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Effects of Electron-Electron Interactions on Nuclear Spin-Lattice Relaxation Rates and Knight Shifts in Alkali and Noble Metals*

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Nuclear-magnetic-resonance data for the alkali and noble metals are discussed in terms of Moriya's theory of exchange-enhanced spin-lattice relaxation rates. The available evidence suggests that the relaxation-rate enhancement resulting from collective electron effects is ~20% smaller in lithium and sodium than predicted by the theory for the case of a δ-function-potential electron-electron interaction. This small disparity is attributed to a nonzero interaction range whose magnitude is estimated to be less than an atomic radius. During the course of this study, low-temperature Knight-shift and spin-lattice relaxation data have been obtained for ^{39}K, ^{85}Rb, ^{87}Rb, and ^{133}Cs in the respective metals. The results suggest that the exchange enhancements of the conduction-electron spin susceptibilities in these metals are comparable to those in lithium and sodium. Similar conclusions apply in the case of the noble metals.

I. INTRODUCTION

THE Knight-shift K and nuclear spin-lattice relaxation time T_1 for a nucleus with gyromagnetic ratio γ_n coupled to a system of noninteracting conduction electrons obey the Korringa relation $\gamma_n{}^2K^2T_1T=\text{const}$,[1] provided that the s-contact interaction represents the only hyperfine coupling mechanism between the electronic and nuclear spins. In practice, the Korringa relation is seldom satisfied. Even in the monovalent alkali metals, where the requirement of a dominant s-contact interaction should be reasonably well satisfied, the experimental values of K^2T_1T are appreciably larger than predicted. These disparities have generally been attributed to repulsive electron-electron interactions which are known to enhance the spin susceptibility of an electron gas relative to its independent particle value. Early efforts[2] to correct the Korringa relation for these exchange effects focused attention on the Knight shift which is enhanced by the same factor as the uniform conduction-electron spin susceptibility. However, when applied to the simple metals lithium and sodium this correction to the Korringa relation was found to be inadequate. The magnitudes of the exchange enhancement factors required to bring theory and experiment into agreement were appreciably smaller than those inferred from direct measurements of the uniform spin susceptibilities. This result provided evidence that the nuclear spin-lattice relaxation rate is also enhanced by electron-electron interactions, the magnitude of the enhancement being smaller, however, than that of the square of the Knight shift. Pines[2] attempted to take approximate account of this enhancement by replacing the bare-electron density of states which appears in the rate expression by its many-body value. This approach, however, is incorrect since the electron-phonon enhancement of the density of states is accompanied by a corresponding reduction in the hyperfine constant.[3] Subsequently, Moriya[4] gave a correct treatment of the exchange-enhanced nuclear spin-lattice relaxation rate in terms of the wave number and frequency-dependent susceptibilities of the interacting electron gas. He obtained numerical values for the enhancement of the relaxation rate for metals with spherical Fermi surfaces and δ-function electron-electron interaction potentials (treated in the usual random-phase approximation) which, for the first time, seemed to provide a quantitative explanation for the difference between observed and calculated Korringa products (K^2T_1T) in lithium and sodium. Because of this success, it seemed that the nuclear-magnetic-resonance (NMR) technique might provide a useful method for the determination of exchange-enhanced spin susceptibilities of simple metals. For example, when applied[5] to NMR Knight-shift and spin-lattice relaxation data for the noble metals copper, silver, and gold, Moriya's theory yielded reasonable values for the respective exchange-enhancement parameters. Recently, however, we have discovered an error in Moriya's numerical results. In its corrected form, the theory predicts enhancement factors for the spin-lattice relaxation rate that are too large to be consistent with measured values of K^2T_1T.

The principal purpose of this paper is to present a critical comparison of Moriya's theory of exchange-enhanced nuclear spin-lattice relaxation rates with experimental data for the alkali and noble metals. This comparison is based in part on new low-temperature NMR data for potassium, rubidium, and cesium. A

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[1] J. Korringa, Physica **16**, 601 (1950).

[2] D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1.

[3] See, for example, V. Jaccarino, in *Proceedings of the International School of Physics, Enrico Fermi, Course XXXVII*, edited by W. Marshall (Academic Press Inc., New York, 1967), p. 365.

[4] T. Moriya, J. Phys. Soc. Japan **18**, 516 (1963).

[5] A. Narath, Phys. Rev. **163**, 232 (1967).

review of the relevant theory is given in Sec. II. Experimental details are described in Sec. III. The experimental results obtained in the present study combined with those of previous measurements are compared against theory in Sec. IV. Our conclusions are summarized in Sec. V.

II. REVIEW OF THEORY

The contact hyperfine interaction between a nuclear spin $\mathbf{I}_i$ and conduction-electron spins $\mathbf{S}_j$ may be written

$$\mathcal{H}=-\tfrac{1}{3}(8\pi)\gamma_e\gamma_n\hbar^2\mathbf{I}_i\cdot\sum_j\mathbf{S}_j\delta(\mathbf{r}_{ij}),\qquad(2.1)$$

where γ_e and γ_n are the electronic and nuclear gyromagnetic ratios, respectively, and the $\mathbf{r}_{ij}$ are appropriate position coordinates. The interaction (2.1) gives rise to a shift in the field for nuclear resonance:

$$\Delta H=(\gamma_n\hbar)^{-1}\sum_{\mathbf{k},\sigma}A_{\mathbf{kk},\sigma\sigma}m_\sigma f_{\mathbf{k},\sigma},\qquad(2.2)$$

where $m_\sigma=\pm\frac{1}{2}$ is the spin-projection quantum number and $f_{\mathbf{k},\sigma}$ is the Fermi distribution function for a state of wave vector $\mathbf{k}$ and spin orientation σ. The generalized contact hyperfine coupling parameter $A_{\mathbf{kk}',\sigma\sigma'}$ is defined in terms of the amplitudes $u_{\mathbf{k},\sigma}(0)$ of the conduction-electron wave functions at the nucleus by

$$A_{\mathbf{kk}',\sigma\sigma'}=\tfrac{1}{3}(8\pi)\gamma_e\gamma_n\hbar^2u_{\mathbf{k},\sigma}(0)^*u_{\mathbf{k}',\sigma'}(0).\qquad(2.3)$$

The fluctuations associated with the transverse part of the interaction (2.1) give rise to a nuclear spin-lattice relaxation rate

$$T_1^{-1}=(2/\hbar^2)\int_{-\infty}^{+\infty}d\tau\cos(\omega_0\tau)\langle\{\mathcal{H}^+(\tau)\mathcal{H}^-(0)\}\rangle,\qquad(2.4)$$

where ω_0 is the nuclear Larmor frequency and the bracketed term is the symmetrized, transverse autocorrelation function of the hyperfine interaction.

In the independent-particle approximation, (2.2) and (2.4) reduce to the following standard form, provided only that the hyperfine interaction parameters are independent of σ (i.e., $A_{\mathbf{kk}',\sigma\sigma'}=A_{\mathbf{kk}'}$):

$$K_0\equiv\Delta H/H=(2/|\gamma_e\hbar|)H_{\text{hfs}}\chi_0,\qquad(2.5)$$

$$(T_{1,0})^{-1}=4\pi\gamma_n^2\hbar k_BT[H_{\text{hfs}}N(0)]^2,\qquad(2.6)$$

where k_B is Boltzmann's constant, T is the absolute temperature, and

$$H_{\text{hfs}}=-(\gamma_n\hbar)^{-1}\langle A_{\mathbf{kk}}\rangle,\qquad(2.7)$$

the average being taken over all states at the Fermi level. Since the uniform conduction-electron spin susceptibility χ_0 and the density of electronic states at the Fermi level $N(0)$ are related in this approximation by

$$\chi_0=\tfrac{1}{2}(\gamma_e\hbar)^2N(0),\qquad(2.8)$$

one obtains immediately the Korringa relation[1]

$$K^2T_{1,0}T=\mathcal{S},\qquad(2.9)$$

$$\mathcal{S}\equiv(\gamma_e/\gamma_n)^2(\hbar/4\pi k_B).\qquad(2.10)$$

In the presence of electron-electron interactions, the expressions (2.2) and (2.4) can be simplified easily only if two important assumptions can be made: (1) The effects due to electronic exchange and correlation can be represented by an effective potential $V(\mathbf{q})$ whose magnitude depends at most on the momentum transfer $\hbar\mathbf{q}$ between interacting electrons. (2) The wave-vector dependence of the hyperfine interaction parameters can be approximated by $A_{\mathbf{k+q},\mathbf{k}}=A_{\mathbf{q}}$. This assumption should be valid only for metals in which the Fermi surface is nearly spherical and is contained within the first Brillouin zone. These severe restrictions can only be justified in the case of the alkali metals and perhaps to a lesser extent the noble metals.

The first of these assumptions permits the sum in (2.2) to be separated as for the noninteracting case. The Knight shift K is therefore still given by (2.5) provided that the uniform spin susceptibility χ_0 is replaced by its many-body value χ. If the enhancement of χ_0 is expressed in terms of the usual Stoner factor $(1-\alpha)^{-1}$, where $\alpha=[2V(0)/(\gamma_e\hbar)^2]\chi_0$, the Knight shift may be written

$$K=K_0(1-\alpha)^{-1}.\qquad(2.11)$$

The second assumption leads to an expression for the spin-lattice relaxation rate of the form[4]

$$T_1^{-1}=(2\hbar^2)^{-1}\sum_{\mathbf{q}}|A_{\mathbf{q}}|^2\int_{-\infty}^{+\infty}d\tau\cos(\omega_0\tau)\times\langle\{S_{\mathbf{q}}^+(\tau)S_{-\mathbf{q}}^-(0)\}\rangle,\qquad(2.12)$$

where the $S_{\mathbf{q}}(\tau)$ are related to the Fourier components of the time-dependent spatial electronic spin density. They are defined by

$$S_{\mathbf{q}}(\tau)=\tfrac{1}{2}\sum_{\mathbf{k}}\mathbf{a}_{\mathbf{k+q}}^\dagger(\tau)\boldsymbol{\sigma}\mathbf{a}_{\mathbf{k}}(\tau),\qquad(2.13)$$

where $\mathbf{a}_{\mathbf{k}}^\dagger$ and $\mathbf{a}_{\mathbf{k}}$ are two-component creation and annihilation operators, respectively, and $\boldsymbol{\sigma}$ are the Pauli spin matrices. According to the fluctuation-dissipation theorem, the Fourier-transformed spin-correlation function in (2.12) can be expressed in terms of the imaginary part of an appropriate linear response function. This yields

$$T_1^{-1}=(2/\hbar^2)k_BT(\gamma_e\hbar)^{-2}\sum_{\mathbf{q}}|A_{\mathbf{q}}|^2\omega_0^{-1}\chi''(\mathbf{q},\omega_0).\qquad(2.14)$$

The susceptibility function $\chi(\mathbf{q},\omega)$ has the form of the reduced susceptibility of Izuyama *et al.*[6] and refers to

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[6] T. Izuyama, D. Kim, and R. Kubo, J. Phys. Soc. Japan **18**, 1025 (1963).

an electron gas which differs from the real metal only in that the actual spatial distribution of the electrons is replaced by a uniform distribution. This property, which follows from the definition (2.13), has the important consequence that umklapp processes do not affect the reduced susceptibility. It is interesting to note that cross sections for inelastic magnetic scattering of neutrons by itinerant electrons depend on the real susceptibility, which is usually assumed to differ from the reduced susceptibility by the square of a multiplicative, **q**-dependent form factor. This factor is analogous to the coupling constant $A_{\mathbf{q}}$ appearing in the present case. In both cases the factorization of a reduced susceptibility from the relevant response function requires that the individual coupling constants depend only on the wave-vector difference between the initial and final states connected by the perturbation.

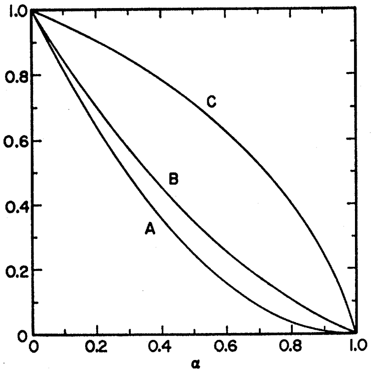

FIG. 1. Plots of calculated reciprocal enhancement factors for (a) K^2, (b) $(T_1T)^{-1}$, and (c) K^2T_1T for the case of a δ-function electron–electron interaction as a function of the interaction parameter α.

The reduced susceptibility function is given in the random-phase approximation by[7]

$$\chi(\mathbf{q},\omega_0)=\chi_0(\mathbf{q},\omega_0)\left[1-(2V(\mathbf{q})/\gamma_e^2\hbar^2)\chi_0(\mathbf{q},\omega_0)\right]^{-1}, \tag{2.15}$$

provided that $V(\mathbf{q})=\text{const}$. For **q**-dependent interaction constants (2.15) is only valid for exchange between localized orbitals (extreme tight binding limit). In the limit of small ω_0 the imaginary part of Eq. (2.15) becomes

$$\chi''(\mathbf{q},\omega_0)=\chi_0''(\mathbf{q},\omega_0)\left[1-(2V(\mathbf{q})/\gamma_e^2\hbar^2)\chi_0'(\mathbf{q},0)\right]^{-2}. \tag{2.16}$$

TABLE I. Comparison of $K(\alpha)$ values with previous results.

α	Present work	Moriya[a]
0	1.0000	1.0000
0.10	0.9565	
0.20	0.9077	0.762
0.30	0.8522	
0.40	0.7885	0.531
0.50	0.7147	
0.60	0.6277	0.313
0.70	0.5233	
0.80	0.3950	0.120
0.90	0.2307	
0.95	0.1276	

[a] Reference 4.

Substituting Eq. (2.16) into Eq. (2.14), and making use of the well-known expressions for the real and imaginary parts of the noninteracting reduced susceptibility, yields

$$T_1^{-1}=\hbar^{-2}k_BT\pi\omega_0^{-1}\times\sum_{\mathbf{q}}|A_{\mathbf{q}}|^2\left[1-(2V(\mathbf{q})/\gamma_e^2\hbar^2)\chi_0F(\mathbf{q})\right]^{-2}\times\sum_{\mathbf{k}}(f_{\mathbf{k}+\mathbf{q}}-f_{\mathbf{k}})\delta(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}+\hbar\omega_0), \tag{2.17}$$

where $f_{\mathbf{k}}$ and $E_{\mathbf{k}}$ refer to the independent-particle states, χ_0 is given in volume units, and $F(\mathbf{q})$ is the static response function for the noninteracting electron gas. The rate expression (2.17) can be simplified for two limiting cases.

Case (a)

We assume that the range of the electron-electron interaction is great enough that the enhancement of the dissipative part of the spin susceptibility is only significant for vanishly small q values [i.e., $V(\mathbf{q})\sim V(0)\delta(\mathbf{q})$]. In this limit the electron-electron interactions have no effect on T_1 and (2.17) reduces to (2.6). The Korringa relation therefore becomes

$$K^2T_1T=\mathcal{S}(1-\alpha)^{-2}. \tag{2.18}$$

TABLE II. Summary of low-temperature frequency-field ratios and Knight shifts for potassium, rubidium, and cesium. The ν/H ratios for the reference compounds are published values as indicated.

	ν(metal)/H (kHz/Oe)	ν(ref)/H (kHz/Oe)	K(%)
^{39}K	0.199176(8)	0.19864(1)[a]	+0.27(1)
^{85}Rb	0.413744(20)	0.411076(1)[b]	+0.649(5)
^{87}Rb	1.40213(3)	1.393127(1)[b]	+0.646(2)
^{133}Cs	0.567235(10)	0.55846(3)[c]	+1.571(7)

[a] Reference 15.
[b] W. E. Blumberg, J. Eisinger, and M. P. Klein, Phys. Rev. **124**, 206 (1961).
[c] R. E. Sheriff and D. Williams, Phys. Rev. **82**, 651 (1951).

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[7] G. Allan, W. M. Lomer, R. D. Lowde, and C. G. Windsor, Phys. Rev. Letters **20**, 933 (1968).

Case (b)

We assume that the interaction potential is of the δ-function form [i.e., $V(\mathbf{q})=\text{const}$]. We also assume that the Fermi surface is spherical, in which case

$$F(\mathbf{q})=\tfrac{1}{2}\{1+[(1-x^2)/2x]\ln[(1+x)/(1-x)]\}, \quad (2.19)$$

with $x=q/2k_F$. In keeping with the spherical model, the hyperfine and enhancement factors in (2.17) may be averaged separately. This leads immediately to

$$T_1^{-1}=(T_{1,0})^{-1}\langle[1-\alpha F(\mathbf{q})]^{-2}\rangle. \quad (2.20)$$

The pointed brackets denote an average over all $\mathbf{q}$ vectors spanning the Fermi surface,

$$\langle[1-\alpha F(\mathbf{q})]^2\rangle=2\int_0^1 dx\, x[1-\alpha F(x)]^{-2}. \quad (2.21)$$

The α dependence of this enhancement factor is compared in Fig. 1 against the α dependence of the square of the Knight-shift enhancement. The relative magnitudes of these enhancements are seen to be strikingly similar except for large values of the interaction parameter. For this reason the Korringa relation appropriate for the present case,

$$K^2T_1T=\mathcal{S}K(\alpha)^{-1} \quad (2.22)$$

[where $K(\alpha)$ is obtained by multiplying (2.21) by $(1-\alpha)^2$], is not strongly dependent on α except when the latter approaches unity. This is illustrated in Fig. 1, as well as in Table I which compares numerical values of $K(\alpha)$ computed during the course of the present work with previously[4] published values. The accuracy of the present results can be easily verified for small values of α. In this range, the leading term in a power-series expansion in α yields the initial slope

$$\lim_{\alpha\to 0}(d/d\alpha)[K(\alpha)]=-2[1-\tfrac{1}{3}(2\ln 2+1)]=-0.409, \quad (2.23)$$

in good agreement with an extrapolated value based on our $K(\alpha)$ values in Table I.

We may conclude that the enhancement of the spin-lattice relaxation rate for a δ-function electron-electron interaction model is quite significant, being even larger than previously[4] estimated. Finally, we emphasize again that the density-of-states function in the relaxation-rate expression (2.6) is the bare electron density and therefore does not include effects due to electron-phonon interactions.

III. EXPERIMENTAL METHODS AND RESULTS

Since the observed hyperfine effects in the heavy alkali metals are influenced significantly by explicit temperature dependences[8] for which the theory reviewed in Sec. II makes no allowance, we have carried out low-temperature Knight-shift and spin-lattice relaxation time measurements for potassium, rubidium, and cesium which we believe to be more accurate than previously available data.

The alkali-metal samples were in the form of small-particle dispersions that were prepared in a dry helium atmosphere by a method similar to that suggested by Gutowsky and McGarvey.[9] The bulk metals[10] were melted in white mineral oil to which a small amount of oleic acid was added. The molten metal and oil were stirred in a high-speed blender for approximately 5–10 min and then allowed to cool to room temperature. After removal of excess oil by filtration, the samples were loaded into perforated sample holders. The perforations allowed the liquid helium to come into direct contact with the oil-coated metal particles thereby eliminating problems associated with eddy-current heating.

As in our earlier experiments,[5] all measurements were performed by crossed-coil transient NMR techniques using phase-coherent rf excitation and gated (boxcar integrator) detection. Magnetic fields to 60 kOe were produced in a compensated NbZr superconducting solenoid.

Knight shifts were determined from the NMR frequency-to-field ratios ν/H that were obtained in the usual manner by measuring the frequency of the interference pattern produced by the nuclear and reference signals under off-resonance conditions. The principal difficulty with this technique arises from the requirement of an accurate magnetic field calibration. A convenient secondary NMR reference for this purpose is provided by the ^{109}Ag resonance in silver metal. In external fields near 50 kOe, the ratio of the 4°K ^{109}Ag frequency to the room-temperature ^{2}H frequency in heavy water ($10^{-4}M$ CuSO_4 doped) is given by[11]

$$\nu^{(109)}(\text{metal})/\nu^{(2)}=0.304715(6), \quad (3.1)$$

where the number in parentheses indicates the estimated uncertainty in the last quoted digit. We have verified the stated accuracy of this result by ^{27}Al NMR measurements in metallic aluminum. At room temperature and 35 kOe we find

$$\nu^{(27)}(\text{metal})/\nu^{(2)}=1.70022(3), \quad (3.2)$$

and at 4°K in the same field

$$\nu^{(27)}(\text{metal})/\nu^{(109)}(\text{metal})=5.57967(15). \quad (3.3)$$

Note added in proof: A recent measurement by R. W. Weinert and R. T. Schumacher, Phys. Rev.

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[8] G. B. Benedek and T. Kushida, J. Phys. Chem. Solids **5**, 241 (1957).

[9] H. S. Gutowsky and B. R. McGarvey, J. Chem. Phys. **20**, 1472 (1952).

[10] The suppliers were as follows: Electronic Space Products, Inc., Los Angles, Calif. (cesium 99.99%); Leico Industries, Inc., New York, N.Y. (cesium 99.99%, rubidium 99.99%); MSA Research Corp., Callery, Pa. (potassium 99.95%).

[11] A. Narath, Phys. Rev. (to be published).

172, 711(1968), gives $\nu^{(27)}(\text{metal})/\nu^{(2)}=1.70024(2)$ at room temperature.

The total change in the ^{27}Al ν/H ratio in the temperature range 4–300°K was found to be at most $\pm 0.001\%$, as might have been expected from the pressure-dependence measurements of Benedek and Kushida.[8,12] Combining the results in (3.2) and (3.3) yields a ^{109}Ag-to-^{2}H frequency ratio of 0.304717, which is in excellent agreement with the directly measured ratio (3.1). Using the known ratio of the proton and deuteron moments, together with[13] $\mu^{(1)}=2.79268\mu_N$ (uncorrected for diamagnetic shielding) and $\mu_N=5.05050\times 10^{-24}$ erg G^{-1}, we calculate

$$\nu^{(2)}/H=0.653561(2)\ \text{kHz/Oe}, \tag{3.4}$$

and hence[14]

$$\nu^{(109)}(\text{metal})/H=0.199150(4)\ \text{kHz/Oe}, \tag{3.5}$$

$$\nu^{(27)}(\text{metal})/H=1.11120(2)\ \text{kHz/Oe}. \tag{3.6}$$

All of our field-strength determinations were based on these two standards.

It is interesting to compare Knight shifts computed from (3.5) and (3.6) with published shifts determined by direct comparisons of the fields for resonance in the metal and in a solution of a suitable reference compound. Using $\nu^{(109)}(\text{ref})/H=0.198089(10)$ kHz/Oe for silver[15] gives $K^{(109)}=+0.535(8)\%$ at 4°K, which may be compared with published room-temperature values of $+0.522(3)\%$ by Sogo and Jeffries[16] and $+0.533(4)\%$ by Brun *et al.*[17] For aluminum, $\nu^{(27)}(\text{ref})/H=1.10942(4)$ kHz/Oe[15] and therefore $K^{(27)}=+0.160(5)\%$, in excellent agreement with Teeter's value[12] of $+0.162\%$.

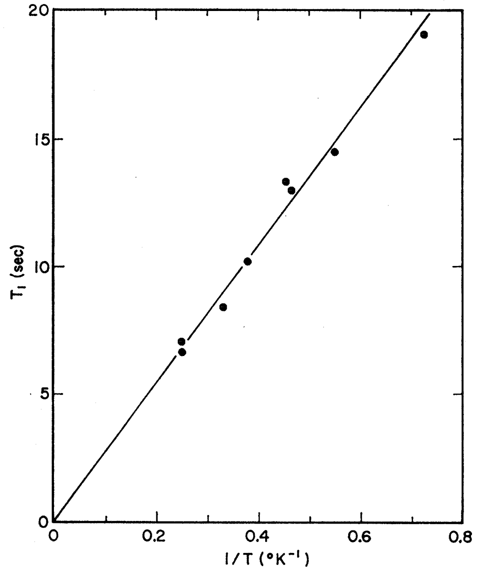

FIG. 2. Experimental spin-lattice relaxation times as a function of inverse temperature for ^{39}K in potassium metal at 9.6 MHz. The solid line represents a best fit to the data and yields $T_1T=27\pm 1$ sec°K.

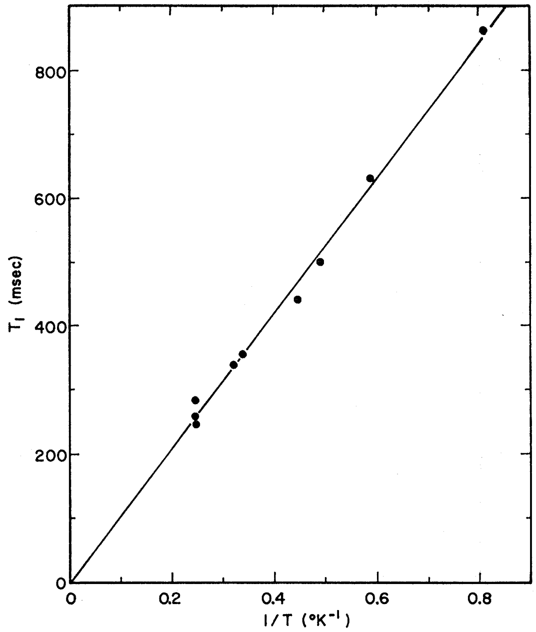

FIG. 3. Experimental spin-lattice relaxation times as a function of inverse temperature for ^{85}Rb in rubidium metal at 10 MHz. The solid line represents a best fit to the data and yields $T_1T=1.06\pm 0.05$ sec°K.

Table II summarizes our 4°K shift data for ^{39}K, ^{85}Rb, ^{87}Rb, and ^{133}Cs. The quoted ν/H ratios for the metals were calculated from the following experimental ratios:

$$\nu^{(133)}(\text{metal})/\nu^{(39)}(\text{metal})=2.8479(1)\quad (\text{at 46 kOe}), \tag{3.7}$$

$$\nu^{(133)}(\text{metal})/\nu^{(85)}(\text{metal})=1.37098(6)\quad (\text{at 26 kOe}), \tag{3.8}$$

$$\nu^{(133)}(\text{metal})/\nu^{(87)}(\text{metal})=0.404553(7)\quad (\text{at 26 kOe}), \tag{3.9}$$

$$\nu^{(133)}(\text{metal})/\nu^{(109)}(\text{metal})=2.84828(2)\quad (\text{at 56 kOe}). \tag{3.10}$$

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[12] D. R. Teeters, thesis, University of California, Berkeley, 1955 (unpublished); see also W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956) Vol. 2.

[13] E. R. Cohen and J. W. M. Dumond, Rev. Mod. Phys. **37**, 537 (1965).

[14] Our ^{27}Al value is in good agreement with the accepted value of 1.112 kHz/Oe; see, for example, R. J. Higgins and Y. K. Chang, Rev. Sci. Instr. **39**, 522 (1968).

[15] V. S. Shirley, Table of Nuclear Moments, in *Hyperfine Structure and Nuclear Radiations* (North-Holland Publishing Co., Amsterdam, 1968).

[16] P. B. Sogo and C. D. Jeffries, Phys. Rev. **93**, 174 (1954).

[17] E. Brun, J. Oeser, H. H. Staub, and C. G. Telschow, Phys. Rev. **93**, 172 (1954).

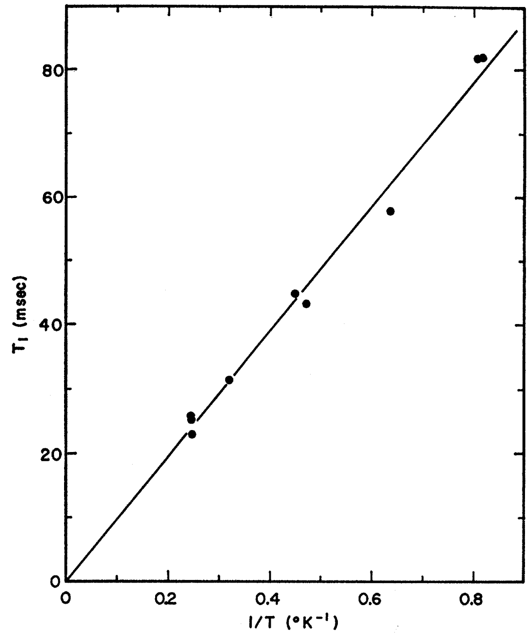

FIG. 4. Experimental spin-lattice relaxation times as a function of inverse temperature for ^{87}Rb in rubidium metal at 10 MHz. The solid line represents a best fit to the data and yields $T_1T=0.098\pm0.005$ sec°K.

In each case the two metallic powders were intimately mixed and the NMR frequencies measured while the magnet remained in the persistent mode. Our results for cesium metal may be compared with earlier measurements by Rupp,[18] $\nu^{(133)}(\text{metal})/H=0.56732(3)$, $K=+1.58(2)\%$, and by Holcomb, *et al.*,[19] $K=+1.58\%$.

Spin-lattice relaxation times were determined by measurements of the echo or free-induction decay amplitudes as a function of time separation from a saturating comb of rf pulses. Care was taken to reduce eddy-current heating of the metallic samples to insignificant levels. The absence of heating effects was verified in every case by repeating the measurements several times using different rf-pulse widths. The experimental results for ^{39}K, ^{85}Rb, ^{87}Rb, and ^{133}Cs are summarized in Figs. 2–5, respectively. In the case of the rubidium isotopes the observed ratio of the relaxation times $T_1(^{85}\text{Rb})/T_1(^{87}\text{Rb})=10.8(7)$ agrees well with the ratio $(\gamma_n^{(87)}/\gamma_n^{(85)})^2=11.5$. Since the nuclear electric-quadrupole moments of ^{85}Rb and ^{87}Rb are quite different, we may conclude that any contributions to the observed relaxation rates in rubidium metal from quadrupolar interactions are small.

Our T_1T values for ^{87}Rb and ^{133}Cs are slightly smaller than those obtained recently by Carver *et al.*[20] For the temperature range 1.4–77°K, these authors reported respective values of 0.13(1) and 0.11(1) sec°K. The discrepancy is most serious for cesium; however, for temperatures below ~4°K the data of Carver *et al.* are consistent with a somewhat smaller value than their published average which was based on the entire temperature interval. In the case of ^{39}K, our measured value of T_1T is significantly larger than the value obtained recently by Kaeck[21] (23.5±1.0 sec°K). Because of the relatively poor signal-to-noise ratio resulting from the low frequency (2.0 MHz) employed in Kaeck's experiments, it is possible that his error estimates were somewhat too small.

IV. DISCUSSION

The results of the present study are summarized in Table III, which also lists results of previous NMR experiments on lithium, sodium, and the noble metals. Column 4 of Table III compares the experimental products K^2T_1T with the predictions of the independent-particle model (2.9), (2.10). In every case the ratio $K^2T_1T/\mathcal{S}$ exceeds unity by a substantial amount. Assuming for the moment that the observed deviations are caused entirely by electron-electron interaction effects, we can use the measured K^2T_1T products to calculate the enhancement of the spin susceptibility for the two models described in Sec. II. The results are listed in the last two columns of Table III. It is evident that the inclusion of an exchange-enhanced spin-lattice relaxation rate in the Korringa relation requires considerably larger values of α to bring the theoretical

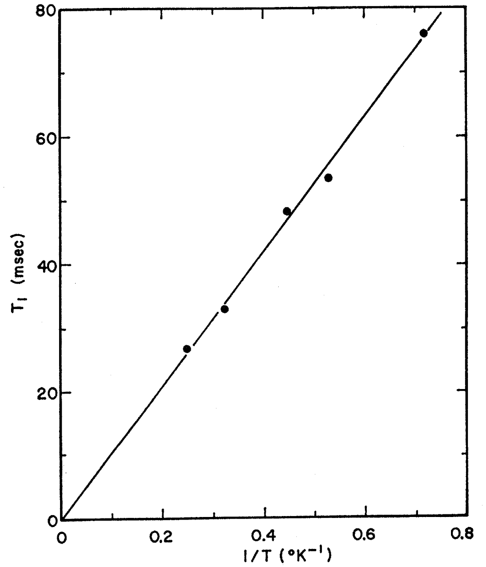

FIG. 5. Experimental spin-lattice relaxation times as a function of inverse temperature for ^{133}Cs in cesium metal at 9 MHz. The solid line represents a best fit to the data and yields $T_1T=0.106\pm0.005$ sec°K. Measurements at 4°K and 25 MHz gave the same result.

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[18] L. W. Rupp, Jr., Rev. Sci. Instr. **37**, 1039 (1966).

[19] D. F. Holcomb, J. A. Kaeck, and J. H. Strange, Phys. Rev. **150**, 306 (1966).

[20] G. P. Carver, D. F. Holcomb, and J. A. Kaeck, Phys. Rev. **164**, 410 (1967).

[21] J. A. Kaeck, Solid State Commun. **6**, 335 (1968).

TABLE III. Summary of alkali and noble-metal NMR data and α parameters derived for two limiting values of the electron–electron interaction range. The lithium data are room-temperature values; all others were obtained near 4°K. The rubidium data are averages for the two isotopes.

Metal	$K(\%)$	$T_1T\gamma_n^2$ (10^8°K sec^{-1}Oe^{-2})	$K^2T_1T/\mathcal{S}$	α from (2.18)	α from (2.22)
Li	+0.0249[a]	47(3)[b]	1.57(7)	0.20(2)	0.59(3)
Na	+0.1085(1)[a,c]	2.5(2)[b,c]	1.60(7)	0.21(2)	0.60(3)
K	+0.27(1)	0.42(2)	1.63(17)	0.22(5)	0.61(7)
Rb	+0.648(3)	0.073(3)	1.62(10)	0.21(3)	0.61(4)
Cs	+1.571(7)	0.0131(7)	1.73(9)	0.24(2)	0.65(3)
Cu	+0.232[a]	0.64(5)[b]	1.83(15)	0.26(3)	0.68(4)
Ag	+0.53(1)	0.149(7)[d,e]	2.22(20)	0.33(3)	0.76(4)
Au	+1.65(2)[d,e]	0.0097(8)[d]	1.40(16)	0.15(5)	0.50(7)

[a] W. D. Knight, in Ref. 12.

[b] A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

[c] Reference 27.

[d] Reference 5.

[e] Reference 11.

K^2T_1T products into agreement with experiment than is the case when only the Knight shift is assumed to be exchange enhanced.

Actually, it seems unlikely that the enhancement of the uniform-spin susceptibility in these nearly-free-electron metals could be as large as predicted by (2.22).[22] This can be verified by making use of the measured conduction-electron spin susceptibilities of lithium[23] and sodium[24] to estimate α for these metals. The unenhanced susceptibilities can be calculated from

$$\chi_0=\chi_P(m_0^*/m_0), \qquad (4.1)$$

where χ_P is the Pauli spin susceptibility of a free-electron gas of specified density and m_0^*/m_0 is the appropriate band effective mass ratio. The latter does not include electron-phonon effects and therefore cannot be obtained from experimental electronic specific-heat coefficients. Instead, we have used the thermal effective masses calculated by Ham.[25] These are listed for lithium and sodium together with calculated values of χ_P, χ_0, and the experimental susceptibilities χ_{expt} in Table IV. The corresponding α parameters, which are also shown in Table IV, have magnitudes that are approximately midway between those listed in the last two columns of Table III. One is therefore forced to conclude that the δ-function potential model for the conduction electrons leads to an overestimate of the associated spin-lattice relaxation rate. The magnitude of this discrepancy can be estimated by using (2.20) together with

$$T_{1,0}T=\mathcal{S}K_0^{-2}=\mathcal{S}[(1-\alpha)K]^{-2}, \qquad (4.2)$$

to calculate T_1T. The resulting values for lithium and sodium are compared in Table IV with the experimental relaxation times. The discrepancies between $(T_1T)_{\text{calc}}$ and $(T_1T)_{\text{expt}}$ are clearly outside the combined errors. It is significant that the calculated enhancements of the relaxation rates exceed the observed enhancements by only ~20%. The discrepancies in the α parameters are much larger because of the relatively weak dependence of $K(\alpha)$ on α.

The validity of the above conclusions depends in a sensitive way on the accuracy of the χ_{expt} and m_0^*/m_0 values for lithium and sodium which were used in the calculation of the respective α parameters. In regard to the experimental spin susceptibilities, the published values are supported by the work of Ryter, who made direct measurements of the hyperfine fields in lithium[26] and sodium[27] metals. These measurements were based

TABLE IV. Comparison of calculated and observed nuclear spin-lattice relaxation times for lithium and sodium.

	Li	Na
χ_P (10^{-6} emu/g)	1.471	0.650
m_0^*/m_0	1.66[a]	1.00[a]
χ_0 (10^{-6} emu/g)	2.441	0.650
χ_{expt} (10^{-6} emu/g)	3.84±0.18[b]	1.12±0.05[c]
α	0.36±0.03	0.42±0.03
$K_0(\%)$	0.0158±0.0007	0.063±0.005
$(T_1T)_0$ (sec°K)	69.7±6.5	9.5±1.5
$(T_1T)_{\text{calc}}$ (sec°K)	34.4±0.8	4.1±0.1
$(T_1T)_{\text{expt}}$ (sec°K)	42±2[d]	5.1±0.2[d,e]

[a] Reference 25.

[b] Reference 23.

[c] Reference 24.

[d] A. G. Andersen and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

[e] Reference 27.

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[22] See, for example, the theoretical estimates of the alkali metal spin susceptibilities by D. Pines (Ref. 2).

[23] R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1956).

[24] R. T. Schumacher and W. E. Vehse, J. Phys. Chem. Solids **24**, 297 (1963).

[25] F. S. Ham, Phys. Rev. **128**, 2524 (1962).

[26] C. Ryter, Phys. Rev. Letters **5**, 10 (1960).

[27] C. Ryter, Phys. Letters **4**, 69 (1963).

on observed hyperfine shifts of the conduction-electron spin resonance resulting from dynamically enhanced nuclear polarizations. Spin susceptibilities calculated from Ryter's hyperfine fields and the known Knight shifts are in excellent agreement with the values quoted in Table IV. The reliability of the effective mass ratios is somewhat more difficult to assess. Fortunately, in the case of sodium, the deviation of the Fermi surface from a free-electron sphere is small[28] and mass corrections arising from the lattice potential must therefore also be small in this metal. Since the α parameters listed in Table IV for lithium and sodium have nearly identical magnitudes as expected from the essentially identical $K^2T_1T/\mathcal{S}$ ratios, Ham's band mass for lithium is at least consistent with the NMR data.

One also needs to be concerned about the effects of other hyperfine interactions on the alkali-metal Knight shifts and spin-lattice relaxation rates. Orbital and spin dipolar interactions can be safely ignored. Contact interactions with exchange polarized core-s electrons, on the other hand, are not necessarily small. In the case of the $1s^22s$ state of atomic lithium, Cohen *et al.*,[29] using an exchange perturbation method, have calculated direct and core-polarization contributions to the hyperfine constant of 286 and 87 MHz, respectively; for the $1s^22p$ state the same authors obtained a core-polarization hyperfine constant of -8.5 MHz. Similar results have also been obtained by Gaspari *et al.*[30] from the related nuclear moment perturbation scheme. Gaspari *et al.* also applied the moment perturbation method to a calculation of core-polarization hyperfine corrections in lithium metal using the conduction-electron wave functions of Kohn and Callaway.[31] The results of this calculation suggested that the s and p core-polarization contributions to the lithium Knight shift nearly cancel, their magnitudes being $+23$ and -28% of the direct contact contribution, respectively.

The s core-polarization corrections can be incorporated as a scale factor in the contact hyperfine constants A_q, since they cannot be distinguished experimentally from the direct contact interaction. Consequently, the model developed in Sec. II is unaffected by core polarization arising from the s wave part of the conduction-electron wave functions. Core polarization due to the p-wave part, however, introduces complications. Since s and p states belong to different irreducible representations of the cubic point group, spin-lattice relaxation contributions from s and p hyperfine interactions do not interfere; the total rate $1/T_1$ is thus the sum of the individual s and p rates, each of which is related in the independent-particle model to the square of the associated Knight shift. Since the p core-polarization shift in lithium metal is evidently several times smaller than the total s shift, the corresponding p contribution to $1/T_1$ is quite small. It is further reduced by an orbital degeneracy factor,[32] which in the present case is $\frac{1}{3}$. While p core-polarization contributions to the spin-lattice relaxation rate are sufficiently small to be ignored for the present purpose, their influence on the Korringa relation nevertheless may be significant. According to Gaspari *et al.*[30] the Knight shift in lithium is reduced by p core polarization to 77% of its s-electron value. Such a reduction would *decrease* the experimental Korringa product K^2T_1T to approximately 59% of its s-electron value. The corresponding α parameters are consequently increased to 0.39 and 0.81 for the two limiting cases discussed in Sec. II. The first of these [case (a)] is essentially identical to the experimental value given in Table IV. Since it is quite unlikely that the electron–electron interactions yield zero enhancement of the nuclear spin-lattice relaxation rate, we must conclude that either Ham overestimated the lithium band mass or Gaspari *et al.* overestimated the p core-polarization hyperfine term. Of these alternatives, the latter is probably the more important in view of the specific-heat derived band mass[25] of $\sim$2.0 for bcc lithium. In any event, it is important to reemphasize that any p core-polarization contribution to the Knight shift (provided that it is negative) increases the disparity between α values inferred from the NMR data for the case of a δ-function interelectronic potential and those obtained from the experimental conduction-electron spin susceptibilities.

As concerns p core-polarization effects in sodium and the heavier alkalis, it is probable that they are relatively less important in these metals than in lithium. This follows from the expected reversal in the sign of the polarization at the nucleus in passing from the $1s$ shell to the outermost core-s shell. (Such partial cancellation effects are knownt o occur in the case of d core-polarization hyperfine interactions.[33]) Of relevance to the NMR results in sodium are recent moment perturbation calculations by Shyu *et al.*[34] for aluminum in which the $1s$ and $2s$ polarizations due to the p-wave component of the conduction-electron wave functions at the Fermi level were found to be essentially equal in magnitude but of opposite sign.

Finally, there exists the possibility that the Knight shifts may be in significant error because of differential chemical shifts between the metal and the reference

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[28] M. J. G. Lee, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966*, edited by M. P. Malkov (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967) Vol. III, p. 295.

[29] M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) **73**, 811 (1959).

[30] G. D. Gaspari, W.-M. Shyu, and T. P. Das, Phys. Rev. **134**, A852 (1964).

[31] W. Kohn and J. Callaway, Phys. Rev. **127**, 1913 (1962).

[32] Y. Yafet and V. Jaccarino, Phys. Rev. **133**, A1630 (1964).

[33] A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, Chap. IV.

[34] W. Shyu, T. P. Das, and G. D. Gaspari, Phys. Rev. **152**, 270 (1966).

substance. For example, Figger *et al.*[35] have recently concluded, on the basis of atomic beam magnetic-resonance measurements of the nuclear dipole moments of ^{63}Cu, ^{65}Cu, and ^{87}Rb, that chemical shifts in general may be significantly larger in many instances than might be inferred from NMR measurements in various compounds. Although this complication must be carefully considered when a quantitative interpretation of NMR shift data is attempted, it is unreasonable to attribute a significant fraction of the observed differences between the K^2T_1T product and $\mathcal{S}$ to this effect.

The above considerations lead to the conclusion that the results summarized in Table IV give a reliable measure of the exchange enhancement of $1/T_1$ for sodium and probably also for lithium. In the case of lithium, the actual relaxation enhancement may be slightly smaller than indicated because of a possibly significant negative p core-polarization contribution to the Knight shift. The δ-function random-phase-approximation (RPA) model therefore overestimates the relaxation enhancement. In other words, the exchange enhancement of $\chi''(\mathbf{q}, \omega)$ in the small ω limit falls more rapidly with increasing q than predicted by that model. Thus, the electron–electron interactions, at least in lithium and sodium, have a nonzero range and hence cannot be accurately represented by a wave-number-independent interaction constant. In order to examine the sensitivity of the predicted relaxation enhancement on the range of the electron–electron interaction, we have assumed that $V(\mathbf{q})$ in (2.15) can be approximated by the Fourier coefficients of a screened Coulomb potential $V(\mathbf{r}) \propto r^{-1} \exp(-\lambda r)$. The interaction constant α in (2.21) was therefore replaced by $\alpha(\mathbf{q}) = \alpha(0)[1+(q/\lambda)^2]^{-1}$. Using this form, agreement with the experimental relaxation rate in sodium was obtained for $\lambda/2k_F = 1.1$ (i.e., $1/\lambda = 0.23r_s$, where r_s is the average atomic radius in the metal). This result has only qualitative significance because (2.15) applies only in the tight binding limit unless $V(\mathbf{q}) = \text{const}$. The tight-binding model, however, is inappropriate for nearly free-electron metals such as the alkalis. In the RPA treatment of exchange interactions between free electrons[36] the susceptibility $\chi(\mathbf{q}, \omega)$ cannot be obtained in simple closed form since the response to a perturbation of wave number $\mathbf{q}$ depends in that case on $V(\mathbf{q}')$ for all $\mathbf{q}'$ values. As a consequence of this coupling, the $\mathbf{q}$ dependence of the $\chi(\mathbf{q}, \omega)$ enhancement will be less rapid than predicted by (2.15). Thus, the screening length obtained above for sodium only represents a lower limit.

Our conclusions concerning the effective electron–electron interaction range may be compared with those offered recently by Allan *et al.*[7] for the d-spin susceptibility of paramagnetic nickel. For $\mathbf{q}$ values in the range 0–$\sim k_F$ these authors showed that the available neutron scattering data[37] are consistent with a $V(\mathbf{q})$ which remains essentially constant. Our results for sodium, on the other hand, imply a reduction in $V(\mathbf{q})$ of $\gtrsim 20\%$ at $\mathbf{q} = k_F$ relative to the $q = 0$ value.

The most surprising result of the present study is the experimental observation of nearly identical values of $K^2T_1T/\mathcal{S}$ for all five alkali metals. This behavior was not anticipated because of the expected decrease in the magnitude of the Stoner factor $(1-\alpha)^{-1}$ with increasing atomic number among the alkalis. In the first place, the effective exchange potential $V(0)$ is believed to decrease significantly as the average electronic separation increases over the range appropriate for the alkali metals.[2] This decrease is a consequence of more complete mutual cancellation of exchange and correlation effects as the conduction-electron density is reduced. Furthermore, the independent-particle susceptibility $\chi_P m_0^*/m_0$ also tends to decrease for the heavier alkali metals. In the sequence lithium to cesium the susceptibilities (in 10^{-6} cgs volume units) are predicted to be 1.32, 0.66, 0.58, 0.60, and 0.81, respectively. These values are again based on band masses calculated by Ham.[25] The cesium value is probably too high, as noted recently by Kaeck[38] in connection with a study of alkali-metal spin susceptibilities based on Knight-shift measurements in liquid binary alloys of Na, K, Rb, and Cs. It is not clear why the experimental $K^2T_1T/\mathcal{S}$ ratios do not approach unity in going from lithium to cesium. It is possible that the results simply reflect a change in the wave-number-dependent enhancement of $\chi''(\mathbf{q}, \omega)$ due to variations in the effective screening radius. Positive non-s core-polarization contributions to the Knight shifts in the heavy alkalis may also be contributing factors, although this seems less likely. Further speculations must necessarily await the appearance of additional information concerning the spin susceptibilities of the alkali metals.

In Table III we list for comparison previously published NMR data for the noble metals. These data are of interest because the noble metals are monovalent, as are the alkali metals. They are the only other metals for which the assumptions contained in the theoretical model of Sec. II may have some validity. Because the noble-metal Fermi surfaces make contact with the zone boundaries, the non-s admixture into the conduction-electron wave functions at the Fermi level is undoubtedly greater than in the case of the alkali metals. For this reason the effects of core-polarization hyperfine

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[35] H. Figger, D. Schmitt, and S. Penselin, in *Actes du Colloque International du CNRS sur La Structure Hyperfine Magnétique des Atoms et des Molécules* (Edition du Centre National de la Recherche Scientifique, Paris, 1967).

[36] P. A. Wolff, Phys. Rev. **120**, 814 (1960).

[37] J. W. Cable, R. D. Lowde, C. G. Windsor, and A. D. B. Woods, J. Appl. Phys. **38**, 1247 (1967).

[38] J. A. Kaeck, Phys. Rev. **175**, 897 (1968); this conclusion is also consistent with the results of recent de Haas–van Alphen effect measurements on cesium by K. Okumura and I. M. Templeton, Proc. Roy. Soc. (London) **A287**, 89 (1965).

interactions on the Korringa relation are much more difficult to evaluate. It is interesting to note, however, that the experimental $K^2T_1T/\mathcal{S}$ ratios have magnitudes that are quite similar to those for the alkali metals. This observation supports the view that the conduction-electron spin susceptibilities of Cu, Ag, and Au are enhanced significantly by electron–electron interactions. Our earlier estimates[5] of the magnitudes of the respective exchange enhancements are of course invalid, since they were based on Moriya's[4] $K(\alpha)$ values.

V. SUMMARY

Available NMR data for the alkali metals provide strong evidence that Knight shifts as well as spin-lattice relaxation rates in these simple metals are strongly exchange enhanced by collective electron effects. In both cases predictions based on the RPA contact interaction model are in surprisingly good agreement with the experimental observations in lithium and sodium. The small difference between the measured relaxation rates in lithium and sodium, and those calculated from Moriya's theory of exchange-enhanced nuclear spin-lattice relaxation rates, can be attributed to a decrease in the potential $V(\mathbf{q})$ for large $\mathbf{q}$ values. The corresponding electron–electron interaction range inferred from the NMR data is $\gtrsim 23\%$ of an atomic radius.

Although the δ-function-potential model yields reasonably accurate enhancement factors for the nuclear spin-lattice relaxation rate in simple metals, the accuracy is clearly not sufficient to permit reliable α parameters to be determined from the experimental Korringa products. This is especially true for small values of α where the exchange enhancements of $(T_1T)^{-1}$ and K^2 have similar magnitudes, and $K(\alpha)$ consequently is relatively weakly dependent on α.

The conclusions offered above are based primarily on an analysis of available data for lithium and sodium. Since the experimental $K^2T_1T/\mathcal{S}$ ratios for the heavier alkali metals and the noble metals are essentially the same as for lithium and sodium, it is reasonable to conclude that the conduction-electron spin susceptibilities in all of these metals are substantially enhanced by electron–electron interactions. A more definitive interpretation of the NMR data will require an evaluation of the strength of non-*s* hyperfine interactions in these metals. In general, these interactions are expected to yield negative contributions to the Knight shift and hence increase the disparity between the observed Korringa products and predictions based on the independent-particle model.

It is obvious that exchange-enhancement effects must also be carefully considered when detailed interpretations of hyperfine interactions in transition metals and polyvalent simple metals are attempted. A straightforward extension of the present treatment to these more complicated situations will probably not be adequate, however, since it is unlikely that the approximations inherent in Moriya's theory will remain valid.

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