

In Table V we summarize the relevant parameters, the observed shifts  $\langle x \rangle$  and the calculated shifts  $x_0$  of the emission lines for our alloy targets with FeAl structure.

We have not corrected the spectra obtained with the Fe<sub>3</sub>Al target for self-absorption. There, too, the centers of emission lines and of self-absorption cross sections

do not coincide. But the effects of self-absorption are greatly diminished by the magnetic splitting. The maximum cross section is only about  $\frac{1}{6}$  of that in paramagnetic FeAl structure targets, and the shifts due to self-absorption do not exceed the experimental uncertainty of the line centers.

## Low-Temperature Pressure-Dependence Studies of Knight Shifts and Nuclear Spin-Lattice Relaxation Rates in Cesium and Rubidium Metals\*

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Measurements of the Knight shift  $K$  and nuclear spin-lattice relaxation-time  $T_1$  have been carried out on <sup>133</sup>Cs and <sup>87</sup>Rb as a function of hydrostatic pressure to 50 000 psi at 4°K. For <sup>133</sup>Cs, atmospheric-pressure data were also obtained at 27 and 76°K. The cesium Knight shift and relaxation rate are enhanced by about 18 and 24%, respectively, at the maximum pressure. This corresponds to a 13% increase in the Korringa product  $K^2T_1T$ , which is attributed to an increase in the exchange enhancement of the spin susceptibility resulting from a strong volume dependence of the band effective mass. The experimental volume and temperature derivatives of  $K$  in cesium metal yield an explicit temperature dependence at 4°K given by  $(\partial \ln K / \partial T)_V = -(0.8 \pm 0.1) \times 10^{-4} \text{K}^{-1}$ .

### I. INTRODUCTION

THE spin susceptibilities  $\chi$  of the alkali metals are enhanced significantly relative to the independent-particle susceptibilities  $\chi_0 = \chi_P m_0^*/m_0$  (where  $\chi_P$  is the Pauli free-electron susceptibility, and  $m_0^*/m_0$  is the band effective mass ratio) by collective-electron effects. This has been demonstrated by a variety of experimental techniques. The early measurements of the lithium susceptibility by Schumacher and Slichter,<sup>1</sup> and that of sodium by Schumacher and Vehse,<sup>2</sup> were based on determinations of the absolute areas under the conduction-electron spin-resonance absorption curves. Ryter<sup>3,4</sup> subsequently obtained essentially identical values for these susceptibilities from measurements of hyperfine-induced  $g$  shifts of the conduction-electron resonances. Estimates for the alkali-metal spin susceptibilities have also been obtained by Kaeck,<sup>5</sup> who inferred the dependence of  $\chi$  on atomic volume from the systematic variation of the alkali Knight shifts in liquid binary alloys. The enhancement factors have been determined more directly by Schultz and Dunifer<sup>6</sup>

for sodium, potassium, rubidium, and cesium from observations of spin-wave sidebands in the transmission conduction-electron spin-resonance spectra. An interesting feature of the available experimental results is the relatively weak dependence of the collective-electron enhancement on atomic volume. Whereas the latter increases by a factor of 2.8 in the sequence sodium to cesium, the ratio  $\chi/\chi_P$  increases by a factor of only  $\sim 1.3$ . Moreover, it is likely that a significant fraction of the observed increase in  $\chi/\chi_P$  simply reflects a band-structure enhancement of the independent-particle susceptibility  $\chi_0$  of cesium and to a lesser extent that of rubidium. It is noteworthy that a recent calculation by Rice<sup>7</sup> yielded nearly identical  $\chi/\chi_P$  ratios for sodium and potassium, in good agreement with experiment.

That the enhancement of the alkali-metal spin susceptibilities due to electron-electron interactions is nearly constant has also been inferred recently from measurements<sup>8</sup> of the nuclear magnetic resonance (NMR) shifts  $K$  and spin-lattice relaxation rates  $T_1^{-1}$ . The experimental Korringa products  $K^2T_1T$  were shown to exceed the independent-particle prediction  $\mathcal{S}$  by approximately 60% in all five alkali metals. In nearly free-electron metals, and in the absence of non- $s$  hyperfine interactions, the ratio  $K^2T_1T/\mathcal{S}$  depends only on the electron-electron interaction. A convenient measure of the strength of this interaction is the Stoner enhance-

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<sup>1</sup> R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1956).

<sup>2</sup> R. T. Schumacher and W. E. Vehse, J. Phys. Chem. Solids **24**, 297 (1963).

<sup>3</sup> C. Ryter, Phys. Rev. Letters **5**, 10 (1960).

<sup>4</sup> C. Ryter, Phys. Letters **5**, 69 (1963).

<sup>5</sup> J. A. Kaeck, Phys. Rev. **175**, 897 (1968).

<sup>6</sup> S. Schultz and G. Dunifer, Phys. Rev. Letters **18**, 283 (1967); and private communication. The susceptibilities are obtained by combining the spin-wave data with the effective masses given

by C. C. Grimes and A. F. Kip, Phys. Rev. **132**, 1991 (1963); C. C. Grimes, G. Adams, and P. H. Schmidt, Bull. Am. Phys. Soc. **12**, 414 (1967).

<sup>7</sup> T. M. Rice, Phys. Rev. **175**, 858 (1968).

<sup>8</sup> A. Narath and H. T. Weaver, Phys. Rev. **175**, 373 (1968).

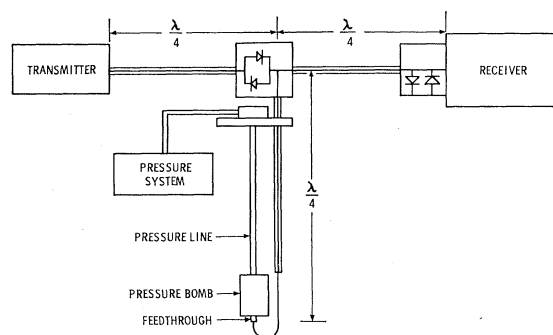


FIG. 1. Schematic diagram of high-pressure pulsed NMR spectrometer.

ment factor  $\alpha$ , defined by  $\chi/\chi_0 = (1-\alpha)^{-1}$ . The functional dependence of  $K^2 T_1 T/S$  on  $\alpha$  is unfortunately not known with sufficient accuracy to allow absolute values of  $\alpha$  to be determined from the NMR data. On the other hand, it is possible to infer relative values of  $\alpha$  since  $-(\partial/\partial\alpha)[S/(K^2 T_1 T)]$  is of order unity,<sup>8,9</sup> at least for the alkali metals. The NMR results therefore suggest that  $\alpha$  has essentially the same magnitude for all the alkali metals.

We have now extended our nuclear-resonance experiments to a determination of the low-temperature, hydrostatic-pressure dependence of  $K$  and  $T_1$  in rubidium and cesium. Of these two metals, cesium is of particular interest in view of the expected rapid increase of its effective-mass ratio with decreasing volume.<sup>10</sup> Because of its high compressibility,<sup>11,12</sup> cesium therefore affords an opportunity to study the influence of band-structure effects on  $\alpha$ . The pressure-dependence measurements were restricted to low temperatures in order to eliminate the need to consider possible changes in the explicit temperature-dependent contributions to the observed hyperfine effects.

## II. EXPERIMENTAL METHODS AND RESULTS

As in our earlier experiments,<sup>8</sup> all measurements were performed by transient NMR techniques using phase-coherent rf excitation and gated detection. Because of the small volume of the pressure bomb, a single transmitting-receiving coil was employed. Isolation between

receiver and transmitter was achieved by connecting the coil in a bridge circuit as described by Lowe and Tarr.<sup>13</sup> All measurements were performed at a frequency of 26 MHz. Magnetic fields were produced in a compensated NbZr superconducting solenoid which was equipped with a liquid-nitrogen-shielded sample dewar. Temperatures of 4, 27, and 76°K were attained by immersing the sample in liquid helium, neon, and nitrogen, respectively. Knight shifts were calculated from the experimental frequency-to-field ratios  $\nu/H$ , which were determined from the frequency of the interference pattern produced by the nuclear and rf reference signals under off-resonance conditions. The interference pattern was digitally stored in a Fabri-Tek 952/1062 signal averager. The field calibrations were based on the <sup>133</sup>Cs NMR in cesium metal<sup>8</sup> and the <sup>27</sup>Al NMR in aluminum metal,<sup>8,14</sup> using

$$\nu^{(133)}(\text{metal})/H = 0.56723 (1) \text{ kHz/Oe}, \quad 4.0^\circ\text{K} \quad (2.1)$$

$$\nu^{(27)}(\text{metal})/H = 1.1112 (1) \text{ kHz/Oe}, \quad 4-76^\circ\text{K}. \quad (2.2)$$

The <sup>133</sup>Cs and <sup>87</sup>Rb Knight shifts were calculated by comparing the experimental  $\nu/H$  ratios against the following reference ratios<sup>15,16</sup>:

$$\nu^{(87)}(\text{reference})/H = 1.393127 (1) \text{ kHz/Oe}, \quad (2.3)$$

$$\nu^{(133)}(\text{reference})/H = 0.55846 (3) \text{ kHz/Oe}, \quad (2.4)$$

where the numbers in parentheses indicate the error in the last quoted digit. Spin-lattice relaxation times were determined by monitoring the echo or free-induction amplitudes with a boxcar integrator as a function of time separation from a saturating comb of rf pulses.

Hydrostatic pressures at 4°K were achieved by freezing the sample into solid helium.<sup>17</sup> Pressures to 4 kbar were developed by a 15:1 intensifier and measured with a 0-100 kpsi Heise gauge. The helium was frozen isobarically so that the gauge reading represented the pressure at the freezing point. This reading was corrected<sup>18</sup> for pressure changes in the bomb during the subsequent isochoric cooling to 4°K. The corrected pressures  $P$  have an estimated absolute accuracy of  $\pm 4\%$ . The sample was contained in a thin-walled 0.2-in.-diam, 2.0-in.-long phenolic cylinder along whose length was wound a 6-turn rf coil. This sample cylinder was mounted on a high-pressure feed-through devised by Schirber and Shanfeldt<sup>19</sup> and inserted into the bottom of a beryllium-copper pressure bomb. The feed-through provided the necessary electrical contact between the rf coil and the external apparatus. The top of the bomb

TABLE I. Atmospheric pressure data for <sup>133</sup>Cs in cesium metal.

	$\nu/H$ (kHz/Oe)	$K$ (%) <sup>a</sup>	$T_1 T$ (sec°K)
4°K	0.567235 (10)	1.571 (2)	0.106 (5)
27°K	0.567198 (10)	1.564 (2)	0.107 (5)
76°K	0.567115 (10)	1.550 (2)	...

<sup>a</sup> The quoted uncertainties in  $K$  do not include possible errors in the reference  $\nu/H$  ratio.

<sup>9</sup> H. T. Weaver, thesis, Auburn University, 1969 (unpublished).

<sup>10</sup> F. S. Ham, Phys. Rev. **128**, 2524 (1962).

<sup>11</sup> C. A. Swenson, Phys. Rev. **99**, 423 (1955).

<sup>12</sup> M. S. Anderson, E. J. Gutman, J. R. Packard, and C. A. Swenson, J. Phys. Chem. Solids **30**, 1587 (1969).

<sup>13</sup> I. J. Lowe and C. E. Tarr, J. Sci. Instr. **1**, 320 (1968).

<sup>14</sup> R. J. Higgins and Y. K. Chang, Rev. Sci. Instr. **39**, 522 (1968).

<sup>15</sup> R. E. Sheriff and D. Williams, Phys. Rev. **82**, 651 (1951).

<sup>16</sup> W. E. Blumberg, J. Eisinger, and M. P. Klein, Phys. Rev. **124**, 206 (1961).

<sup>17</sup> The pressure system used in this work was developed by J. E. Schirber; for details, see W. J. O'Sullivan and J. E. Schirber, Phys. Rev. **151**, 484 (1966).

<sup>18</sup> J. S. Dugdale, Nuovo Cimento Suppl. **9**, 27 (1958).

<sup>19</sup> J. E. Schirber and D. W. Shanfeldt, Rev. Sci. Instr. **39**, 270 (1968).

TABLE II. Summary of high-pressure data for  $^{133}\text{Cs}$  in cesium metal at 4.0°K.

$P$ (kpsi)	$V/V^{(0)}$	$K/K^{(0)}$	$T_1/T_1^{(0)}$	$\frac{K^2 T_1 T}{(K^2 T_1 T)^{(0)}}$
1.0	0.998	1.0020 (5)		
1.8	0.995	1.0032 (5)		
3.2	0.991	1.0059 (5)		
4.2	0.987	1.005 (5)	0.97 (2)	0.98
4.6	0.987	1.0085 (5)		
6.9	0.980	1.0142 (5)		
9.2	0.973	1.0183 (5)		
11.5	0.966	1.0258 (5)		
12.7	0.963	1.038 (5)	0.95 (2)	1.02
18.8	0.947	1.058 (5)	0.92 (2)	1.03
22.1	0.938	1.067 (5)	0.91 (2)	1.04
27.4	0.925	1.101 (5)	0.91 (2)	1.10
31.3	0.916	1.121 (5)	0.86 (2)	1.08
32.2	0.914	1.1210 (5)		
42.3	0.892	1.152 (5)	0.82 (2)	1.09
42.7	0.891	1.1640 (5)		
47.5	0.881	1.197 (5)	0.80 (2)	1.15

was connected to a rigid stainless-steel pressure line which provided the required mechanical rigidity for the probe. The experimental arrangement is illustrated in Figs. 1 and 2.

Powdered samples were prepared by melting the metals<sup>20</sup> in white mineral oil and stirring with a high-speed (15 000 rpm) blender as described earlier.<sup>8</sup> The excess oil was then filtered off and the samples were loaded into the phenolic cylinder. That the presence of the oil coating produced no anomalous effects was verified by the repeatability of the data. In particular, each high-pressure point was bracketed by two low-pressure (5 kpsi) measurements. No detectable change was ever observed in the second low-pressure result.

The zero-pressure  $^{133}\text{Cs}$  data are summarized in Table I. The experimental Knight shifts vary linearly with temperature. The slope  $(\partial K/\partial T)_P = -2.9(3) \times 10^{-6} \text{K}^{-1}$  is in excellent agreement with the high-temperature slope obtained by Gutowsky and McGarvey.<sup>21</sup> Although the 0°K intercepts differ slightly, the discrepancy lies within the uncertainty of the  $^{133}\text{Cs}$  reference  $\nu/H$  ratio used in the present work. The two sets of data are also in good agreement with the recent work of Carver *et al.*,<sup>22</sup> whose measurements spanned the entire range from 4°K to room temperature. The 4°K pressure data are summarized in Table II. The corresponding volume dependences are based on the equation of state of cesium as determined by Anderson *et al.*<sup>12</sup> The most significant feature of the  $^{133}\text{Cs}$  results is the fact that the square of the Knight shift increases more rapidly with

<sup>20</sup> The suppliers were Electronic Space Products, Inc., Los Angeles, Calif. (cesium 99.99%) and Leico Industries, Inc., New York, N. Y. (cesium 99.99% and rubidium 99.99%).

<sup>21</sup> B. R. McGarvey and H. S. Gutowsky, *J. Chem. Phys.* **21**, 2114 (1953).

<sup>22</sup> G. P. Carver, D. F. Holcomb, and J. A. Kaeck, *Phys. Rev.* **164**, 410 (1967).

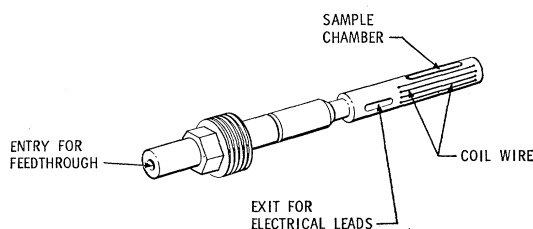


FIG. 2. Sample holder showing orientation of the rf coil.

decreasing atomic volume than does the spin-lattice relaxation rate. It is evident that the 12% volume reduction achieved in our experiments results in an increase in the Korringa product  $K^2 T_1 T$  of more than 10%.

The  $^{87}\text{Rb}$  data are summarized in Table III. The pressure-to-volume conversion is based on the work of Swenson.<sup>11</sup> We were unable to detect a change of  $T_1 T$  with pressure, which is not surprising in view of the weak pressure dependence of  $K$ .

### III. DISCUSSION

Because of the nearly free-electron character of the alkali-metal conduction bands, the hyperfine coupling is dominated by the Fermi contact interaction.<sup>23</sup> For this case, the independent-electron model yields

$$K_0 = A\chi_0\Omega, \quad (3.1)$$

$$T_{1,0}^{-1} = (A\chi_0\Omega)^2 T S^{-1}, \quad (3.2)$$

where  $A$  is a hyperfine coupling constant,  $\chi_0$  is the spin susceptibility per unit volume,  $\Omega$  is the atomic volume, and  $S$  is the Korringa constant defined by

$$S \equiv (\gamma_e/\gamma_n)^2 (\hbar/4\pi k_B). \quad (3.3)$$

Within this approximation it is obvious that the Korringa product  $K_0^2 T_{1,0} T (\equiv S)$  is independent of volume. In real metals, collective electron effects enhance both the Knight shift<sup>24</sup> and spin-lattice relaxation rate.<sup>25</sup> The enhanced quantities may be represented by

$$K = K_0(1-\alpha)^{-1}, \quad (3.4)$$

$$T_1^{-1} = T_{1,0}^{-1}(1-\alpha)^{-2} K(\alpha), \quad (3.5)$$

 TABLE III. Summary of high-pressure data for  $^{87}\text{Rb}$  in rubidium metal at 4.0°K.

$P$ (kpsi)	$V/V^{(0)}$	$K/K^{(0)}$
0.0	1.000	1.00000 (5); $K^{(0)} = 0.646\%$
4.2	0.990	1.00309 (5)
13.8	0.969	1.01084 (5)
23.0	0.952	1.01393 (5)
32.2	0.933	1.01857 (5)
41.4	0.917	1.02631 (5)

<sup>23</sup> C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row Publications, New York, 1963).

<sup>24</sup> P. A. Wolff, *Phys. Rev.* **120**, 814 (1960).

<sup>25</sup> T. Moriya, *J. Phys. Soc. Japan* **18**, 516 (1963).

where  $K(\alpha)$  is a correction factor and  $\alpha$  is a measure of the strength of the electron-electron interaction. It follows immediately that variations in the Korringa product (for the case of a single hyperfine mechanism considered here) can only result from changes in  $K(\alpha)$ . In the limiting cases of zero and infinite interaction range,  $\alpha$  is the only parameter which enters into  $K(\alpha)$  and hence into the enhancement of  $K$  and  $T_1^{-1}$ . For the first case  $K(\alpha)$  has been numerically evaluated<sup>8,25</sup> in the random-phase approximation [ $1 \geq K(\alpha) \geq 0$ ]; in the second case  $K(\alpha) = (1-\alpha)^2$ . For realistic interaction ranges,  $K(\alpha)$  depends in a complicated and only approximately known way on the details of the interaction. Our discussion will therefore be restricted to a consideration of the volume dependence of  $\alpha$  and the qualitative effects of this volume dependence on  $K(\alpha)$ .

An alternative explanation for the observed volume dependence of  $K^2T_1T$  based on a change in the nature of the hyperfine interaction, such as an increased admixture of  $p$  character into the wave function at the Fermi level, is not very plausible. Such an explanation requires that the  $p$ -core-polarization hyperfine field be positive and have an appreciable magnitude relative to the  $s$ -contact hyperfine field. A positive  $p$ -core-polarization contribution would tend to increase the Korringa product because of the absence of interference effects between  $s$  and  $p$  contributions to the spin-lattice relaxation rate. We believe, however, that this explanation cannot account for the large increase in  $K^2T_1T$ . For example, Mahanti and Das<sup>26</sup> have estimated recently that the  $p$ -core-polarization contribution to the cesium Knight shift, although positive, amounts to only 3% of the measured shift. This result supports our contention that the  $s$ -conduction-electron interactions (i.e., direct  $s$  contact plus  $s$  core polarization) provide the principal hyperfine coupling mechanisms in the alkali metals and that the observed changes in  $K^2T_1T$  must therefore be caused by changes in  $\alpha$ .

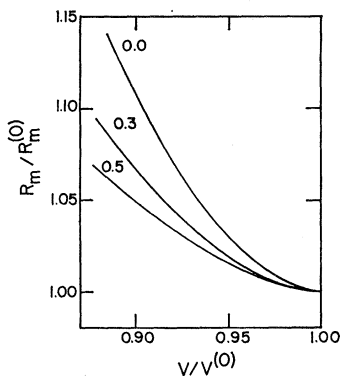


FIG. 3. Plot of the volume dependence of the band effective mass ratio of cesium at 4°K obtained from a smooth fit of the Knight-shift data for three values of  $\alpha^{(0)}$ .

<sup>26</sup> S. D. Mahanti and T. P. Das, Bull. Am. Phys. Soc. **14**, 331 (1969); S. D. Mahanti (private communication).

In an attempt to account for the experimental volume dependence of  $K$  and  $T_1T$  in somewhat greater detail, we rely on the following model. The hyperfine constant  $A$  is assumed to vary as  $\Omega^{-1}$  (i.e., simple volume renormalization), which closely approximates the predictions of Brooks<sup>27</sup> for small volume changes. The enhancement factor  $\alpha$  is assumed to have the form

$$\alpha = \rho\chi_0 = \rho\chi_P R_m, \quad (3.6)$$

where  $\rho$  is an appropriate electron-electron interaction parameter,  $\chi_P$  is the Pauli susceptibility (in volume units), and  $R_m$  is the band effective-mass ratio ( $m_0^*/m_0$ ). The volume dependence of  $\chi_P$  is given by  $\Omega^{-1/3}$ , while that of  $R_m$  is to be determined experimentally. No simple model exists for predicting the volume dependence of  $\rho$ . However, the observation that  $\alpha$  is nearly constant for the alkali-metal sequence Na, K, Rb, and Cs, despite an increase in the atomic volume by a factor of 2.8, allows us to assume that  $\rho\chi_P$  is independent of volume. The slight increase in  $\alpha$  for Cs suggested by the spin-wave data of Schultz and Dunifer<sup>6</sup> can probably be attributed to an increase in  $R_m$ . In any event, the maximum variation in  $\rho\chi_P$  consistent with the available data is too small to affect our conclusions. The central feature of our model is therefore the contention that the volume dependence of  $\alpha$  in cesium metal arises principally from a rapid increase in the band effective-mass ratio  $R_m$ .

The volume dependence of  $R_m$  can be estimated from the Knight-shift data. Combining (3.4) and (3.6) yields

$$R_m/R_m^{(0)} = f(V)\{1 + \alpha^{(0)}[f(V) - 1]\}^{-1}, \quad (3.7)$$

where

$$f(V) = (V/V^{(0)})^{1/3}(K/K^{(0)}). \quad (3.8)$$

The superscript zero denotes zero pressure. Figure 3 shows a smooth fit of  $R_m/R_m^{(0)}$  to the data for three values of  $\alpha^{(0)}$  (0, 0.3 and 0.5). These values span the range allowed by the uniform spin susceptibility. For cesium Dunifer and Schultz<sup>6</sup> find  $\chi/\chi_P = 2.01 \pm 0.13$ . Since this ratio is given by  $R_m(1-\alpha)^{-1}$ , we conclude that  $\alpha^{(0)} = 0.5$  if  $R_m = 1.0$ , and  $\alpha^{(0)} = 0.3$  if  $R_m = 1.4$ . An inspection of the data shows that the initial value of  $d \ln R_m / d \ln V$  is very small [ $-0.13(3)$  for  $\alpha = 0.5$ ], which suggests that the initial value of  $R_m$  is near unity. Hence, the actual value of  $\alpha^{(0)}$  probably lies in the range 0.4–0.5. It should be noted that our qualitative estimate of  $R_m^{(0)}$  is in disagreement with Ham's predicted value of 1.74.<sup>10</sup> The volume dependence of  $R_m$  inferred from our experimental results is also weaker than obtained by Ham. These disparities are not surprising since it is now known that Ham's calculation greatly overestimates the distortion of the cesium Fermi surface.<sup>28</sup> In view of the approximate nature of (3.6), a detailed com-

<sup>27</sup> See calculations of Brooks quoted in Ref. 30.

<sup>28</sup> K. Okumura and J. M. Templeton, Proc. Roy. Soc. (London) **287**, 89 (1965).

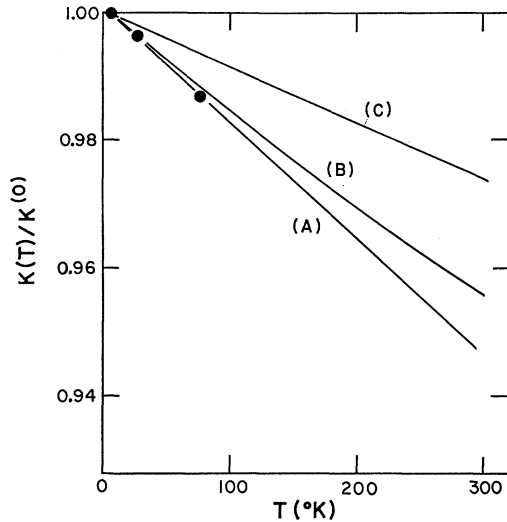


FIG. 4. The temperature dependence of the cesium knight shift: (A) Experimental data; the points were obtained in the present study, while the solid line represents the data of Refs. 21 and 22. (B) Calculated temperature dependence including both the explicit volume and explicit temperature contributions. The band effective mass has been assumed to be volume-independent. (C) Explicit temperature dependence.

parison between our results and Ham's predictions would, of course, be meaningless.

As an independent check on our conclusions we may examine the temperature dependence of the zero-pressure Knight shift. Because of the apparent weak dependence of  $R_m$  on volume near  $P=0$ , we assume that  $R_m$  is unaffected by thermal expansion. The observed variation of  $K$  with  $T$  must therefore be attributed to explicit temperature effects and/or explicit volume effects on  $\chi_P$  and  $A$ . The former can be calculated from our data using the exact relation

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \left(\frac{\partial \ln K}{\partial \ln V}\right)_T \left(\frac{\partial \ln V}{\partial T}\right)_P + \left(\frac{\partial \ln K}{\partial T}\right)_V. \quad (3.9)$$

From Table I we have<sup>29</sup>

$$\left(\frac{\partial \ln K}{\partial T}\right)_{P=0} = -1.85 \times 10^{-4} \text{K}^{-1},$$

and from Table II,  $(\partial \ln K / \partial \ln V)_T = -0.60$ . The thermal expansion coefficient<sup>12</sup> at 4°K is  $1.69 \times 10^{-4} \text{K}^{-1}$  so that  $(\partial \ln K / \partial T)_V = -0.84 \times 10^{-4} \text{K}^{-1}$  with an estimated uncertainty of  $\pm 0.1 \times 10^{-4} \text{K}^{-1}$ . The same calculation has been applied by Benedek and Kushida<sup>30</sup> to their room-temperature data. They obtained the wrong sign for  $(\partial \ln K / \partial T)_V$ , however, because of inaccurate thermal-expansion data available at that time. Ku-

<sup>29</sup> This value is based on the observed linear variation of  $K$  with temperature in the range 4–76°K. This procedure is expected to yield a reliable 4°K estimate for  $(\partial \ln K / \partial T)_P$  because of the nearly constant magnitude of the thermal expansion coefficient of cesium between 4 and 76°K (Ref. 12).

<sup>30</sup> G. B. Benedek and T. Kushida, J. Phys. Chem. Solids **5**, 241 (1958).

shida<sup>31</sup> subsequently corrected their estimate to  $-0.7 \times 10^{-4} \text{K}^{-1}$ , which is essentially the same as our 4°K value. We shall therefore assume that  $(\partial \ln K / \partial T)_V$  is temperature independent, at least near atmospheric pressure. The resulting contribution to the observed Knight-shift variation is shown in Fig. 4. In the approximation used here, the explicit volume dependence of  $K$  due to thermal expansion is given by  $\Omega^{-1/3}$ . (The volume thermal expansion in the range 4–300°K amounts to  $\sim 5\%$ .) Adding the explicit-volume term to the explicit-temperature term yields a total temperature dependence which is in reasonable agreement with experiment as shown in Fig. 4. The agreement can be improved, of course, by permitting  $R_m$  to decrease very slightly with increasing temperature. For example, if we choose  $d \ln R_m / d \ln V = -0.13$ , as suggested by the initial slope of  $R_m$  with respect to  $V$  at 4.0°K for  $\alpha = 0.5$ , we obtain an additional 1.3% reduction in the calculated room-temperature Knight shift, which compares with a required reduction of  $\sim 0.9\%$ . Thus, our qualitative conclusion that thermal expansion effects on  $\alpha$  are relatively unimportant, when compared to the strong volume dependence at high pressures, remains unchanged. Finally, we note that the weaker initial volume dependence of  $K$  at room temperature<sup>29</sup> is consistent with our model. In particular, the experimental value  $(\partial \ln K / \partial \ln V)_T = -0.32$  coincides with the assumed  $\Omega^{-1/3}$  variation of  $A \chi_P \Omega$ , suggesting that  $d \ln R_m / d \ln V$  is negligibly small at room temperature as expected. Unfortunately, the room-temperature analysis is complicated by the possibility that the observed volume effects may be influenced by changes in the explicit-temperature contributions.

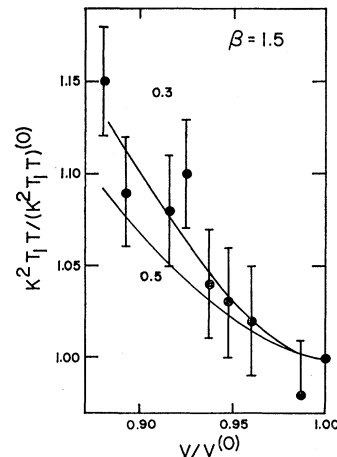


FIG. 5. Volume dependence of the cesium Korrington product at 4.0°K. The points are the experimental results. The solid lines are the calculated variations for  $\beta = 1.5$  and two different values of  $\alpha^{(0)}$ , as discussed in the text.

<sup>31</sup> See T. Kushida's private communication in T. Muto, S. Kobayashi, M. Watanabe, and H. Kozima, J. Phys. Chem. Solids **23**, 1303 (1962).

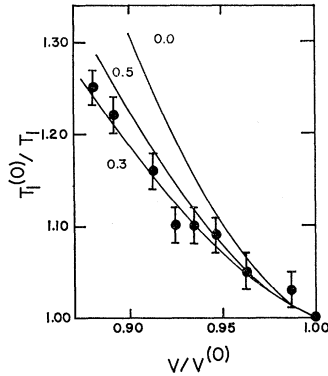


FIG. 6. Volume dependence of the cesium spin-lattice relaxation rate at 4.0°K. The solid lines are calculated for  $\beta=1.5$  and  $\alpha^{(0)}$  values as indicated.

Having gained some confidence in the essential correctness of our model, we return to a consideration of the volume dependence of the Korringa product. Using (3.4) and (3.5) we obtain for sufficiently small volume changes

$$K^2 T_1 T / (K^2 T_1 T)^{(0)} = 1 + \beta [(R_m / R_m^{(0)}) - 1], \quad (3.10)$$

where

$$\beta \equiv -d \ln K(\alpha) / d \ln \alpha. \quad (3.11)$$

Unfortunately, the parameter  $\beta$  is not accurately known. For example, the long-range limit for the electron-electron interaction yields  $\beta$  values of 0.85 and 2.0 for  $\alpha^{(0)}$  values of 0.3 and 0.5, respectively. The  $\delta$ -function limit gives 0.25 and 0.61, respectively. Because of this wide range of values we have chosen  $\beta=1.5$  in order to obtain a reasonable fit to our data for illustrative purposes as shown in Fig. 5. If we had chosen  $\rho$  rather than  $\rho \chi_P$  to be constant, the required value of  $\beta$  would have been 1.2. A similar calculation for the spin-lattice relaxation rate yields the results shown in Fig. 6.

We now turn to a brief consideration of the  $^{87}\text{Rb}$  pressure data. It is noteworthy that the initial volume dependence of  $K$  is significantly smaller than in the case of cesium. Assuming  $\alpha=0.4$ , the measured value  $(\partial \ln K / \partial \ln V)_T \approx -0.3$  implies an effective-mass variation,  $d \ln R_m / d \ln V$ , of  $\sim 0$  for  $A \propto \Omega^{-1}$  and  $-0.16$  for  $A \propto \Omega^{-0.7}$ .<sup>27</sup> As in the case of cesium, the room-temperature volume derivative  $(\partial \ln K / \partial \ln V)_T \approx -0.1$  is much smaller than the 4°K value. Because of the relatively small volume dependence of  $K$  it was not possible to detect significant changes in  $T_1$ . Hence, we are unable to comment on the possible importance of volume effects on  $\alpha$  and  $R_m$  in rubidium.

#### IV. SUMMARY

Although our interpretation of the experimental data is not unique, the internal consistency achieved in the cesium analysis allows several tentative conclusions to be drawn. (1) The exchange enhancement  $(1-\alpha)^{-1}$  of the cesium spin susceptibility increases strongly with decreasing volume at 4°K. (2) The increase in  $\alpha$  is a consequence of the rapid increase in the average band effective-mass ratio  $R_m$  at 4°K. (3) The low-temperature value of  $R_m$  lies in the range 1.0-1.2. (4) Increasing the volume from its 4°K value results in little, if any, decrease in  $\alpha$ .

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