

(6.8 kG) for which

$$q\bar{v} = 3\omega_c. \quad (51)$$

The magnitude of these resonances depends upon the magnitude of w_1^\pm and since w_1^+ corresponding to Eq. (50) is larger than w_1^- corresponding to Eq. (51) for all values of k_z , the resonance at $B_0=6.8$ kG is obscured. (By making w_1^\pm unrealistically large, resonances at $B_0=6.8$ kG appear.) These resonances disappear at lower frequencies and lower collision times. In the $\langle 111 \rangle$ directions w_1^\pm is very small for all k_z and, hence, these resonances are essentially unobservable in all the curves of Figs. 11–13.

The peak in the coefficient of attenuation in the $\langle 100 \rangle$ directions which occurs at 3.0 kG for a frequency of 110 Mc/sec and at corresponding lower fields for lower frequencies (see Figs. 8 and 9) may be identified with the peak observed by Boyd and Gavenda⁷ and discussed by other authors.^{7,26} This peak is associated with the presence of the Bessel functions in the conductivity tensor and, hence, should be described in quantum-mechanical language as a geometrical resonance. That is, it results from a variation in the matrix elements rather than a variation in the resonant denominator.

²⁶ S. G. Eckstein, Phys. Rev. Letters **16**, 611 (1966).

Nuclear Quadrupole Coupling, Knight Shift, and Spin-Lattice Relaxation Time in Beryllium Metal*

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The nuclear quadrupole coupling and Knight shift of Be⁹ have been measured in high-purity beryllium metal at room temperature and at 77°K in magnetic-field strengths up to 25 kOe. The nuclear quadrupole coupling constant is found to have the value $e^2qQ/h = 61.8 \pm 1.8$ kHz, independent of temperature. By contrast, the best estimate of the lattice contribution to the quadrupole coupling is found to be 68 ± 6 kHz, which implies that the conduction-electron contribution opposes that of the lattice. The Knight shift is found to have the values $K_{Be} = -0.0025 \pm (6)$ at 300°K and $K_{Be} = -0.0035 \pm (6)$ at 77°K (in percent); the uncertainty given is the standard deviation of the measurements. Measurements of the spin-lattice relaxation time at two temperatures indicate that $T_1 T = 1.66 \times 10^4$ sec °K with an uncertainty of 10%. These experimental observations can be interpreted in terms of direct-contact and core-polarization contributions, from a predominantly p -like band, which partially cancel to yield the small Knight shift.

INTRODUCTION

THE nuclear quadrupole coupling in beryllium metal has been of interest both from the solid-state and nuclear standpoints. From the theoretical standpoint, the calculation of the coupling constant in beryllium by Pomerantz and Das¹ was the first to include, in an explicit manner, the contribution of the conduction electrons to the electric field gradient (EFG). That calculation, combined with the measured value of the coupling constant reported by Knight,² yielded a value for the quadrupole moment of Be⁹ which was for some time the only available value for this quantity. Quite recently, atomic beam measure-

ments³ have yielded an independent value for $Q(\text{Be}^9)$ which differs significantly from that derived by Pomerantz and Das.

We report here on new measurements of the quadrupole coupling in beryllium, in which we have obtained a value 25% greater than that reported by Knight.² Nonetheless, this measured coupling is still less than that calculated on the basis of the atomic beam value of Be⁹ and the lattice contribution to the EFG. Whereas the calculation of Pomerantz and Das indicated that the conduction-electron contribution to the EFG was of the same sign as the lattice contribution, the present results suggest that the two contributions are very likely of opposite sign. This is interesting in view of the fact that in essentially all other metallic cases the relative sign of the lattice and conduction-electron contribution is unknown.

Similarly, the unusually small Knight shift, which

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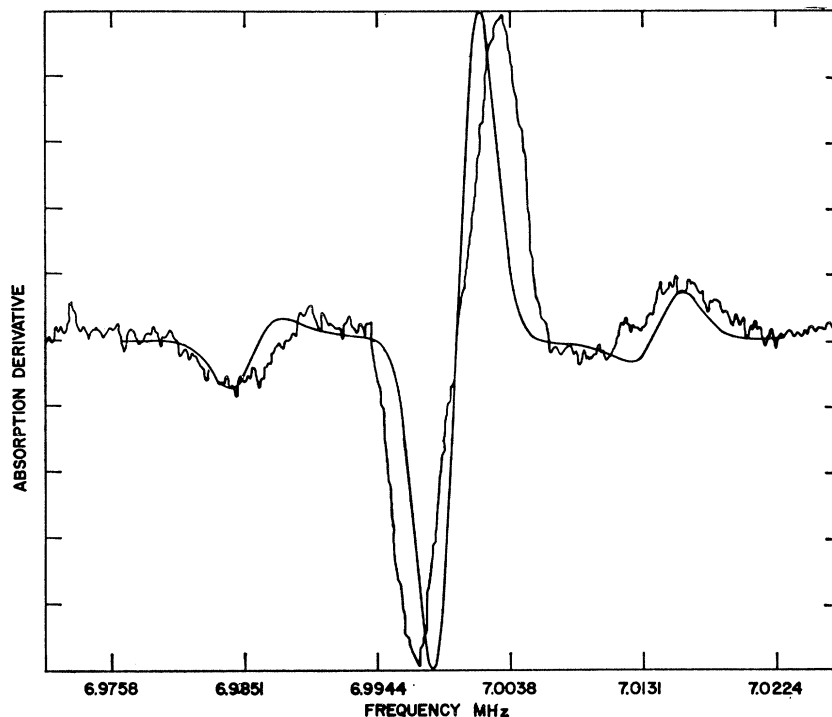
[§] Present address: University of Washington, Seattle, Washington.

¹ M. Pomerantz and T. P. Das, Phys. Rev. **119**, 70 (1960).

² W. D. Knight, Phys. Rev. **92**, 539 (1953).

³ A. G. Blachman and A. Lurio, Bull. Am. Phys. Soc. **11**, 343 (1966).

FIG. 1. Synthetic resonance derivative of the Be^9 nuclear-magnetic-resonance spectrum in beryllium superimposed on the experimental trace. The (nominal) resonance frequency is 7.00 MHz, and the sample is commercial-grade beryllium (sample I).



had been reported^{4,5} for beryllium, led to a number of theoretical papers seeking an explanation of this.⁶⁻⁸ We have also made new measurements of the Knight shift, and we find that it is, indeed, small but *negative*. This result is particularly interesting when considered together with the spin-lattice relaxation time T_1 , which does not appear to have been measured previously. We find that T_1 is unusually long (~ 50 sec at 300°K), and that T_1T is evidently constant. These facts may be understood in terms of the partial cancellation of the direct-contact and core-polarization contributions to the Knight shift. The magnitude of the direct-contact contribution, however, must be significantly less than the value obtained in a recent calculation by Shyu *et al.*,⁸ in order for the spin-lattice relaxation process to be as ineffective as it is. Moreover, it appears that the (negative) core-polarization contribution from p -like electrons dominates both the shift and the relaxation. This conclusion does not appear to be inconsistent with the present understanding of the Fermi surface of beryllium.⁹

In the following, the measurement of the quadrupole coupling and its comparison with theory are taken up

⁴ C. H. Townes, C. Herring, and W. D. Knight, *Phys. Rev.* **77**, 852 (1950).

⁵ W. D. Knight, *Solid State Phys.* **2**, 93 (1956).

⁶ V. Wood and F. J. Milford, *J. Phys. Chem. Solids* **23**, 160 (1962).

⁷ W. Schneider, L. Jansen, and L. Etienne-Amberg, *Physica* **30**, 84 (1964).

⁸ Wei-Mei Shyu, G. D. Gaspari, and T. P. Das, *Phys. Rev.* **141**, 603 (1966).

⁹ T. L. Loucks and P. H. Cutler, *Phys. Rev.* **133**, A819 (1964).

first. The Knight-shift and relaxation-time measurements are then considered, and these measurements are compared with theoretical expectations.

QUADRUPOLE COUPLING

Experimental

We have measured the quadrupole coupling constant in beryllium using several samples of the metal of differing purity and at several different magnetic-field strengths up to 25 kOe. The coupling is, in any case, so weak that the second-order effects on the central transition of the spectrum are not discernable at resonance frequencies above 4 MHz. Extremely low rf levels must be employed in observing the resonance due to the very long spin-lattice relaxation time in the metal (roughly 50 sec at 300°K and 200 sec at 77°K). Figure 1 shows a recorded (derivative) tracing of the Be^9 spectrum at a resonance frequency of 7.18 MHz.¹⁰ The central transition of the resonance in this trace is somewhat broadened by the relatively large modulation amplitude in order to emphasize the satellite peaks. Also shown in the figure is a synthetic resonance derivative based on the first-order perturbation-theoretic resonance envelope appropriate to a powder sample distribution for a spin- $\frac{3}{2}$ nucleus, and using the parameter

¹⁰ It is interesting to note that a similar recorded tracing of the resonance was published by T. J. Rowland [in *Progress in Material Science*, edited by Bruce Chalmers (Pergamon Press, Inc., New York, 1961), Vol. 9, p. 30]. That figure includes a calibration scale which, applied to the separation of the satellite derivative maxima, yields a coupling constant of 100 Oe or 60 kHz.

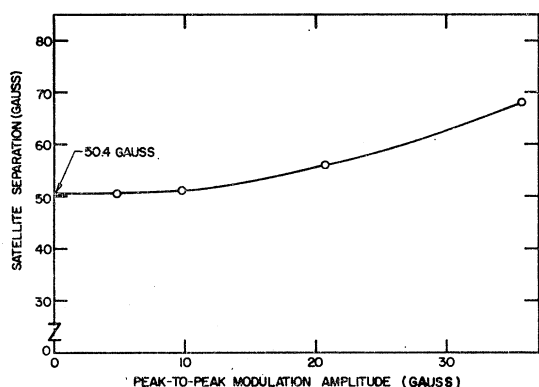


Fig. 2. Satellite separation (splitting) of the Be^9 nuclear magnetic resonance in beryllium as a function of modulation amplitude.

values: $e^2qQ/h = 0.0604$ MHz, $\sigma = 4.50$ Oe, where e^2qQ is the quadrupole coupling and σ is the full width at half-maximum intensity of the (Gaussian) resonance shape.

For most of the measurements, actual computer fitting was not employed. Rather, the satellite spacing was measured directly on the derivative recording. As has been noted in several papers,^{11,12} when the $3 \cos^2\theta - 1$ function which describes the angular dependence of a satellite resonance in a single crystal is folded with the dipolar line-shape function and averaged over all angles in the manner appropriate to a powder specimen, the maxima in the absorption derivative occur very close to the $\theta = 90^\circ$ singularities. The apparent spacing of the satellites can be increased by over-modulation, and this effect is demonstrated in Fig. 2 which shows the measured satellite spacing as a function of modulation amplitude. It is clear that for moderate to small modulation amplitudes, very little distortion of the splitting occurs.

Representative experimental measurements of the quadrupole coupling are summarized in Table I. Both samples of beryllium were obtained from the Brush Beryllium Corporation, the principal difference being in the iron content. Sample I (Brush grade Sp-100-C) contained 900 ppm iron (by weight, hence, 150 ppm atomic), whereas the high-purity sample (II) contained

TABLE I. Representative measurements of the quadrupole splitting of the Be^9 NMR spectrum in beryllium metal.

Sample	Temperature (°K)	Frequency (MHz)	$e^2qQ/2h$ (kHz)
II ^a	300	7.000	30.9
II	300	15.000	30.8
II	77	9.000	30.9
I ^b	300	7.180	30.2

^a High-purity beryllium, 140 ppm Fe.

^b Brush Beryllium Corporation grade Sp-100-C, 900 ppm Fe.

¹¹ F. Borsa and R. G. Barnes, *J. Phys. Chem. Solids* **25**, 1305 (1964).

¹² J. A. Ibers and J. D. Swalen, *Phys. Rev.* **127**, 1912 (1962).

only 140 ppm iron (by weight, hence, 23 ppm atomic). Not all the measurements made with sample I have been summarized in Table I. There is some evidence of a systematic difference between the results obtained from the two samples, the splitting in the less pure metal being typically about 0.5 kHz less than that in the purer metal. Although the scatter in the measured values is quite small, a conservative estimate of the possible systematic error involved in locating the derivative peaks might be ± 1 Oe. The measurements with the high-purity metal then lead to the result that $e^2qQ/h = 61.8 \pm 1.8$ kHz for Be^9 in beryllium, independent of temperature.

Theoretical

In a metal, the net electric-field gradient at a nuclear site is the sum of a lattice contribution (enhanced by the antishielding effect) and a conduction-electron contribution¹³:

$$eq_{\text{net}} = V_{zz \text{ net}} = V_{zz \text{ lat}} + V_{zz \text{ ce}}$$

$$= eq_{\text{lat}}(1 - \gamma_\infty) - eq_{\text{ce}},$$

where the minus sign is introduced because the conduction-electron contribution arises from a distribution of negative charges, and

$$q_{\text{ce}} = Z \left\langle \int \psi^* (3z^2 - r^2) r^{-5} \psi dr \right\rangle_{k \leq K_F}$$

For the specific case of beryllium, the lattice contribution to the EFG is given by the sum

$$q_{\text{lat}} = \sum_{i \neq 0} 2(3z_i^2 - r_i^2)/r_i^5, \quad (1)$$

taken over all beryllium ions except the one at the origin. It is assumed that the beryllium ions are divalent. For the hexagonal-close-packed lattice this sum is a function of the lattice parameter a and also of the c/a ratio of the unit cell. Das and Pomerantz have given the general expression for the hcp case,¹⁴

$$q_{\text{lat}} = Z[0.0065 - 4.3584(c/a - 1.6330)]a^{-3}, \quad (2)$$

where Z is the ion valence. For beryllium at room temperature, Pearson¹⁵ gives $c/a = 1.5677$ and $a = 2.2810$ Å, leading to the result $q_{\text{lat}} = 0.2911 Za^{-3}$. Some estimate of the uncertainty in the lattice sum can be obtained by comparing the value obtained with (2) with that obtained using the plane-wise summation method of de Wette.¹⁶ de Wette has given the result, $q_{\text{lat}} = 0.2928 Za^{-3}$, using $c/a = 1.5679$. With this value of c/a , we obtain from (2), $q_{\text{lat}} = 0.2902 Za^{-3}$; thus, the difference

¹³ D. R. Torgeson and R. G. Barnes, *Phys. Rev.* **136**, A738 (1964).

¹⁴ T. P. Das and M. Pomerantz, *Phys. Rev.* **123**, 2070 (1961).

¹⁵ W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958).

¹⁶ F. W. de Wette, *Phys. Rev.* **123**, 103 (1961).

in final value obtained with the two summation approximations is essentially 1%.

This direct lattice contribution is modified by the Sternheimer antishielding factor according to

$$q = (1 - \gamma_\infty) q_{\text{lat}}. \quad (3)$$

In the case of Be, this factor is actually a shielding factor in that $\gamma_\infty > 0$. Pomerantz and Das used the value $\gamma_\infty = +0.185$.¹ Somewhat more recently, Sternheimer calculated $\gamma_\infty = +0.189$ by a different method.¹⁷ The difference in these values is only 2%, but we shall employ Sternheimer's value for the sake of using the most recent numbers available. The final value for the EFG at the nucleus, due to the ion lattice, is then

$$eq = 1.918 \times 10^{13} \text{ esu cm}^{-3}.$$

Recent atomic beam experiments by Blachman and Lurio³ have given $Q(\text{Be}^9) = +(0.049 \pm 0.003) \times 10^{-24} \text{ cm}^2$, and combining this with the above result for eq , we find for the "lattice" contribution to the quadrupole coupling,

$$e^2qQ/h = 0.068 \pm 0.006 \text{ MHz}.$$

This calculated value, which takes no account of the conduction-electron contribution to the EFG, exceeds in magnitude the observed coupling constant, and this result implies that the sign of the conduction-electron contribution, $V_{zz \text{ ce}}$, must be opposite to the sign of the lattice contribution, $V_{zz \text{ lat}}$.

KNIGHT SHIFT AND T_1

Experimental

In previous measurements, the Knight shift in beryllium metal was found to be anomalously small. Townes, Herring, and Knight reported the value, $K_{\text{Be}} < 0.002\%$,⁴ and later, Knight reported $K_{\text{Be}} = 0.000\%$.⁵ An unpublished measurement by Gager and Milford yielded $K_{\text{Be}} \leq 0.001\%$. Our measurements have been made at room temperature and at liquid-nitrogen temperature and in field strengths to 25 kOe. Nuclear induction (crossed-coil) spectrometers were used, and in all cases the resonance frequency was crystal stabilized. Frequency measurements were made with a Computer Measurements Corporation frequency counter. We find that the shift is *negative* with respect to the Be^{++} ion in aqueous solution.

Measurements of the shift were made both with respect to a saturated aqueous solution of BeCl_2 and with respect to the deuteron resonance in a $\text{D}_2\text{O}-\text{H}_2\text{O}$ mixture. In this connection, we find for the frequency ratio $\nu(\text{Be}^9)_{\text{BeCl}_2}/\nu(\text{H}^2)$ the value $0.915387 \pm (2)$, whereas Sheriff and Williams had previously obtained $0.915475 \pm (70)$ using a super-regenerative oscillator spectrometer.¹⁸ Our value is in good agreement with that which

¹⁷ R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959).

¹⁸ R. E. Sheriff and D. Williams, Phys. Rev. **82**, 651 (1951).

TABLE II. Summary of Knight-shift and T_1 measurements on high-purity beryllium metal.

Temperature (°K)	Resonance frequency (nominal value) (MHz)	Knight shift (%)	T_1 (sec)
77	9.000	-0.0035 ± 0.0006	
120	6.500		140 ± 15
300	9.000	-0.0025 ± 0.0006	
300	6.500		55 ± 5

is obtained by combining the value for $\nu(\text{Be}^9)_{\text{BeF}_2}/\nu(\text{H}^1)$ of Dickenson, *et al.*,¹⁹ $[0.1405187 \pm (20)]$ with the very accurate value of the proton-deuteron moment ratio measured by Wimett $[\nu(\text{H}^2)/\nu(\text{H}^1) = 0.3070121 \pm (15)]$.²⁰ The result is that $\nu(\text{Be}^9)_{\text{BeF}_2}/\nu(\text{H}^2) = 0.915395 \pm (6)$. The difference between this value and our value may reflect a chemical shift, and is in any case, no larger than the uncertainty in the Knight-shift value.

The "best" measurements were made on the high-purity metal (sample II) in a nominal magnetic-field strength of 15 kOe, reflecting better magnetic-field stability. Room temperature and liquid-nitrogen temperature results are summarized in Table II. These data are seen to just overlap, so that it is not clear at this stage if the shift has a measurable temperature dependence.

Measurements of the spin-lattice relaxation time T_1 were made at two temperatures (120 and 300°K) using a two-pulse sequence and an rf bridge configuration.²¹ These experiments confirmed the results of previous saturation studies made with the cw technique.²² The results of the measurements are summarized in Table II, and lead to the conclusion that $T_1 T = (1.66 \pm 0.15) \times 10^4 \text{ sec}^\circ\text{K}$ over this temperature range. Very recently, Sagalyn *et al.* have obtained the result $T_1 T = (1.8 \pm 0.1) \times 10^4 \text{ sec}^\circ\text{K}$ for the range 77–300°K,²³ in good agreement with our result.

Neither the quadrupole coupling nor T_1 appear to be affected by the sample purity within the range of the two specimens considered. This suggests that the impurity atoms are very likely not dissolved in the Be lattice but are present as inclusions of oxide, etc. The electric-field gradient in particular appears to be very homogeneous, since the derivative amplitude of the observed quadrupolar satellites agrees very well with the calculated (synthetic) derivative, as shown in Fig. 1, which is based on the ideal intensity ratios. Calculations and measurements on other metals show that this

¹⁹ W. G. Dickenson and T. F. Wimett, Phys. Rev. **75**, 1769 (1949).

²⁰ T. F. Wimett, Phys. Rev. **91**, 499 (1953).

²¹ D. E. Barnaal and I. J. Lowe, Rev. Sci. Instr. **34**, 143 (1963).

²² L. W. Mohn, M. S. thesis, Iowa State University, 1964 (unpublished).

²³ P. L. Sagalyn, J. A. Hofmann, and M. E. Schillaci, Bull. Am. Phys. Soc. **7**, 916 (1966).

agreement is very quickly destroyed by relatively slight EFG inhomogeneity.²⁴

Theoretical

The conduction-electron contributions to the Knight shift and to the relaxation time can arise from four magnetic interactions:

- (a) the Fermi-contact interaction (direct-contact interaction) with electrons in partly filled *s* states;
- (b) the contact interaction with electrons in filled *s* states (core electrons) due to core polarization;
- (c) the spin-dipolar interaction with electrons in partly filled non-*s* states;
- (d) the orbital interaction with electrons in partly filled non-*s* states.

In all cases, only those conduction-electron states near the Fermi level are involved. The first two interactions are responsible for positive and negative contributions, respectively, to the Knight shift, and it is the possible mutual cancellation of these terms which has been investigated as affording an explanation of the extremely small shift in beryllium.⁸ Interactions (c) and (d) give rise to an anisotropy in the shift in noncubic metals which is typically of the order of 10% of the isotropic shift. We have found no evidence for Knight-shift anisotropy in beryllium and will not consider this point further.

The total nuclear spin-lattice relaxation rate is given by the sum of the rates associated with the separate interactions (a)–(d). In the tight-binding approximation, all of these individual rates may be expressed in the form $(T_1T)^{-1} = \text{const}$, and of these interactions, the contact interactions (a) and (b) are the most strongly relaxing. In the case of beryllium, we note first that the calculated direct-contact shift obtained by Shyu *et al.*⁸ ($K_s = +0.016\%$) leads to $(T_1T)_s = 5.2 \times 10^3 \text{ sec } ^\circ\text{K}$ via the Korringa relation²⁵

$$(T_1T)_s = (\hbar/4\pi k)(\gamma_e/\gamma_n)^2 K_s^{-2} \quad (4)$$

which applies to the direct-contact interaction. This rate is 25 times more rapid than what is observed, and implies a room temperature T_1 of roughly 2 sec rather than 50 sec. The Knight shift clearly cannot result from cancellation of contributions of this magnitude (0.016%).

The relation between the core-polarization contributions to the shift and to the relaxation rate has been established by Yafet and Jaccarino.²⁶ They obtained the “Korringa-like” relation

$$(T_1T)_{\text{cp}} = (\hbar/4\pi kq)(\gamma_e/\gamma_n)^2 K_{\text{cp}}^{-2}, \quad (5)$$

where q is a reduction factor given by the reciprocal of

²⁴ R. G. Barnes and B. R. McCart, *Bull. Am. Phys. Soc.* **12**, 315 (1967).

²⁵ J. Korringa, *Physica* **16**, 601 (1950).

²⁶ Y. Yafet and V. Jaccarino, *Phys. Rev.* **133**, A1630 (1964).

the orbital degeneracy of the band. For a pure *p* band, $q = \frac{1}{3}$. If we assume for the moment that the measured shift results entirely from the *p*-band core-polarization contribution, we obtain $(T_1T)_{\text{cp}} = 4.4 \times 10^4 \text{ sec } ^\circ\text{K}$ which is only three times longer than what is observed.

The spin-dipolar and orbital interactions also contribute in general to $(T_1T)^{-1}$. For a pure *p* band, Obata has obtained the relation²⁷

$$(T_1T)_{\text{sp-dip+orb}} = (5\hbar/52\pi k)[\gamma_e\gamma_n\hbar^2\rho(E_F)\langle r^{-3} \rangle]^2, \quad (6)$$

where $\rho(E_F)$ is $\frac{1}{6}$ the usual density-of-states $N(E_F)$,²⁷ and $\langle r^{-3} \rangle$ refers to the $2p$ state. For Be^{2+} , $\langle r^{-3} \rangle = 1.16 \times 10^{24} \text{ cm}^{-3}$.²⁸ The value of $N(E_F)$ may be determined from the specific-heat coefficient γ measured recently by Ahlers²⁹ [$\gamma = 0.1714 \times 10^4 \text{ erg/mole } ^\circ\text{K}^2$]. These values lead to $(T_1T)_{\text{sp-dip+orb}} = 56.5 \times 10^4 \text{ sec } ^\circ\text{K}$. The spin-dipolar and orbital contributions to the relaxation, and, hence, to the shift, are therefore not altogether negligible; however, they are just comparable to the uncertainty in the measurements.

An approximate and simple resolution of the contributions to the Knight shift and to the relaxation rate can be made by neglecting the orbital and spin-dipolar parts. We then have the two conditions to be satisfied by the data:

$$K_{\text{obs}} = K_s + K_{\text{cp}}$$

and

$$(T_1T)_{\text{obs}}^{-1} = (T_1T)_s^{-1} + (T_1T)_{\text{cp}}^{-1},$$

with the relations between the rates and the shifts given by Eqs. (4) and (5). Taking $K_{\text{obs}} = 3 \times 10^{-6}$ and $(T_1T)_{\text{obs}} = 1.6 \times 10^4$, we obtain $K_s = +1.4 \times 10^{-5}$ and $K_{\text{cp}} = -4.4 \times 10^{-5}$.

DISCUSSION

The most striking features of these measurements are the unusually long relaxation time T_1 and the very small negative Knight shift of the resonance. A comparable situation is not known for any other element metal (apart from some semiconductors and metalloids). A close parallel to the beryllium case is, however, found in the spin-resonance properties of Li, Na, etc. in the metallic tungsten bronzes, and an interpretation of these measurements in terms of a predominantly non-*s*-band picture has been given recently by Narath.³⁰ Our values for K_s and K_{cp} indicate that the conduction-electron character at the Fermi surface in beryllium must be strongly *p*-like. In this respect, it may be relevant to compare, at least qualitatively, the Fermi surface of beryllium⁹ with that of the very similar metal, magnesium.³¹ Magnesium is “well behaved” insofar as

²⁷ Y. Obata, *J. Phys. Soc. Japan* **18**, 1020 (1963).

²⁸ R. G. Barnes and W. V. Smith, *Phys. Rev.* **93**, 95 (1954).

²⁹ G. Ahlers, *Phys. Rev.* **145**, 419 (1966).

³⁰ A. T. Fromhold, Jr., and A. Narath, *Phys. Rev.* **136**, A487 (1964).

³¹ L. M. Falicov, *Phil. Trans. Roy. Soc. (London)* **A255**, 55 (1962).

its Knight shift and T_1 are concerned, the Knight shift of magnesium being $+0.111\%$,³² so that it appears that in this case the direct-contact contribution K_s to the total Knight shift is substantial and dominant. The Fermi surface of beryllium differs from that of magnesium in the important aspect that the third-zone "lens" figure at Γ enclosing electrons in magnesium³¹ is completely absent in beryllium.⁹ Correspondingly, the energy of the Γ_4^- representation in beryllium lies above the Fermi energy, whereas in magnesium it lies below. The relatively large positive direct-contact contribution calculated by Shyu *et al.*,⁸ is based on the Γ_4^- representation. By contrast, the state H_1 (near the "cigars") gives a small negative shift.⁸ It would appear⁹ that the Fermi surface in beryllium is mainly in the vicinity of the symmetry points H , K , and M . All of these points probably have very little s character, so that the predominantly non- s character of the Knight shift and relaxation time appear qualitatively plausible.

³² T. J. Rowland, in *Progress in Material Science*, edited by Bruce Chalmers (Pergamon Press, Inc., New York, 1961), Vol. IX, p. 14.

The fact that the quadrupole coupling in beryllium, even though larger than Knight's value by 25%, is still smaller than the theoretical estimate based on the lattice contribution to the field gradient and a new independent value of the quadrupole moment is indeed surprising. It indicates that the conduction-electron contribution to the gradient opposes that due to the lattice of point charges. In view of the appreciable p -like character of the conduction-electron wave function at the Fermi surface, deduced from the Knight shift and T_1 results, a substantial conduction-electron contribution to the field gradient may be reasonable.

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Exchange Potential for Nearly Free Electrons

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The approximation of the exchange potential which varies as the cube root of the density is examined. The optimum value of the coefficient in this expression, i.e., the value which minimizes the total energy of the system, is determined for a sinusoidal perturbation upon a system of free electrons as a function of the wavelength of the perturbation. For very long waves the coefficient assumes the value proposed by Gaspar. However, over a range of wavelengths which, in relation to the Fermi energy, are more appropriate for conduction electrons in a metal, the coefficient increases, well beyond Slater's original value, and then experiences a fairly sharp cutoff. Beyond this range the coefficient tends to vanish for decreasing wavelengths. A higher-order approximation incorporating this characteristic is also presented.

THE Hamiltonian for a system of $2N$ electrons,

$$\mathcal{H} = -\sum_{i=1}^{2N} [\nabla_i^2 - w(\mathbf{r}_i) - q \sum_{j=i+1}^{2N} r_{ij}^{-1}],$$

where w arises from external forces, $q = 2me^2/\hbar^2$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, assumes in the one-particle—or Hartree-Fock—approximation the form

$$\mathcal{H}_0 = \sum_{i=1}^{2N} H(\mathbf{r}_i),$$

whereupon the total wave function Ψ for the system in the ground state becomes the Slater determinant constructed from the N solutions with the lowest eigen-

values ϵ_n of the equation

$$H\psi_n = \epsilon_n\psi_n. \quad (1)$$

The total energy of the system is found from $E = \langle \Psi | \mathcal{H} | \Psi \rangle$.

Substituting for the exchange operator the function $A(\mathbf{r})$ proposed by Slater¹ gives

$$H(\mathbf{r}_1) = -\nabla_1^2 + w(\mathbf{r}_1) + 2q \int d\mathbf{r}_2 \rho(\mathbf{r}_2) r_{12}^{-1} - A(\mathbf{r}_1), \quad (2)$$

where, with respect to

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_{n=1}^N \psi_n^*(\mathbf{r}_1) \psi_n(\mathbf{r}_2), \quad (3)$$

$$\rho(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r}),$$

¹ J. C. Slater, *Phys. Rev.* **81**, 385 (1951).