thermoluminescence data. None of the measurements took into account any dependence of the half-life of the F' center on the concentration of F' centers.

The analysis of this work yields an activation energy in essential agreement with those previously reported. At first sight this would appear puzzling, since the early measurements did not consider the concentration dependence of the half-life. Our analysis only deduced an activation energy for low concentrations of F' centers (less than $10^{16}/\mathrm{cm}^3$), where the half-life was indicated to be independent of the F' concentration. Pick's measurement of the activation energy of the F' center was for initial F' concentrations of less than $10^{16}/\mathrm{cm}^3$. Thus, his measurement was also in the concentration-independent region, and could be expected to agree with our result.

It is of interest to speculate on the reason why the half-life of the F' center is dependent on the concentration of the F' centers. It is possible that for high concentrations of F' centers, other F' centers or vacancies are sufficiently close to a given F' center to polarize it, which in turn might affect the stability of the center. Such an effect would depend on the distance between centers, which would be concentration dependent.

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Effects of Temperature on the Magnetic Hyperfine Properties of Beryllium[†]

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The temperature dependence of the Fermi contact and exchange core-polarization (ECP) contribution to Knight shift K and nuclear-spin relaxation time T_1 in beryllium has been studied. The variation in the spin density shows a similar trend to that in cadmium, namely, the s content of the conduction-electron wave function Ψ_k increases with temperature at the expense of a decrease in the p content. Combining both direct and ECP contributions, K increases by 2.3% and T_1T decreases by 8% from 0 to 300 °K. The results are compared with the available experimental data.

The hyperfine properties of metals that depend upon the wave functions of the conduction electrons on the Fermi surface are of particular interest, because they serve as sensitive indices of the nature of the energy bands constituting the Fermi surface and of the associated electronic wave functions. In the case of alkali metals, the Fermi surface is spherical and is inside the first Brillouin zone. However, for the group-II hcp metals in the extended zone scheme, the Fermi surface intersects the second Brillouin zone substantially and is composed of several bands with varying degrees of angular symmetry. The nuclear-magnetic-resonance properties of the various divalent hcp metals provide very interesting trends.

Recently, the unusual temperature dependence of the Knight shift[1] K in Cd has been explained by changes in the $s\,(l=0)$ content of the conduction-electron wave functions which are brought about by the temperature variation of the ionic potential produced by electron-phonon interaction. In Be, the lightest of the hcp metals, K has been explained by the combination of direct, exchange core-polarization[2] (ECP), and Landau-type orbital contributions.[3] Since the conduction electrons in Be at 0 °K are very p-like[2] and the ECP contribution of a p

electron is about one-third of that of an s electron, one expects the contributions arising from changes in p character to be non-negligible compared to the changes arising from the s character. This is in contrast to the situation in Cd, where the ECP contribution to K was small[4] (only 10% of the direct contribution).

The Knight shift in Be has been measured by Barnaal *et al.*[5] at two temperatures. At 77 °K, $K=(-0.0035 \pm 0.0006)\%$, whereas at 300 °K, $K=(-0.0025 \pm 0.0006)\%$. The latter result is in good agreement with the result of Anderson *et al.*[6] at 300 °K, namely, $K=(-0.0027 \pm 0.0006)\%$.

The error limits in the results of Ref. 5 make it difficult to draw conclusions regarding the nature of the temperature dependence. If one ignores the error ranges, it may appear that there is a strong variation, almost a 40% change in going from 77 to 300 °K. On the other hand, there is also the possibility that the temperature dependence is much weaker and the apparent difference between the mean values at the two temperatures has no real significance because of the size of the error limit involved. The available relaxation-time data[5] at the two temperatures are more in keeping with a weak temperature dependence or constancy of K in the temperature range 77–300 °K. However, this conclusion is not definitive because of the difference in the T_1T values obtained by two investigators [namely,[5] $(1.66 \pm 0.15)\times 10^4$ and[7] $(1.8 \pm 0.1)\times 10^4$ deg sec] and the error ranges in the two measurements.

The present paper is aimed at exploring theoretically the nature of the variation of K and T_1T with temperature, with the object of throwing light on the question of whether or not the temperature variation of K and T_1T is shrouded by experimental error. This investigation involves us in a study of the relative importance of the s and p contributions to K through core-polarization effects. While the extent of changes in the nature of the Fermi surface is expected to be much smaller for Be than for Cd because of the larger Debye temperature ($\Theta_D \sim 1250$ °K), the qualitative variation is expected to be similar because of the similarity of the Fermi surface in the two cases, the coronet in Be being closely analogous to the monster in Cd.

Tripp[8] has attempted a study of the Fermi-surface dimensions in Be as a function of temperature using a similar procedure to that adopted by Keffer *et al.*[9] and later by Kasowski and Falicov[1] for Cd. Rather small but finite changes of the Fermi-surface dimensions were found[8] from 0 to 300 °K. One expects somewhat more significant changes in the spin density, because the energy has an average dependence on the potential while the s and p character of the conduction-electron wave function could be more sensitive to the nature of the potential.

In our calculation of the spin density, the volume thermal expansion was taken into account by the use of parameters c and a appropriate to the temperature,[10] while the electron-phonon interaction was introduced by simply modifying the lattice structure factor at 0 °K, $S_0(G)$ being changed to $S_T(G)=S_0(G)e^{-W(G,T)}$, where

$$W(G,T)=D(T)G^2\,.$$

The quantity[1] $D(T)$ was obtained[8] at various temperatures by analyzing the normal phonon modes of the solid. For the evaluation of the spin density at the nuclei, one has to average both over the temperature-dependent Fermi surface and over the nuclear positions, which are influenced by the thermal vibrations. The temperature dependence of both these factors is determined by $S_T(G)$. The influence of the temperature-dependent structure factor on the spin density occurs in two ways. First, with increasing temperature, $S_T(G)$ leads to a reduction in anisotropy of the potential. Thus, the strength of the mixing between two momentum states produced by the potential weakens with increasing temperature, resulting in an increase in the s content of the conduction-electron wave functions. This would cause K to increase with temperature. Second, because of the thermal vibrations of the nuclei, the probability of finding an electron at the nuclear site decreases. Thus, the density $\langle |\Psi_k(0)|^2\rangle_{\rm av}$ at any point on the Fermi surface and at any temperature will decrease with the rise of temperature. Hence, there is a competition between these two effects. The former is known to be dominant in cadmium,[1] causing a net rise of K with temperature.

The results for the spin densities averaged over the Fermi surface and including both direct and ECP contributions are presented in Table I for a number of temperatures from 0 to 300 °K. From the direct contribution to spin density S_d, it is noticed that there is very little change in the angular character of the wave functions from 0 to 100 °K. However, from 100 to 300 °K, the s content of the conduction-electron wave function increases by about 6%. This is also noticed from the increase of the ECP contribution to the spin density from the s part of the conduction-electron wave function ($S^s_{\rm ECP}$). While the p contribution to the ECP spin density, $S^p_{\rm ECP}$, is individually larger than $S^s_{\rm ECP}$, the rate of temperature variation of $S^p_{\rm ECP}$ is found to be only about one-third of that of $S^s_{\rm ECP}$. This result could be explained by realizing that while the relative changes in s and p characters are comparable, the ECP contribution per p electron is about one-third smaller[11] than that per s electron. The d contribution to the ECP mechanism is orders of magnitude smaller than $S^s_{\rm ECP}$

TABLE I. Direct and exchange core-polarization contribution to spin density (in units of $1/\Omega_0$) in solid beryllium as a function of temperature.

Temperature (°K)	S^s_{ECP}	S^p_{ECP}	S^d_{ECP}	S_{ECP}	S_d	$S = S_{\mathrm{ECP}} + S_d$
0	0.0191	−0.0413	−0.0021	−0.0243	0.1054	0.0811
100	0.0191	−0.0413	−0.0021	−0.0243	0.1055	0.0812
200	0.0194	−0.0412	−0.0021	−0.0239	0.1070	0.0831
300	0.0202	−0.0409	−0.0021	−0.0228	0.1116	0.0888

and S^p_{ECP} and does not contribute appreciably to the temperature dependence. From Table I, the ECP mechanism is seen to make a net contribution of about 18% of the temperature variation of the total spin density S over the temperature range 0–300 °K.

The Knight shift and the nuclear-spin relaxation time T_1T were calculated using the spin densities in Table I and standard expressions[12] in the literature. The results are presented in Table II. The calculation of K assumes both the spin susceptibility χ_s (the experimental value, 0.2×10^{-6} cgs volume units, being used) and the orbital contribution K^{orb} to be constant in the temperature range chosen. Of these approximations, the former is justified because of Tripp's calculations[8] on the Fermi surface, which indicates that the Fermi surface does not change significantly, and hence one does not expect the density of states to change appreciably.

As regards the second approximation, K^{orb} is mainly of the Landau type and is not very sensitive to the angular character of the wave function. This would not be the case if there were significant contributions from the Van Vleck–Ramsey mechanism.[13] In studying the temperature variation of T_1T, we have considered only the contributions to the spin density from the direct and s parts of ECP terms. This does not introduce any serious error in view of the relative weakness of the p-type ECP effect on T_1T.[12,14]

The theoretical results for K indicate that virtually no change is predicted from 0 to 100 °K, and only about a 2.3% increase (including the sign, actually a decrease in magnitude) in going from 0 to 300 °K. The 9.5% change in $K^d + K^{cp}$ is damped by the constancy of the substantial orbital contribution to K. However, there is about an 8% decrease in T_1T in going from 0 to 300 °K. The greater percentage change in T_1T occurs because there is no large orbital contribution present as there is in the case of K.

In comparing with experiment, it appears that if one ignores the standard deviation, then the experimental variation observed by Barnaal *et al*. between 77 and 300 °K is 0.001%, which is a factor of 10 larger than the theoretical number in Table II. It is possible, as pointed out at the outset, that the experimental variation is indeed much smaller than what one gets from the quoted mean, since the range of error is comparable to the observed variation. Any possible reduction in the range of experimental error would help clarify this comparison between theory and experiment. A similar comment applies to the experimental temperature variation of T_1T, which seems to be constant from both measurements, within the ranges of experimental error. The theoretical variation from 0 to 300 °K is 0.08×10^4 deg sec.

The understanding of the situation *vis à vis* theory and experiment could also be improved if measurements could be made at temperatures higher than 300 °K, particularly at a substantial fraction of the Debye temperature, $\Theta_D \sim 1250$ °K, where the variation is expected to be much stronger. The measurements of T_1T offer greater hope in this respect, because of the expected larger percentage variation.

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TABLE II. Knight shift and relaxation time in solid beryllium as a function of temperature.

Temperature (°K)	K^d (%)	K^{cp} (%)	$K^d + K^{cp}$ (%)	$K = K^d + K^{cp} + K^{\mathrm{orb}}$ [a] (%)	T_1T (deg sec)
0	0.96×10^{-3}	-0.22×10^{-3}	0.74×10^{-3}	−0.00300	0.98×10^{4}
100	0.96×10^{-3}	-0.22×10^{-3}	0.74×10^{-3}	−0.00300	0.97×10^{4}
200	0.98×10^{-3}	-0.22×10^{-3}	0.76×10^{-3}	−0.00298	0.95×10^{4}
300	1.02×10^{-3}	-0.21×10^{-3}	0.81×10^{-3}	−0.00293	0.90×10^{4}

[a] $K^{\mathrm{orb}} = -0.00374\%$ (Ref. 3) was assumed to be constant from 0 to 300 °K.

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