Oscillatory Field Dependence of the Knight Shift in a Monocrystal of Tin*

S. A. KHAN,† J. M. REYNOLDS, AND R. G. GOODRICH
Department of Physics, Louisiana State University, Baton Rouge, Louisiana
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A detailed experimental investigation of the magnetic-field dependence of the Knight shift in a monocrystal of white tin has been performed. The measurements were made at 1.2°K and in magnetic fields ranging from 10.5 to 16.2 kG. The Knight shift is found to oscillate at the de Haas-van Alphen (dHvA) frequency, and in the range of fields investigated, exhibits two periods of 3×10^{-7} and 5.8×10^{-7} G^{-1}. The values and angular variations of these periods are in satisfactory agreement with the data on the tin Fermi surface obtained from other experiments and from a pseudopotential calculation of the band structure. The magnetic-field dependence of the amplitude of the oscillations has been investigated for both periods. The amplitude of the shorter-period component increases, and that of the longer-period component decreases, with increasing magnetic field. The decrease in amplitude of the longer-period oscillation is attributed to the effects of magnetic breakdown. The observed amplitudes are in satisfactory agreement with the assumption that the Knight-shift oscillations are due to oscillations in the ground-state wave functions of the contributing electrons rather than oscillations in the susceptibility as has been previously suggested. Measurements of the dHvA susceptibility oscillations in the same sample used for the Knight-shift measurements give further support to this viewpoint, since the field variation of the amplitude of the susceptibility oscillations is drastically different from the corresponding field dependence of the oscillatory Knight shift.

I. INTRODUCTION

IN an earlier paper,[1] the results of a study of the field dependence of the Knight shift σ in a monocrystal of white tin were reported. It was found that above 11 kG, σ exhibits easily observable oscillations, which are periodic in reciprocal field. The results of an extended field-dependent investigation of σ in tin at 1.2°K are reported here.

The major contribution to σ comes from the hyperfine interaction of the nuclear magnetic moment with the spins of the electrons occupying states close to the Fermi level. The difference in the observed nuclear magnetic resonance (NMR) frequency ν for a given nucleus situated in a conductor and the free-atom frequency ν_0 divided by ν_0 is given essentially by the magnetic shielding constant

$$(\nu-\nu_0)/\nu_0=\sigma=-H^{-1}(\delta F/\delta\mu_n)\mu_{n=0}\,, \tag{1}$$

where F is the free energy, H is the applied magnetic field, and μ_n is the nuclear magnetic moment. In the limit of small magnetic fields and considering only spin effects, this expression may be evaluated to first order in μ_n to yield the Townes, Herring, and Knight[2] expression for the Knight shift

$$\sigma=(8\pi/3)\chi_p\langle|\psi(0)|^2\rangle_{\text{av}}\Omega\,, \tag{2}$$

where Ω is the atomic volume, χ_p is the paramagnetic spin susceptibility of the conduction electrons, and $\langle|\psi(0)|^2\rangle_{\text{av}}$ is the ground-state wave functions of the conduction electrons averaged over the Fermi surface and evaluated at the nucleus. Das and Sondheimer[3] have evaluated Eq. (1) including both the spin and orbital moments of the conduction electrons and obtain, for free electrons,

$$\sigma=(8\pi/3)(\chi_d+\chi_p)\,, \tag{3}$$

where χ_d is the diamagnetic susceptibility of the conduction electrons. Here it is assumed that $\langle|\psi(0)|^2\rangle_{\text{av}}\Omega=1$. These authors then conjecture that Eq. (3) will remain valid for the oscillatory as well as the steady part of the susceptibility, and that an oscillatory Knight shift might be observable. Oscillations in σ from this effect have been further commented on by Kaplan[4] and by Rodriguez.[5] Their estimates show that the Knight-shift oscillations arising from the variation of the density of electron states should be observable in fields of the order of 3×10^4 G and at temperatures of about 2°K.

An exact calculation of the above effect by Stephen[6] shows that the major contribution to the oscillatory component comes from the diamagnetic term in Eq. (3), and for the mass of the electron equal to the free-electron mass the paramagnetic component has no oscillatory terms. The amplitude of the oscillatory diamagnetic term is independent of the applied field and the paramagnetic term exhibits oscillations for parabolic energy bands increasing in amplitude as $H^{1/2}$, where H is the strength of the applied magnetic field. Using a generalization of the effective-mass approximation, Dogopolov and Bystrik[7] arrived at the same conclusions as Stephen concerning the field dependence of the amplitude of

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† On leave from Aligarh Muslim University, Aligarh, India.

[1] J. M. Reynolds, R. G. Goodrich, and S. A. Khan, Phys. Rev. Letters 16, 609 (1966).

[2] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. 77, 852 (1950).

[3] T. P. Das and E. H. Sondheimer, Phil. Mag. 5, 529 (1960).

[4] J. I. Kaplan, J. Phys. Chem. Solids 23, 826 (1962).

[5] S. Rodriguez, Phys. Letters 4, 306 (1963).

[6] M. J. Stephen, Phys. Rev. 123, 126 (1961).

[7] D. G. Dolgopolov and P. S. Bystrik, Zh. Eksperim. i Teor. Fiz. 46, 593 (1964) [English transl.: Soviet Phys.—JETP 19, 404 (1964)].

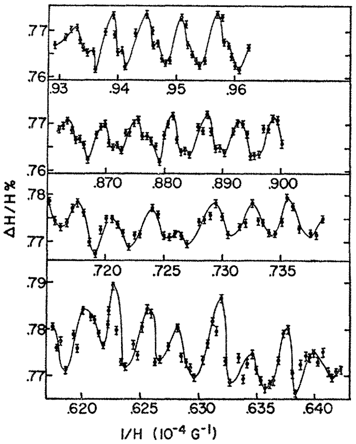

FIG. 1. The Knight shift versus reciprocal field for four ranges of the magnetic field applied along the [001] direction.

the oscillatory part of the Knight shift $\tilde{\sigma}$ and showed that for a chemical potential of order 10^{-13} erg and magnetic fields of order 10^4 G, $\tilde{\sigma}$ should have an amplitude 10^{-3} times as large as σ.

In all of the above considerations, σ is assumed to arise from the susceptibility factor in Eq. (2) with the wave-function factor remaining independent of the applied field. The fact that in metals the conduction electron ground-state wave functions are not independent of the applied magnetic field has been the subject of much discussion in the past few years in connection with the interpretation of experiments which measure the various properties of the Fermi surface of metals and semiconductors, especially when the metal is exhibiting magnetic breakdown.[8] Recently, Glasser[9] has considered the first-order effects of the lattice potential on the ground-state wave functions of electrons in metals as a function of magnetic field, and has shown that reasonable agreement with the oscillatory-Knight-shift experimental results can be obtained for sufficiently high magnetic fields.

Knight-shift measurements on powdered samples of tin have been reported by McGarvey and Gutowsky,[10] by Bloembergen and Rowland,[11] and by Karimov and Shchegolev.[12] The first monocrystal experiments were performed by Jones and Williams,[13] who determined the anisotropy of both the Knight shift and the NMR linewidth in white tin. During the course of their experiments, a preliminary search for the oscillatory component of the Knight shift was carried out, but no reproducible effect could be determined over the rather limited field range that they investigated.[14]

II. EXPERIMENTAL DETAILS

The sample was prepared from a zone-refined bar of white tin obtained from Cominco Products Incorporated, Spokane, Washington (quoted purity: 99.9999%). A large monocrystal cut from this bar exhibited a residual resistance ratio of $R_{300°K}/R_{4.2°K} \approx 27\,000$. The bar contained a large crystal which was cut out, oriented, and reshaped into a parallelepiped approximately 20 mm×17 mm×10 mm with the tetragonal axis within 1° of normal to the largest face. Laue back-reflection x-ray photographs were used for orienting the crystal, and cutting and planing were done by spark erosion. Although a light acid etch indicated that the entire piece was single crystal, x-ray photographs were taken at several points to ensure that the crystal was not twinned. In order to increase the effective surface area and reduce the eddy-current losses, this piece was then cut into 25 wafers of about the same thickness with the [001] direction contained in the plane of the wafers and perpendicular to an edge. Identifying marks were made on one of the surfaces of the parallelepiped before it was cut, so that the wafers could be reassembled with the axes orientation preserved. The spark damage was removed by etching in 40% hydrochloric and 10% nitric acid. The final average size of the wafers was 17 mm×10 mm×0.3 mm. These wafers were sandwiched together in proper order with a 0.013-mm-thick Mylar sheet placed between each of them. Small quantities of Q dope were between the layers and a coating of Q dope covered the entire sample so that it would be strengthened. The over-all size of the resultant sandwich was 17 mm×10 mm×9 mm. The rf coil was wound from No. 30 multistrand copper wire over a 0.025 mm-Mylar sheet on a form of the same size as the sample. The coil was removed from the form and placed around the sample during measurements. The coil form made the coil rigid, reduced the

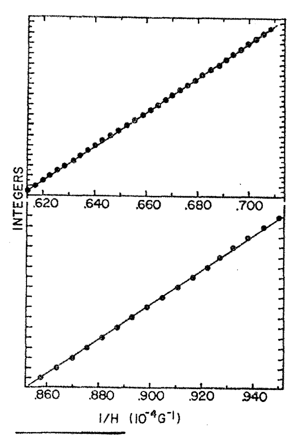

FIG. 2. Reciprocal field values of maximum Knight shift versus integers. The upper curve is for the short-period oscillations (3.0×10⁻⁷ G⁻¹), and the lower curve is for the long period oscillations (5.8 ×10⁻⁷ G⁻¹).

[8] M. H. Cohen and L. M. Falicov, Phys. Rev. Letters **5**, 544 (1960).
[9] M. L. Glasser, Phys. Rev. **150**, 234 (1966).
[10] B. R. McGarvey and H. S. Gutowsky, J. Chem. Phys. **21**, 2114 (1953).
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[13] E. P. Jones and D. Ll. Williams, Phys. Letters **1**, 109 (1962).
[14] E. P. Jones and D. Ll. Williams, Can. J. Phys. **42**, 1499 (1964).

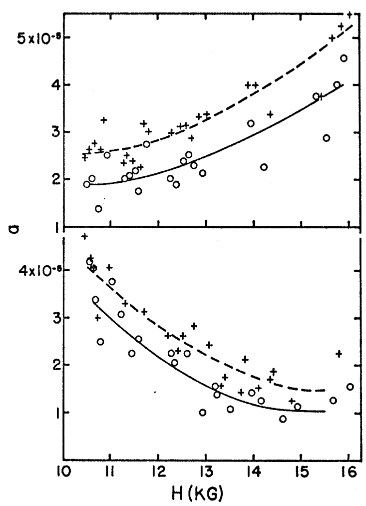


FIG. 3. Plot of the amplitude a of the Knight-shift oscillations $\bar{\sigma}$ versus magnetic-field strength for the field along the [001] axis. The upper curve is for the short-period oscillations (3.0×10^{-7} G^{-1}) and the lower curve is for the long-period oscillations (5.8×10^{-7} G^{-1}).

possibility of straining the sample, and improved the Q of the oscillator.

The sample used in this experiment was not the same as the one used previously.[1] However, it was cut from the same zone-refined bar: residual resistance ratio $(R_{300°K}/R_{1.2°K})\approx27\,000$. It was found that the sample previously used was misoriented by approximately 10°, which accounted for the discrepancy between the observed periods and the periods shown in other effects.

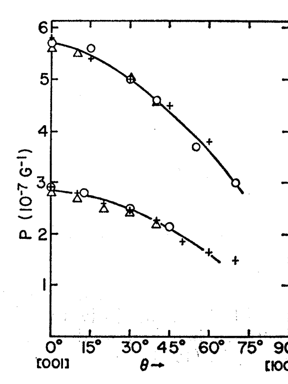
All measurements were made at a temperature of 1.2°K. The magnet used was a low-impedance iron-core magnet capable of producing a field strength of 26.5 kG. At fields below 20 kG, where all of the NMR measurements were performed, the field homogeneity over the volume of the sample was found to be better than one part in 10^5. The derivative of the rf absorption with respect to field versus applied magnetic field was recorded using a standard Pound-Knight-Watkins marginal oscillator,[15] lock-in amplification, and field modulation. Data were recorded every 15 kc/sec between 16.5 and 25.9 mc/sec covering a field range from 10.5 to 16.2 kG. The procedure used to obtain the Knight shift at each value of H was to set the oscillation frequency and sweep the magnetic field over a 5-G range centered on the expected resonant field. Each of the resonance curves obtained in this manner was then analyzed for the center field and changes in line shape. The line shape and width (~1.5 G) remained constant within experimental error for all data reported here. The dispersion of the resonant frequency during the NMR resonance was monitored on an electronic-frequency counter and was found to be negligible compared to oscillations in the absorption as a function of applied field.

III. RESULTS

The Knight shift exhibits two sets of oscillations periodic in reciprocal field in most of the field range investigated. The longer period is dominant at fields around 11 kG, whereas the shorter period becomes dominant as the field is increased. In Fig. 1, both oscillations are shown in different field ranges from which an increase in the short-period amplitude and a decay in long-period amplitude is evident. The inverse-field values versus integers for both periods are shown in Fig. 2. The reciprocals of the slopes of these straight lines give the average values of the two periods. A detailed analysis of the amplitude of these oscillations was carried out over the entire range of the magnetic field. A point-by-point study of the amplitude was carried out at the maxima and minima of this envelope in several field ranges, and the results are shown in Fig. 3. The crosses represent the amplitude at the points of maxima and the circles at the minima of the over-all envelope. The average behavior is indicated by the dashed and continuous curves, respectively. The amplitude of the long-period oscillations decreases as the magnetic field increases, whereas the short-period oscillations show a continuous growth in amplitude with increasing magnetic field. Because of the wide scatter of these points no attempt has been made to fit these curves to a power law in H; however, from inspection of Fig. 3 the power is apparently greater than unity.

The angular dependence of the periods and amplitudes were studied for both the long- and short-period oscillations in different field ranges. The results of several runs are summarized in Figs. 4 and 5. In Fig. 4, the dependence of the period on angle is depicted for both the short- and the long-period oscillations. In Fig. 5, the average dependence of the amplitude on angle for these oscillations is shown. It is evident from Fig. 4 that the long period decreases rapidly as the angle θ between the [001] direction and the magnetic-field direction is increased. The short period shows a less rapid decrease. The linear fit of the square of the period of the long-period oscillations versus $\cos^2\theta$ (Fig. 6) indicates an

FIG. 4. Angular variation of the measured periods of the Knight-shift oscillations for the magnetic field applied in the (100) plane. The upper curve is for the long-period oscillations (5.8×10^{-7} G^{-1}) and the lower curve is for the short-period oscillations (3×10^{-7} G^{-1}).



[15] G. D. Watkins, Ph.D. thesis, Harvard University, 1952 (unpublished); E. P. Jones, Ph.D. thesis, University of British Columbia, 1963 (unpublished).

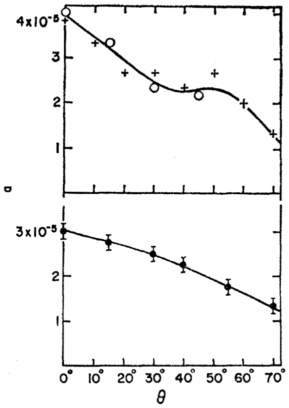


FIG. 5. Variation of amplitudes a of $\tilde{\sigma}$ with orientation of magnetic field in the (100) plane. The upper curve is for short-period oscillations (3.0×10^{-7} G^{-1}) and the lower curve is for the long-period oscillations (5.8×10^{-7} G^{-1}).

approximately cylindrical surface with its axis along [001], giving rise to the long-period oscillations.

The average Knight shift displays an over-all increase with increasing magnetic field as is shown in Fig. 7. This type behavior was also noted by Jones and Williams[14,15] in a lower range of magnetic field. Although the over-all increase in σ of 0.015% is evident in the extended field range of Fig. 7, it was not a noticeable effect over the field range necessary for a few oscillations of the Knight shift and thus was not taken into account in analyzing the amplitudes of the oscillatory components of σ.

For the purposes of comparison, measurements of the de Haas-van Alphen (dHvA) oscillations in the magnetization **M** were carried out on the same sample as that on which the Knight-shift measurements were made.[16] The field-modulation technique[17] was used and a signal proportional to the second derivative of the magnetization was recorded. All measurements were performed at 1.2°K using a modulation frequency of 130 Hz and a modulation amplitude of 1 G. The skin depth of the modulation field for these samples in the field range 10–20 kG was calculated to be several times the thickness of each wafer. In addition, the phase of the detected signal relative to the phase of the applied modulation field was monitored during sweeps of the magnetic field and found not to change during the field sweep. A typical recorder trace is shown in Fig. 8. The resolution of these oscillations at fields above 2 kG and the small amount of observed beating for a single period indicates that the sandwiched sample was indeed strain-free and well oriented. When detecting the

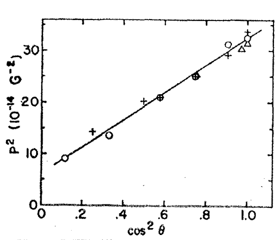


FIG. 6. The square of the period of the long-period (5.8×10^{-7} G^{-1}) oscillations versus the square of the cosine of the angle between the magnetic field and the [001] axis.

[16] These measurements were performed at the suggestion of Dr. David Shoenberg (private communication).

[17] D. Shoenberg and P. J. Stiles, Proc. Roy. Soc. (London) **A281**, 62 (1964).

second derivative of the magnetization, the individual oscillations are attenuated by a factor of $(P_i^2H^4)^{-1}$, where P_i is the period in reciprocal field of the ith oscillation.[18] To obtain the correct field dependence of the magnetization, the amplitude must be multiplied by $P_i^2H^4$ for each period. However, to compare the amplitudes with the Knight-shift measurements the field variation of the susceptibility M/H must be obtained. This requires a point-by-point multiplication of the amplitudes by $P_i^2H^3$. The periods were analyzed by standard methods and their amplitudes were plotted as a function of H after being multiplied by $P_i^2H^3$; the results are shown in Fig. 9.

IV. DISCUSSION

A. Comparison of Periods of Oscillations with the Fermi Surface of Tin

In this section, the experimental results of Sec. III are compared with the Fermi surface of tin.[19] A cross-sectional view of this Fermi surface in the basal plane is shown in Fig. 10. The two periods observed, 5.8×10^{-7} and 3×10^{-7} G^{-1} for the field along the [001] direction, are in agreement with periods expected from the hole

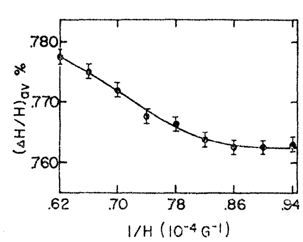


FIG. 7. The average Knight shift versus reciprocal field for the field directed along the [001] axis.

orbits $3\delta_1$ and $3\delta_2$, respectively. The $3\delta_2$ orbit is on the knobs of the third-zone-hole cylinders which appear according to the pseudopotential calculation of Weisz[20] of the band structure of Sn and had previously been ascribed to the 5 μ electron orbits existing in the nearly-free-electron model as given by Gold and Priestley.[19] The approximate cylindrical nature of the central portion of the third-band-hole surface defining the orbit $3\delta_1$ is apparent from the angular variation of the longer period shown in Fig. 4 and the p^2 versus $\cos^2\theta$ plot of Fig. 6. The angular variation of the shorter period is less rapid than the cosine (Fig. 4), suggesting a convex surface. This is consistent with the $3\delta_2$ orbit on the knobs of the third-zone cylinders. According to this interpretation, an amplitude maximum in the short-period oscillations due to mixing of the second harmonic of one period with the fundamental frequency of the other is to be expected at the magnetic-field inclination where the period of the $3\delta_2$ orbit on the knobs is half that of the $3\delta_1$ orbit centered at the point X. As shown in Fig. 5, an indication of this at an angle between 40°

[18] L. R. Windmiller, Phys. Rev. **149**, 472 (1966).

[19] A. V. Gold and M. G. Priestley, Phil Mag. **5**, 1089 (1960).

[20] G. Weisz, Phys. Rev. **149**, 504 (1966).

and 50° from the [001] direction is present. Thus, the periods obtained from the oscillatory Knight shift are in satisfactory agreement with those expected from the Fermi surface of tin.

B. Amplitude of the Oscillations

In this section, the observed amplitude of the oscillatory parts of the Knight shift $\tilde{\sigma}$ is compared to the theoretical estimates of its components as calculated by various authors.

The most detailed calculation of the susceptibility contributions to the Knight shift was done by Stephen.[6] He calculated the exact free energy including the complete hyperfine interaction in the scaler-effective-mass

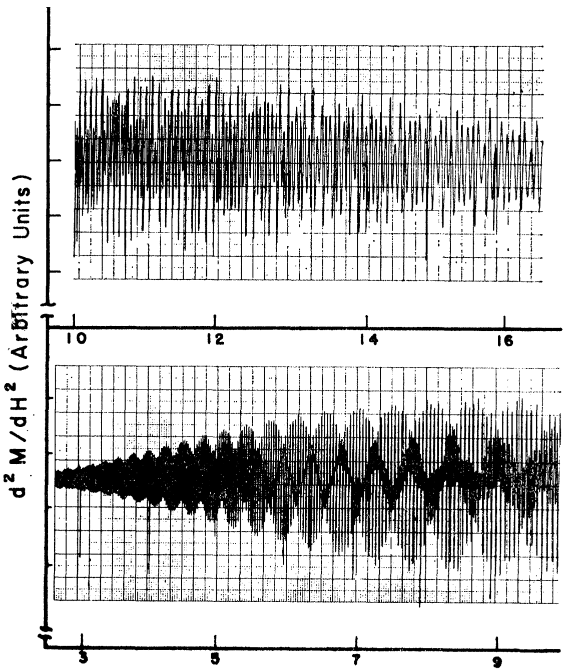


FIG. 8. Recorder trace of the second derivative with respect to H of the magnetization as a function of the magnetic field for the field directed along the [001] axis.

approximation, and obtained the following expressions for the paramagnetic and diamagnetic components of $\tilde{\sigma}$:[21]

$$\tilde{\sigma}_p=\frac{4\pi^2N\mu_0{}^2}{V\zeta_0}kT\left(\frac{1}{\mu_0H\zeta_0}\frac{m}{m^*}\right)^{1/2}\times\sum_{n=1}^{\infty}\frac{(-1)^n\sin(n\pi m^*/m)\cos(n\pi\zeta_0/\mu_0{}^*H-\frac{1}{4}\pi)}{n^{1/2}\sinh[(n\pi^2/\mu_0{}^*H)kT]},\quad(4)$$

[21] An integral occurring in Stephen's calculations of $\tilde{\sigma}$ is in error by a factor of -2 and has been corrected here. For details see M. L. Glasser, J. Math. Phys. 5, 1150 (1964).

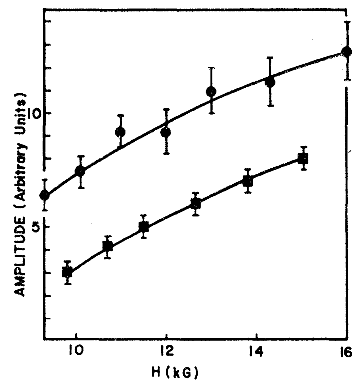


FIG. 9. Variation of the computed amplitude of the dHvA susceptibility as a function of the magnetic field strength, the field being along the [001] axis. The upper curve is for the long-period oscillations (5.8×10^{-7} G^{-1}), and the lower curve is for the short-period oscillations (3.0×10^{-7} G^{-1}).

$$\tilde{\sigma}_d=-\frac{6N\pi^3\mu_0{}^*kT}{V\zeta_0H}\times\sum_{n=1}^{\infty}\frac{(-1)^nI(n)\cos(n\pi m^*/m)\sin n\pi\zeta_0/\mu_0{}^*H}{\sinh[(n\pi^2/\mu_0{}^*H)kT]},\quad(5)$$

with

$$\zeta_0=\left(9\pi\frac{N^2}{V^2}\right)^{1/3}\frac{\pi\hbar^2}{2m^*},\quad I(n)=\int_0^1 ds[s(1-s)]^{1/2}|\sin n\pi s|,$$

where ζ_0 is the Fermi energy, k is the Boltzmann constant, T is the absolute temperature, m^* is the effective mass of the carriers, $\mu_0{}^*$ is the effective Bohr magneton,

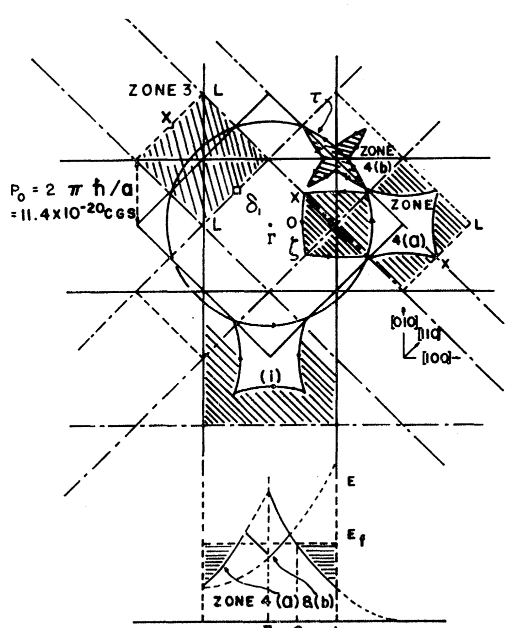


FIG. 10. Basal cross section of the Fermi surface of tin in the extended zone scheme showing the freak orbit (i) generated as a result of magnetic breakdown connecting orbits $3\delta_1$ and $4a\zeta$.

N/V is the density of the electrons taking part in the interaction, and $I(n)$ is an integral expression which has been evaluated numerically by Glasser.[22] The region of interest in this case is where $\pi^2 kT/\mu_0^* H<1$, and only the first terms of the sum in Eqs. (4) and (5) are important. This condition is met in the liquid-helium-temperature range and in fields of 10^4 G where the amplitudes of the first terms are

$$\tilde{\sigma}_p \simeq (4N/V)(\mu_0/\zeta_0)^{3/2}(m/m^*)^{1/2}\mu_0^* H^{1/2}, \tag{6}$$

$$\tilde{\sigma}_d \simeq (6N\pi\mu_0^{*2}/V\zeta_0)I(1), \tag{7}$$

where $I(1)\simeq 0.3$.[22] Putting in values for the carriers observed in tin shows that in a magnetic field of 10^4 G,

$$\tilde{\sigma}_p \simeq 10^{-3}\tilde{\sigma}_d,$$

and hence only $\tilde{\sigma}_d$ need be considered. This, however, probably underestimates $\tilde{\sigma}_p$ since V^{-1} is used instead of $|\psi(0)|^2$ to obtain the numerical result. In $\tilde{\sigma}_d$ there is neither a field nor a temperature dependence of the amplitude.

Dolgopolov and Bystrik[7] retained only the Fermi-contact part of the hyperfine interaction in the interaction Hamiltonian and obtained an expression for the oscillatory part of the Knight shift in terms of the local curvature of the Fermi surface. Their result is

$$\tilde{\sigma} = \frac{8\mu_0}{3\pi\sqrt{2}\pi}\left(\frac{e}{ch}\right)^{3/2}(\sqrt{H})\left|\frac{\partial^2 S}{\partial p_z^2}\right|_m^{-1/2} \times \sum_{n=1}^{\infty}\frac{\psi(n\lambda)}{n^{3/2}}\cos\left[\frac{nc}{ehH}S_m(\zeta_0)\pm\tfrac{1}{4}\pi - 2\pi n\gamma\right] \times \sin\left[\frac{n}{2m_0}\frac{\partial S(\zeta_0)}{\partial \zeta_0}\right], \tag{8}$$

with

$$\psi(n\lambda)=n\lambda/\sinh n\lambda,$$
$$\lambda=(\pi ckT/ehH)\partial S_m(\epsilon)/\partial\epsilon.$$

Here, S_m is the area of an extremal section of the Fermi surface, e is the charge on an electron, $2\pi h$ is Planck's constant, c is the velocity of light in free space, γ is a small phase correction which is equal to $\frac{1}{2}$ for the case of free electrons, p_z is the z component of the electron's momentum; ϵ is the electron energy, and $[|\partial^2 S/\partial p_z^2|_m]^{1/2}$, where the derivative is taken at the extremal point, is a nondimensional quantity representing the anisotropy of the Fermi boundary surface: It is equal to $(2\pi)^{1/2}$ for the case of a spherical surface. The amplitude of $\tilde{\sigma}$ increases as $H^{1/2}$ in this expression. A numerical estimate of the amplitude is obtained by comparing Eq. (8) to the oscillating part of the magnetic susceptibility $\tilde{\chi}_p$.[23] This gives

$$\tilde{\sigma} \simeq \frac{8\pi\mu_0}{3}\frac{\partial S_m(\zeta)}{\partial\zeta}\frac{1}{S_m(\zeta)}\chi_p H.$$

[22] M. L. Glasser, J. Math. Phys. 43, 158 (1964).

[23] I. M. Lifshitz and A. M. Kosevich, Zh. Eksperim. i Teor. Fiz. **29**, 730 (1955) [English transl.: Soviet Phys.—JETP **2**, 636 (1956)].

Since here only the paramagnetic contribution is being considered, the paramagnetic contribution to Eq. (3) can be used to obtain

$$\tilde{\sigma} \simeq \mu_0\frac{\partial S_m(\zeta)}{\partial\zeta}\frac{1}{S_m(\zeta)}\sigma_p H$$
$$\simeq \mu_0(H/\zeta)\sigma_p. \tag{9}$$

For tin in a field of 10^4 G the largest this can be is $\tilde{\sigma}=10^{-7}$. For a parabolic energy band this result agrees with Stephen's $\tilde{\sigma}_p$.

In the nearly-free-electron approximation, Glasser[9] obtains an expression for the oscillatory part of the Knight shift by expanding the free energy of the electrons in powers of the lattice potential $V(\mathbf{r}) = \sum_K V_K e^{i\mathbf{K}\cdot\mathbf{r}}$, where $\mathbf{K}$ is a reciprocal lattice vector. The validity of this calculation is limited to two regions of magnetic field: (1) weak fields where $\mu_0 H \ll V_K$ and (2) high fields where $\mu_0 H \gg V_K$, and $K \neq 2K_F$, where K_F is the radius of the free-electron sphere. Oscillatory behavior is obtained only in the high-field limit, with the result

$$\tilde{\sigma}=\tfrac{1}{2}(\mu_0 H)^{1/2}\left[\frac{8\pi}{3}\mu_0^2\left(\frac{m}{2\pi h^2}\right)^{3/2}\right] \times \sum_K \frac{V_K}{\zeta}\left[\theta_0^{-3/2}\cos\left(\frac{\pi\xi_0}{\mu_0 H}+\tfrac{1}{4}\pi\right)\right] - \sum_{k=1}^{\infty}\left\{\frac{(k+1)}{|k\pi+\theta|^{3/2}}\cos\left(\frac{\pi\xi_k^+}{\mu_0 H}+\tfrac{1}{4}\pi\right) + \frac{(k-1)}{|k\pi-\theta_0|^{3/2}}\cos\left(\frac{\pi\xi_k^-}{\mu_0 H}+\tfrac{1}{4}\pi\right)\right\}, \tag{10}$$

where

$$\xi_0=(1/2\pi)\epsilon(\mathbf{K})g_1(\theta_0),\quad \xi_k^{\pm}=k\zeta\pm\xi_0,$$
$$\epsilon(\mathbf{K})=(h^2/2m)K_z^2+(h^2/2m)(K_x^2+K_y^2),$$
$$g_1(\theta_0)=\tfrac{1}{2}a\theta_0-(a-1)^{1/2},$$
$$a=4\zeta/\epsilon(\mathbf{K})\quad\text{and}\quad\cos\theta_0=(2-a)/a.$$

It is seen that the amplitude of the oscillations increases as $H^{1/2}$ in this expresion.

If the result is applied to an orbit around a symmetry point on the zone boundary, the amplitude of the oscillations is

$$r=\frac{\mathrm{amp}\tilde{\sigma}}{\sigma(H=0)}=\frac{\mathrm{amp}\tilde{\sigma}}{\frac{1}{3}8\pi\chi_p}=\frac{\delta(\pi\mu_0 H)^{1/2}}{8(\zeta\theta_0)^{3/2}}, \tag{11}$$

where δ is a band gap and θ_0 is the angular aperture of the particular sheet of the Fermi surface as seen from the center of the zone. For an angular aperture of a few degrees this expression leads to a value of the amplitude in close agreement with the observed value. This close agreement may be fortuitous since to obtain convergence of the perturbation expansion giving rise to Eq. (10) a high-field approximation ($\mu_0 H \gg V_k$) must be used. The present experiment does not satisfy this requirement in the range of fields investigated. Equation (10) is only correct to first order in V_K and Glasser[24] has pointed out that to second order in V_K the amplitude of the oscillation can be written as $CH^{3/2}(1-e^{-H_0/H})$, where C is a constant. This suggests that, were the calculation to be carried to infinite order in V_K, the behavior would actually be exponential rather than algebraic in the magnetic field.

The numerical results of all the calculations evaluated at 10^4 G are summarized in Table I. Glasser's calculations give the best agreement with the observed value of the amplitude at this field for the case of tin. Stephen's estimates, based on diamagnetic effects in the magnetic susceptibility, are almost an order of magnitude too small.

Since both the diamagnetic-susceptibility factor and the wave-function factor give estimates of the amplitude which are within an order of magnitude of the observed amplitude, the field dependence of the amplitude is considered to determine the major contributing component. The theories of Glasser[9] and of Dolgopolov and Bystrik[7] predict a $H^{1/2}$ field dependence for the oscillation amplitude under normal conditions, i.e., not considering the effect of magnetic breakdown. In Stephen's calculation, the paramagnetic component is three orders of magnitude smaller than the diamagnetic component and has a field dependence of $H^{1/2}$. The more dominant diamagnetic oscillations have no field dependence. Experimentally, however, the amplitude is found to depend on the magnetic field. In the case of the short-period oscillation (3×10^{-7} G^{-1}), the amplitude increases with the magnetic field. This rules out the possibility of the oscillations being due to oscillations in the diamagnetic susceptibility. However, a diamagnetic contribution to the wave-function factor has not been examined. Further support to the argument that the Knight-shift oscillations do not arise from the susceptibility terms is found from the magnetization measurements. As can be seen from a comparison of Figs. 3 and 9, the field dependences of the amplitudes of $\tilde{\sigma}$ and $\tilde{\chi}$ are in opposite directions for the $3\delta_1$ orbit and they are of different powers for the $3\delta_2$ orbit. In all the calculations of $\tilde{\sigma}$ it is tacitly assumed that the electron system in the metal is acted on by the externally applied field **H**. Shoenberg has shown that this not the case, and that one should actually include the magnetic induction **B** in the free-energy calculation. In order to properly include this effect in the theory, careful account must be taken of the demagnetizing factors of the samples on which the measurements are performed. The sample used in the present experiment is a series of wafers separated by insulating sheets. Since the insulating sheets are much thinner than each wafer of Sn and the rf penetrates the insulating sheets, the net result can be approximated by a solid rectangular parallelepiped being penetrated throughout by the rf fields. The crystallographic orientation of the sample was such that (Sec. II) the field dependence of the amplitude $\tilde{\sigma}$ as shown in Fig. 3 was obtained by applying the field perpendicular to one of the faces of the sample. In this case, the field at different points in the sample will be continuously variable from nearly $\mathbf{H}+2\pi\mathbf{M}$ at a point at the center of one of the faces perpendicular to the field to **H** at points on surfaces parallel to the applied field. Since the rf coil completely encloses the sample, the detected NMR signal is an average of measurements made on nuclei being affected by this continuously variable field. Assuming, then, that **B** rather than **H** acts on the nuclei, this should cause the NMR line to be broadened by an amount of order M over and above its width due to various relaxation mechanisms. The measured linewidth is 1.5 G, and changes in this width of 0.2 G can easily be detected. The linewidth is found not to change by as much as 0.4 G for all fields investigated. Nevertheless, the Knight shift oscillates by as much as 2.0 G due to the beating of two dHvA periods. From these considerations it is concluded that the observed $\tilde{\sigma}$ is not simply a result of the field inside the metal oscillating. However, the use of **B** in the calculations of the susceptibility factors in $\tilde{\sigma}$ may bring their behavior into better agreement with the present results. Furthermore, it is seen from the susceptibility measurements that the amplitudes in $\tilde{\sigma}$ do not follow those of the magnetization oscillations.

A simple physical interpretation of the paramagnetic effects may be obtained by considering the spin splitting of the Landau levels in a magnetic field.[25] For a field directed along the [001] axis, there are two neighboring orbits in the same plane, $3\delta_1$ and $4a\zeta$. On the fourth band the ζ orbit is quite extended and the electrons do not remain particularly near any symmetry point in the zone; thus one does not expect these electrons to be characterized by any particular s or p character near the atomic sites. However, on the $3\delta_1$ orbit the electrons remain near the symmetry point X and retain a large amount of s character. In the presence of a strong

TABLE I. A comparison of the observed amplitude of $\tilde{\sigma}$ in Sn to calculations of the various components. All values are for 10^4 G and 1.2°K.

Theory	Amplitude	Ratio calc/obs
Stephen[a] (diamagnetic component)	6.8×10^{-6}	~1/7
Stephen[a] (paramagnetic component)	$\sim10^{-9}$	~1/10 000
Dolgopolov and Bystrik[b]	$\sim10^{-7}$	~1/400
Glasser[c]	4×10^{-5}	~1

[a] See Ref. 6. [b] See Ref. 7. [c] See Ref. 9.

[24] M. L. Glasser (private communication).

[25] The authors are indebted to W. G. Chambers for suggesting this mechanism.

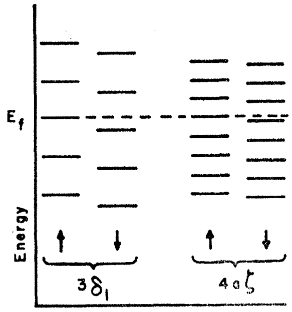


FIG. 11. Energy-level diagram for the spin splitting of Landau levels near the Fermi level in the presence of a strong magnetic field. Levels are shown for electrons on both the $3\delta_1$ and $4a\zeta$ orbits of the Fermi surface.

magnetic field, the Landau levels may be split into spin-up and spin-down states, causing an asymmetric distribution of the two spin states at the Fermi level. This type of energy-level distribution is shown in Fig. 11 for the $3\delta_1$ orbit having a large spin splitting and for the $4a\zeta$ orbit with a larger effective mass, and thus, smaller spin splitting. Since the wave functions of the electrons on the $3\delta_1$ orbit have a large component of s character, they should exert a large influence on the contact term of the hyperfine interaction, and as the magnetic field increases and the different spin orientations pass through the Fermi level, this influence will completely reverse sign at the periodicity of the dHvA period for the $3\delta_1$ orbit. This effect would not present a large distortion in the magnetization oscillations since the major contribution in these is of a diamagnetic origin.

C. Effect of Magnetic Breakdown

The decrease in amplitude of the component of $\bar{\sigma}$ having the longer period ($3\delta_1$ orbit) with increasing magnetic field is attributed to the effect of magnetic breakdown.[8] In the absence of any spin-orbit coupling, the symmetry of the white tin lattice requires the existence of degenerate energy bands along the XL and XP lines on the ⟨110⟩ face of the Brillouin zone.[20,26,27] This degeneracy is preserved only at the points X and L when spin-orbit effects are taken into account, leaving a very small band gap between the third and fourth bands near the point X. Thus, magnetic breakdown occurs at moderate field strengths and couples the $3\delta_1$ orbit on the third band to the $4a\zeta$ orbit on the fourth band which generates the orbit (i) shown in Fig. 10.

The observed component of $\bar{\sigma}$ corresponding to the $3\delta_1$ orbit is found to decrease in amplitude over the range of fields investigated. However, the susceptibility oscillations having the same periodicity do not decrease in amplitude over the same field range. Assuming, then, that the Knight-shift oscillations are indeed due to oscillations in the ground-state wave functions, this behavior indicates that the wave functions are much more sensitive to the amount of tunneling occurring during breakdown than are the susceptibility oscillations. This is compatible with the arguments presented in Sec. IVB, in which the oscillation amplitude is very sensitive to the wave functions having a definite symmetry. Breakdown would cause the $3\delta_1$ electrons to lose this symmetry as they tunnel into the $4a\zeta$ orbit.

[26] S. Mase, J. Phys. Soc. Japan 14, 1538 (1959).
[27] M. Miasek, Phys. Rev. 130, 11 (1963).

V. CONCLUSION

None of the theories of $\bar{\sigma}$ advanced so far completely explains the behavior of the Knight shift as a function of applied field in Sn. Glasser[9] has obtained an expression for the amplitude of $\bar{\sigma}$ which depends on oscillations in the ground-state wave functions of the contributing electrons that gives the correct amplitude at moderate fields. However, his calculation does not include magnetic-breakdown effects which tend to completely dampen oscillations arising from orbits experiencing breakdown in a rather narrow field range. For the observed orbit that does not experience breakdown effects, the observed field dependence of $\bar{\sigma}$ differs from that predicted by Glasser,[9] but nevertheless increases in amplitude with increased field. It is suggested that if Glasser's theory were to be carried to higher order in the lattice potential, better agreement with the field dependence might be obtained. In the various theories which attribute the oscillations to the susceptibility factor in $\bar{\sigma}$, better agreement with experiment may be obtained when accurate values of $|\psi(0)|^2$ are used to obtain numerical results, and when **B** rather than **H** is used to calculate the free energy of the electron system.

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