamagnetic compound or solution, and k is the average of k^{85} and k^{87} . k is obtained from a comparison of g_m and g . g is not entirely independent of the chemical composition of the solution and the range of its value in various substances limits the precision of k . From an experimental point of view our task of determining Δ can therefore be considered to consist in the accurate determination of three ratios of resonance frequencies. The three ratios are (g_m^{85}/g_m^{87}) , (g^{85}/g^{87}) , and say, (g_m^{87}/g^{87}) .

The two samples used were Rb⁺ ions in an aqueous solution and metallic Rb dispersed in mineral oil. The latter sample was made by dispersing the metal by means of a high-speed stirrer in an inert atmosphere at about 60°C and cooling the sample slowly to room temperature with the stirrer still operating to prevent coagulation of the small metal droplets. The former sample was a saturated RbCl solution which was chosen because it showed the narrowest NMR line for Rb from among the three Rb salts investigated. The spread of chemical shifts between RbCl, RbI, and RbHCO₃ was 3 parts in 10⁵. If this spread is taken as the order of magnitude of the chemical shift, it limits the precision to which k (and Δ) can be determined to 5 parts in 10³. As will be seen below, this is too small an error to affect the final precision of Δ .

The experiments were performed at room temperature with a wide-band high-resolution, 12-in. Varian spectrometer without superstabilizer. All resonances were observed by keeping the rf frequency constant and slowly sweeping the magnetic field through its resonance value, approximately 4.8 and 16 Mc/sec for Rb⁸⁵ and Rb⁸⁷, respectively. The field was monitored by a Varian 4400 NMR deuterium probe and the Rb and D signals

* On leave of absence from Lawrence Radiation Laboratory, University of California, Livermore, California.

¹ W. D. Knight, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 93.

² A. Bohr and V. F. Weisskopf, *Phys. Rev.* **77**, 94 (1950).

³ J. Eisinger and V. Jaccarino, *Revs. Modern Phys.* **30**, 528 (1958).

were recorded simultaneously on a Sanborn two-channel recorder.

The metal sample was dispersed finely enough so that the skin effect which mixes the χ' and χ'' modes was unimportant, and the probe was tuned to a pure χ'' signal.

The observed lines were Lorentzian in shape and the half widths of the Rb^{85} and Rb^{87} solution and Rb^{85} and Rb^{87} metal resonances were 0.17, 0.12, 1.7, and 1.7 oe, respectively. The rf power was adjusted to maximum value which did not cause saturation, and the modulation amplitude was set as high as possible without causing line broadening. Mieher⁴ has predicted $T_1(\text{Rb}^{87})/T_1(\text{Rb}^{85})=1.027$ if the quadrupole interaction provides the relaxation mechanism. Our results do not bear out that this is the case in either the metal or RbCl solution.

Our precision was limited by the signal-to-noise ratio of the Rb^{85} metal resonance line, which was about 30:1. We took 18 and 24 traces of the Rb^{85} and Rb^{87} resonances, respectively, half of them with H_0 increasing and the other half with H_0 decreasing. The field difference between the D and Rb samples was monitored and corrected for. Our results are

$$g_m^{85}/g^{85}=1.006527\pm 1.2 \text{ ppm}, \quad (5)$$

$$g_m^{87}/g^{87}=1.006502\pm 0.3 \text{ ppm}, \quad (6)$$

$$g_D/g^{85}=1.5898784\pm 0.6 \text{ ppm}, \quad (7)$$

$$g_D/g^{87}=0.46913152\pm 0.1 \text{ ppm}, \quad (8)$$

where g_D is the effective deuterium g factor and the quoted errors in parts per million are the most probable statistical errors. From (5) and (6)

$$k=\frac{1}{2}(k^{85}+k^{87})=(0.6514\pm 0.0002)\% \quad (9)$$

with an additional uncertainty of about $\pm 0.003\%$ from the uncertainty of the chemical shifts. Using (5) and (6) in (4) we find

$$\Delta_{\text{exp}}=(0.38\pm 0.02)\%.$$

We estimate that if we include the systematic error introduced by a slow change with time in the field difference between the Rb and D sample positions in the course of an experiment, the total error might be in-

creased by 50% so that

$$\Delta_{\text{exp}}=(0.38\pm 0.03)\%. \quad (10)$$

The atomic beam value for $\Delta(s_{\frac{1}{2}})$ is obtained from the hyperfine interaction ratio⁵ and the present value for g^{85}/g^{87} , obtained from (7) and (8);

$$g^{85}/g^{87}=0.2950738\pm 0.0000005, \quad (11)$$

which overlaps the value obtained by other workers⁶ but is somewhat more accurate. In this way one finds

$$\Delta(s_{\frac{1}{2}})=(0.3513\pm 0.003)\%. \quad (12)$$

DISCUSSION

The agreement between (10) and (12) shows that the electrons responsible for the Rb Knight shift and the hyperfine interaction in atomic Rb have the same fractional s character. This is so because $s_{\frac{1}{2}}$ electrons are the only ones which could contribute significantly to the hyperfine structure anomaly Δ . Since the valence electron of Rb is almost certainly in a pure $s_{\frac{1}{2}}$ state, we may conclude that the Knight shift in Rb metal is caused by pure $s_{\frac{1}{2}}$ electrons because an appreciable contribution from non- s electrons would make Δ smaller than $\Delta(s_{\frac{1}{2}})$. This justifies the assumptions made by Townes *et al.*⁷ in explaining the origin of Knight shifts.

The present experiment can also be used as justification for employing the isotope effect of the isotropic part of the Knight shift to measure differences in nuclear magnetization distributions of isotopic pairs which cannot be studied conveniently by the other methods⁸ available for such determinations.

ACKNOWLEDGMENTS

We wish to thank S. Meiboom for being kind enough to put his NMR apparatus at our disposal and E. Wasserman for loaning us the apparatus used in the metal sample preparation.

⁵ S. A. Ochs and P. Kusch, Phys. Rev. **85**, 145 (1952); B. Beder-son and V. Jaccarino, *ibid.* **87**, 228(A) (1952).

⁶ E. Yasaitis and B. Smaller, Phys. Rev. **82**, 750 (1951); N. Adams, T. Wimmert, and F. Bitter, *ibid.* **82**, 343(A) (1951).

⁷ C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

⁴ R. L. Mieher, Phys. Rev. Letters **4**, 57 (1960).