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The nuclear paramagnetic resonance frequency for an atom in the metallic state usually is appreciably greater than the resonance frequency when the atom is in a nonmetallic compound. These frequency shifts are of the order of a few tenths of one per cent, and are hence much too large to be accounted for by a simple difference in magnetic susceptibility of the materials or by differences in diamagnetic correction for the metallic and nonmetallic atoms. It is proposed that such shifts are primarily due to orientation by the magnetic field of the spins of conduction electrons near the top of the Fermi distribution, and the interaction of these electrons with the nuclei. Since the conduction electrons usually have a very large probability density near the nucleus, this may be understood as an enormous concentration of the local magnetic susceptibility of the metal in the vicinity of the nuclei. It may also be compared with and calculated from the magnetic hyperfine structure interactions in an isolated atom. Diamagnetic effects of the same type appear to be very much smaller since the electronic currents responsible for the diamagnetism of the conduction electrons are appreciable only in the outer regions of the atom. We shall show that the coupling between electronic paramagnetism and the nuclei gives approximately the correct magnitude of shift and that in the few cases where information about the wave functions of electrons in the conduction bands is available, the calculated values agree reasonably well with the measured shifts. In other cases, this effect may be used to evaluate the product of the paramagnetic term in the susceptibility by the density of Fermi level electrons at the nucleus.

The fractional shift in nuclear resonance frequency between metal and nonmetal is simply the fractional amount by which the presence of the conduction electrons increases the mean magnetic field strength $H$ at the nucleus. Neglecting the small diamagnetic effect, we consider only the field $\Delta H$ due to the electron spins, which is $8\pi/3$ times the mean density of spin moment at the nucleus. In terms of wave functions of individual electrons in the metal the latter quantity can be written $\chi_p MH \frac{|\psi_F(0)|^2}{|\psi_F(0)|^2}$, where $\chi_p$ is the spin contribution to the macroscopic susceptibility per unit mass, $M$ is the mass of one atom, and $|\psi_F(0)|^2$ is the average probability density at the nucleus for all electronic states on the Fermi surface. Now the hyperfine structure splitting $\Delta \nu$ for an $s$ electron in the free atom is proportional to $|\psi_a(0)|^2$, where $\psi_a$ is the wave function of the $s$ electron in the free atom. Dividing the above expression for $\Delta H$ by the familiar Fermi expression for $\Delta \nu$ gives the fractional frequency shift in terms of a ratio of metallic and atomic wave functions:

$$\frac{\Delta H}{H} = \frac{\hbar c \Delta \nu \mu_p M}{\mu_e (2I + 1)} \frac{|\psi_F(0)|^2}{|\psi_a(0)|^2}$$

where $\hbar c \Delta \nu$ is the hyperfine splitting in energy units, $\mu_e$ is the Bohr magneton, $\mu_I$ is the nuclear moment, and $I$ the nuclear spin.

We have attempted to calculate the theoretical value of the last factor in Eq. 1 for the cases (Na, Li, Be) for which adequate calculations of metallic wave functions are at present available. This factor may be written $\frac{(\psi_o(0)|^2/\psi_a(0)|^2) \bar{s}_k}{\bar{s}_k}$, where $\psi_o$ is the wave function of an electron at the bottom of the conduction band and $\bar{s}_k$ is the mean over the Fermi surface of $s_k = |\psi_k(0)|^2/|\psi_o(0)|^2$.

*Work of C. H. Townes and W. D. Knight largely performed at Brookhaven National Laboratory.
Calculations by the Wigner-Seitz method\(^2\) give \(\psi_0\); \(S_k\) can be determined in either of two ways. The first, suitable only for monovalent metals, is to assume that \(S_k\) is adequately represented by the first two terms of its development in powers of the square of the electronic wave vector \(k\):

\[
s_k = 1 + k^2 \frac{d}{d(k^2)} + \ldots
\]

and to use the expression given by Herring and Hill\(^3\) for \(d\psi_k/d(k^2)\) (Appendix III of this reference; a factor 6 should be inserted before \(\alpha\) in Eq. M.) This method was applied to the case of Na with the aid of wave functions kindly supplied by Dr. Bardeen, and gave \(S_k = 0.70\). Similar calculations were made for Li, but no result will be quoted because it was found that the available wave functions were based on an incorrect potential field for the Li ion. Comparison with the case of Be, to be discussed next, suggests that \(S_k\) for Li may be of the order of 0.4. For Be, which is divalent, the first two terms of Eq. 2 do not give a good approximation, and a second procedure was therefore adopted. This consisted in dividing up the Fermi surface into six portions, estimating an average \(S_k\) for each portion from the values of \(S_k\) directly calculated for states near the Fermi surface (Table VII of reference 3), and combining with suitable weights. This gave \(S_k = 0.32\), and this value did not seem to be particularly sensitive to changes in the technique of averaging.

The quantity \(|\psi_0(0)|^2/|\psi_a(0)|^2\) has approximately the values 1.16, 1.9, and 1.6, for Na, Li, and Be, respectively. For other metals its behavior can be inferred qualitatively by noting how much of the charge of the outermost \(s\) electrons of the free atom lies outside a sphere whose volume equals the atomic volume of the metal; it appears from this that \(|\psi_0(0)|^2/|\psi_a(0)|^2\) should be appreciably smaller for such multivalent metals as Al, Ga, and Pb than for the mono- and divalent ones.

Table 1 gives some experimental values of the relative frequency shift, values of \(\chi p|\psi_F(0)|^2/|\psi_a(0)|^2\) computed from these shifts by use of Eq. 1, and, for Li, Na, and Be, the results of theoretical attempts to calculate this product by the methods outlined above. In all cases of Na, the most uncertain factor is probably the value of \(\chi p\). Though no quantitative comparisons of theory and experiment can be made at present for other metals than these three, it will be noted that the figures in the table are consistent with reasonable values for \(\chi p|\psi_0(0)|^2/|\psi_a(0)|^2\), and \(S_k\). The case of Be is interesting in that the shift is too small to measure, indicating values of \(S_k\) and/or \(\chi p\) still smaller than those calculated. The shift in Pb indicates the considerable size which this paramagnetic effect may have in heavy metals.

### Table 1—Observed Shifts of Nuclear Resonances in Metals Due to Free Electron Paramagnetism, and Comparison With Theory

| Nucleus | Hfs splitting \(\Delta \nu\), in cm\(^{-1}\) for s electron | Observed shift \(\Delta H/H\), per cent | \(\chi p|\psi_F(0)|^2/|\psi_a(0)|^2\) Theory From Eq. 1 |
|---------|-------------------------------------------------|-------------------------------------|------------------------------------------|
| Li\(^{7}\) | 0.027 | 0.04 | 3.0\(*\) | ~2.3 | 2.6 |
| Na\(^{23}\) | 0.060 | 0.10 | 0.88\(†\) | 0.80 | 0.83 |
| Cu\(^{63}\) | 0.40 | 0.23 | ~0.11\(‡\) | 0.077 |
| Be\(^{9}\) | 0.040 | <0.002 | ~0.30\(§\) | ~0.15 | <0.025\(¥\) |
| Pb\(^{207}\) | 3.0 | 1.2 | ~0.10\(‡\) | 0.0067 |
| Al\(^{27}\) | 0.49 | 0.16 | ~0.47\(‡\) | 0.13 |
| Ga\(^{69}\) | 0.86 | 0.44 | ~0.20\(‡\) | 0.055 |

\(*\) Measured value with diamagnetic corrections.\(^4\)
\(†\) Average of measured values with diamagnetic corrections.\(^5\)
\(‡\) Calculated value assuming free valence electrons.
\(§\) Theoretical value.\(^3\)
\(¥\) The small diamagnetic contribution to the shift may increase this limit by a factor of 2 or so.
It is interesting to note that the theoretical calculation of $X_p \bar{E}_k$ is very similar to the calculation of the form of the $L_{2,3}$ X-ray emission bands of a metal. For the intensity of the latter at any given frequency is proportional to the average amount of s function contained in the electronic states from which the transition occurs, multiplied by the number of these states per unit energy, and the latter quantity is proportional to $X_p$.

REFERENCES