"Slater=$\frac{5}{6}$" calculation does show a neck, while the "Slater=1" calculation does not.

Unlike the neck radius, the belly radii are far less sensitive to the location of the Fermi level, and the "Slater=$\frac{5}{6}$" results for the belly radii are in good agreement with those reported by Bohm and Esterling.[4]

The four peaks in the d band observed by Krolikowski are also present in the "Slater=$\frac{5}{6}$" curve (see Fig. 2). Since the experimental curve is based on an optical density of states, the relative heights of the peaks are not necessarily expected to agree with the density of states from the present calculations. However, the locations of the peaks with respect to the Fermi level should be, and are, in agreement.

4. CONCLUSION

It is concluded that although the self-consistent APW method of calculating the energy band structure of silver yields results that, in general, are in reasonable agreement with experimental findings, that agreement is improved when the Slater exchange term is reduced to $\frac{5}{6}$ of its original value.

ACKNOWLEDGMENTS

The author wishes to thank Dr. J. H. Wood for many helpful discussions concerning this work. The interest and comments of Dr. W. E. Spicer are also appreciated. The author also wishes to thank F. W. Schonfeld and W. N. Miner for their help.

PHYSICAL REVIEW VOLUME 172, NUMBER 3 15 AUGUST 1968

Knight Shift in Single-Crystal Mercury*

R. W. WEINERT† AND R. T. SCHUMACHER
Physics Department, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

(Received 26 January 1968; revised manuscript received 15 April 1968)

The Knight shift of the Hg^{199} nucleus in oriented single crystals of mercury has been measured at $T=1.2°K$. The isotropic shift given in terms of ν_{Hg}, the resonant frequency of the Hg^{199} nucleus in the metal, and ν_D, the resonant frequency of the deuterium nucleus, is $(\nu_D)_{293°K}/(\nu_{Hg})_{1.2°K}=0.83856\pm0.00003$. The anisotropic Knight shift was measured and led to the result $(K_\perp-K_\parallel)/K_{iso}=7.8\pm0.3\%$. Field-dependent oscillations of the Knight shift were not seen. Theoretical equations for the oscillation amplitude are discussed for particular oscillation frequencies in Hg and Sn.

I. INTRODUCTION

It was demonstrated in 1962 by Sagalyn and Hofman[1] that with proper attention to the relevant considerations, nuclear resonance signals can be seen without great difficulty in single crystals of metals. Since their original work on Cu and Al, work has been reported on the noncubic metals tin,[2] cadmium,[3] and thallium,[4] and recently on an oscillatory Knight shift in tin[5] and cadmium.[6] We have added to the list the nuclear resonance of the 16.9% abundant isotope Hg^{199} in single-crystal mercury.

Our original intention had been to search for a field-dependent Knight shift such as has been successfully seen in tin[5] and cadmium[6] subsequent to the beginnings of our work. We will report the negative results of our effort in Sec. III of this paper. In addition, we have measured both the isotropic and anisotropic Knight shifts at liquid-helium temperatures. The isotropic shift of Hg^{199} has been measured[7] accurately by observation of the resonance frequency and field in the liquid state (room temperature). The isotropic shift has also been measured,[8] with a relatively large uncertainty of 2%, at helium temperature in polycrystalline mercury. The anisotropic shift has previously only been inferred in Ref. 8 from the linewidth and line shape in polycrystalline samples at relatively low fields and temperatures.

Problems involving experimental technique played a significant role in the conduct of the experiment. We had to overcome a variety of interconnected difficulties brought about by the low abundance of the only spin-$\frac{1}{2}$ isotope, Hg^{199}, the nuclear-resonance techniques required when working with oriented single crystals, and the highly inconvenient fact that mercury is liquid at room temperature. These questions will be discussed briefly in Sec. II of this paper; for many of the details we

---

[*] This work was partially supported by the National Science Foundation, and is based upon a thesis submitted by R. W. Weinert to Carnegie-Mellon University in partial fulfillment of the requirements for the Ph.D. degree.

[†] Westinghouse Predoctoral Fellow. Present address: Westinghouse Research Laboratories, Pittsburgh, Pa. 15235.

[1] P. L. Sagalyn and J. A. Hofman, Phys. Rev. **127**, 68 (1962).

[2] E. P. Jones and D. L. Williams, Phys. Letters **1**, 109 (1962); Can. J. Phys. **42**, 1499 (1964).

[3] H. E. Schone, Phys. Rev. Letters **13**, 12 (1964).

[4] D. L. Williams, Phys. Letters **26**, 79 (1967).

[5] J. M. Reynolds, R. G. Goodrich, and S. A. Khan, Phys. Rev. Letters **16**, 609 (1966); S. A. Khan, J. M. Reynolds, and R. G. Goodrich, Phys. Rev. **163**, 579 (1967).

[6] R. G. Goodrich, S. A. Khan, and J. M. Reynolds, Bull. Am. Phys. Soc. **13**, 485 (1968).

[7] W. E. Blumberg, J. Eisinger, and R. G. Shulman, J. Phys. Chem. Solids **26**, 1187 (1965).

[8] F. Reif, Phys. Rev. **102**, 1417 (1956); **106**, 208 (1957).

refer the reader to the thesis[9] of one of us (R. W. W.). Section III describes the measurement of the Knight shift and the search for field-dependent effects, and these are all related to appropriate theory in Sec. IV.

II. EXPERIMENTAL TECHNIQUES

A. Electronics

The experimental arrangement is shown schematically in Fig. 1. A super-regenerative oscillator[10] (SRO) was used to excite and detect the Hg^{199} resonance in single-crystal mercury, in conjunction with audio-field modulation and synchronous detection equipment. For most of the data to be presented later, the SRO was operated with a duty cycle of $\frac{1}{2}$, a quench frequency of 40 kHz, and with approximately 30 V peak to peak of rf on the sample coil. Measurements of the radio frequency and external magnetic field at resonance were done in the following manner. The SRO was locked to a stable external source of rf while the Hg^{199} resonance was being recorded, and the frequency of the external source was measured with a conventional frequency counter. The field measurement was done by observing the nuclear resonance of Al^{27} in an aluminum metal powder sample placed inside the Dewar and around the mercury sample. The aluminum resonance was detected with a Robinson box,[11] and the frequency of this cw detector was measured directly with a frequency counter. Since the Knight shift of aluminum is known at helium temperatures,[12] relative to the room-temperature value, this frequency measurement yielded the value of the external field at the sample site. The mercury sample and aluminum sample were small in size (less than 1 cm in length and diameter) so that the external field measured with the aluminum metal differed from the actual external field at the mercury sample by less than $1:10^5$.

B. Sample Considerations

Because mercury metal is liquid at room temperature, single crystals of mercury are difficult to work with, and special techniques had to be empolyed to obtain the samples used in this work. The samples were grown from oriented seeds; the technique employed in obtain-

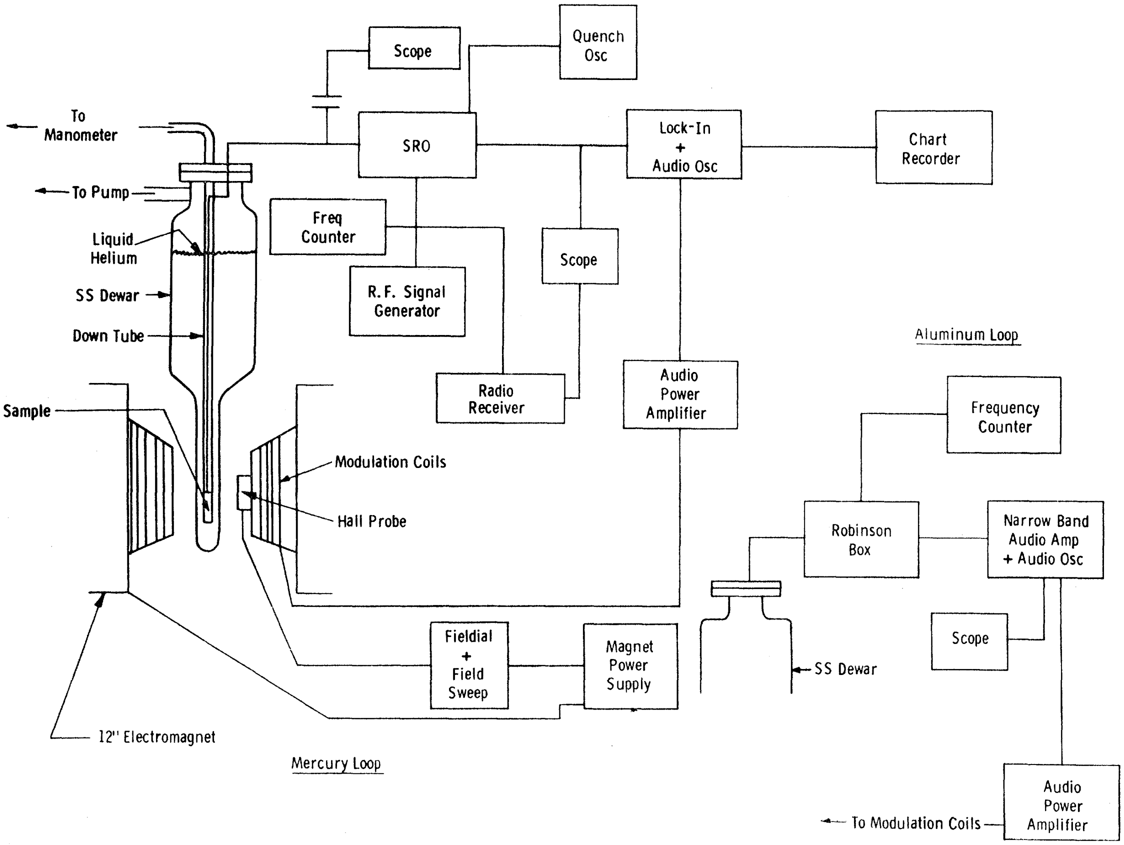

FIG. 1. Equipment used to display and measure the Hg^{199} and Al^{27}resonance in the metal.

---

[9] R. W. Weinert, Ph.D. thesis, Carnegie-Mellon University, 1967 (unpublished).

[10] A. Narath, W. J. O'Sullivan, W. A. Robinson, and W. W. Simmons, Rev. Sci. Instr. 35, 476 (1964).

[11] F. N. H. Robinson, J. Sci. Instr. **36**, 481 (1959).

[12] D. W. Feldman, Ph.D. thesis, University of California, Berkeley, 1959 (unpublished).

ing the seed crystals is discussed in Refs. 13 and 14. Mercury metal freezes at $-38.5°\text{C}$ into a rhombohedral crystal structure with $a=2.9963$ Å and $\alpha=70°\,44.6'$ at 4°K.[15] The two samples on which experiments were done were grown from seeds with the threefold $[111]$ axis and with the $[0\bar{1}1]$ axis along the cylindrical seed axes, respectively. All of the mercury metal used in this work was stated to be 99.99999% pure at obtained from the United Mineral and Chemical Corporation.

Since poor signal-to-noise was anticipated, the rf filling factor was an important consideration when making the coil forms. For obvious reasons no attempt was made to wrap the rf coil directly on the metal as has been done for some metals,[16] but the coil forms used were made of extremely thin-wall C-8 Epoxy tubes. The sample on which the anisotropic Knight-shift data were taken was seeded from the bottom and was split up into four pillars of metal in the interior of the rf coil. Since each pillar grew from the same seed, the orientation of each was identical, as was verified by x ray. For this sample the $[0\bar{1}1]$ axis was parallel to the coil axis and perpendicualr to the external magnetic field H_0 to within 2°. The sample used for the oscillating Knight-shift search was grown in a right circular-cylinder coil form made of C-8 Epoxy with a wall thickness of 0.003 in. The coil consisted of 60 turns of No. 40 copper wire seated in Epoxy. For this sample the $[111]$ axis was parallel to the coil axis to within 2°. For both of the above samples the signal-to-noise ratio at $T\sim1.2°\text{K}$ and $H_0\sim16$ kG was between 10 and 20 when a 4-sec time constant was used at the output of the lock-in detector. Under these same conditions the Hg^{199} resonance in the single crystal could not be seen with the Robinson box or a Knight box.[17]

III. EXPERIMENTAL RESULTS

The isotropic Knight shift of Hg^{199} has previously been measured[18,19] at room temperature using $\text{Hg(NO}_3)_2$ as the diamagnetic reference compound. The resonant frequency of the Hg^{199} nucleus in the metal at room temperature has also been measured[7] in terms of the resonant frequency of the deuterium nucleus in D_2O. The low-temperature results reported here will be expressed in terms of the ratio of the deuterium frequency (ν_D) in D_2O to the metallic Hg resonance frequency (ν_Hg). Measurement of this ratio was a two-step process. First the resonant frequency of the aluminum metal (ν_Al) was measured and compared with the measured ν_D at room temperature. The result of this measurement is

$$(\nu_\text{Al}/\nu_\text{D})_R=1.70024\pm0.00002\,, \tag{1}$$

where R denotes room temperature. Secondly, the ratio of the resonant frequencies of Hg^{199} and aluminum were measured at $T=1.2°\text{K}$. The result of this measurement is

$$(\nu_\text{Al}/\nu_\text{Hg})_{1.2°\text{K}}=1.42571\pm0.00002\,. \tag{2}$$

$(\nu_\text{Al})_{1.2°\text{K}}$ must now be related to the room-temperature ν_D. The Knight shift of aluminum as a function of temperature has been independently measured by Feldman[12] and by Borsa and Barnes.[20] In Ref. 12 it is found that $(\delta K/K_R)_\text{Al}=(1.75\pm0.05)\%$ and from Ref. 20 it is found that $(\delta K/K_R)_\text{Al}=(-7.3\pm2.1)\%$ where $\delta K=(K_R-K_{4.2°\text{K}})$. As yet this discrepancy has not been resolved. Magnetic effects caused by the Dewar may be one explanation. Feldman did his experiment in such a way that Dewar effects were rendered unimportant, whereas Borsa and Barnes do not discuss Dewar effects. Because of this we will work out our results using Feldman's data. We now need to know K_R for aluminum in order to calculate $(\nu_\text{Al})_R/(\nu_\text{Al})_{1.2°\text{K}}$. Using our Eq. (1) and the published value[21] $(\nu_\text{Al}/\nu_\text{D})_R=1.69750\pm0.00008$ for AlCl_3 in an aqueous solution, we find $(K_R)_\text{Al}=(0.161\pm0.006)\%$. Other values which use aqueous solutions of AlCl_3 as the reference compound are $(0.161\pm0.001)\%$,[22] $(0.162\pm0.001)\%$,[23] and $(0.150\pm0.001)\%$.[20] Since our calculation is fairly insensitive to the value of $(K_R)_\text{Al}$, we will not discuss the differences in these values but merely state that we use the most accurate 0.161% value. Therefore using $(\delta K/K_R)_\text{Al}=(1.75\pm0.05)\%$ and $(K_R)_\text{Al}=(0.161\pm0.001)\%$, we find

$$(\nu_\text{Al})_R/(\nu_\text{Al})_{1.2°\text{K}}=1.000028\pm0.000001\,. \tag{3}$$

With the noted discrepancies so far the stated accuracy of the above equation has questionable significance. Finally, combining Eqs. (1), (2), and (3) we find

$$(\nu_\text{D})_R/(\nu_\text{Hg})_{1.2°\text{K}}=0.83856\pm0.00003\,. \tag{4}$$

In obtaining these values for metallic samples, the center of the resonance line had to be identified in the presence of the asymmetry associated with the large sample size to skin-depth ratio.[24] In spite of the commonly accepted lore that line shapes from a SRO are not to be trusted, we observed that the aluminum resonances at room temperature were of normal shape and width on the SRO, just as if a marginal oscillator detector had been in use. The line shapes at low tem-

---

[13] G. B. Brandt, Ph.D. thesis, Carnegie-Mellon University, 1966 (unpublished).

[14] J. M. Dishman, Ph.D. thesis, Carnegie-Mellon University, 1967 (unpublished).

[15] C. S. Barrett, Acta Cryst. **10**, 58 (1957).

[16] H. E. Schone and P. W. Olson, Rev. Sci. Instr. **26**, 843 (1965).

[17] W. D. Knight and R. V. Pound, Rev. Sci. Instr. **21**, 219 (1950).

[18] W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. (N. Y.) **8**, 173 (1959).

[19] W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 98.

[20] F. Borsa and R. G. Barnes, J. Phys. Chem. Solids **27**, 567 (1966).

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

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

[23] D. R. Teeters, Ph.D. thesis, University of California, Berkeley 1955 (unpublished).

[24] P. S. Allen and E. F. W. Seymour, Proc. Phys. Soc. (London) **82**, 174 (1963).

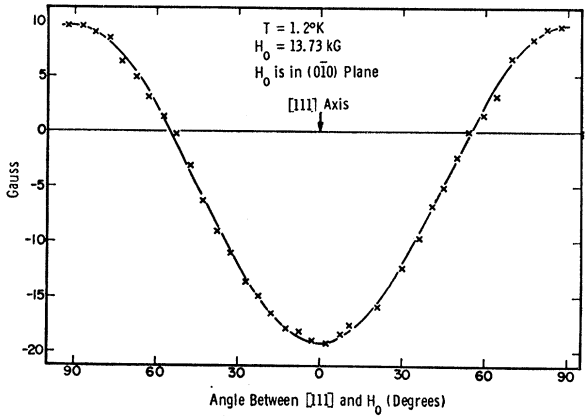

FIG. 2. Anisotropic Knight-shift data for the Hg^{199} nucleus in single crystal mercury. The absolute value of the internal field at the nuclear site corresponding to the 0-G ordinate is $H_0(1+K_{\mathrm{iso}})$.

perature in Hg also had the normal appearance appropriate to an admixture of the dispersive and absorptive mode. We used the correction theory of Ref. 7, which is based entirely on the asymmetry of the resonance itself, to determine the line-center position.

From the published[7] values, $(\nu_{\mathrm{D}}/\nu_{\mathrm{Hg}})_R=0.838247 \pm 0.000015$ and $(K_R)_{\mathrm{Hg}}=(2.724\pm 0.005)\%$, and our data, we obtain

$$\left(\frac{K_R-K_{1.2^\circ\mathrm{K}}}{K_R}\right)_{\mathrm{Hg}^{199}}=(1.4\pm 0.2)\%, \tag{5}$$

where K is the isotropic Knight shift. We use the value of $(K_R)_{\mathrm{Hg}^{199}}$ of Ref. 7, since it is the most accurate value we could find in the literature. It was calculated in Ref. 7 by comparing their measured g value of Hg^{199} in the metal to the free-atom g value.[25] Knight[18] *et al.* report no measurable change ($\pm 2\%$) in the Knight shift of Hg^{199} as the metal changes state from liquid to solid. Since the magnitude of the fractional change in $(K)_{\mathrm{Hg}^{199}}$ between 1.2°K and room temperature is only 1.4% (0.8% if the Al data of Ref. 20 were used), it is difficult to say whether this change is in fact due to temperature or the change of state which occurs between the two temperatures. Until a more accurate measurement is made concerning the change in $(K)_{\mathrm{Hg}^{199}}$ as mercury changes state, this question remains open.

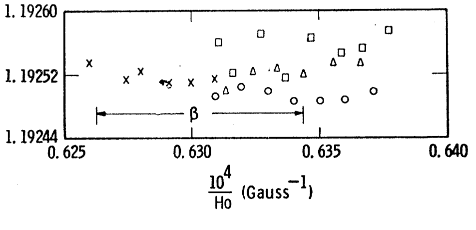

FIG. 3. Oscillating Knight-shift data for β orbits in mercury for $T\sim 1.2$°K and $H_0\sim 16$ kG. $\mathbf{H}_0$ is in the basal plane and along the [$2\bar{1}\bar{1}$]. The period of the β oscillation is also shown. The different points represent separate runs.

The anisotropic Knight-shift data are shown in Fig. 2. The experiment was done at an external field of approximately 13.73 kG and a temperature of 1.2°K. The solid curve corresponds to $K_{\mathrm{an}}[\frac{1}{2}(3\cos^2\theta-1)]$, where θ is the angle between H_0 and the threefold [111] axis, and, from the data,

$$K_{\mathrm{an}}=(-0.140\pm 0.002)\%. \tag{6}$$

A convenient measure of the magnitude of the anisotropy is given by

$$\left(\frac{K_{\parallel}-K_{\perp}}{K_{\mathrm{iso}}}\right)_{T=1.2^\circ\mathrm{K}}=(-7.8\pm 0.3)\%, \tag{7}$$

where $K_{\parallel}=K_{\mathrm{iso}}+K_{\mathrm{an}}$ and $K_{\perp}=K_{\mathrm{iso}}-\frac{1}{2}K_{\mathrm{an}}$. The negative sign indicates that the electron distribution about the Hg^{199} nucleus, for electrons with energy near the Fermi energy, is contracted along the [111] axis and elongated in directions perpendicular to this axis.

The oscillating Knight-shift data are shown in Fig. 3. The orientation of the field was in the [$2\bar{1}\bar{1}$] direction relative to the crystalline axis of mercury. The first zone orbits in reciprocal space responsible for the large de Haas–van Alphen oscillations, seen when H_0 is in this direction, have been labeled as β orbits by Brandt and Rayne.[26] The same notation is used here, and the expected period (in G^{-1}) is shown in Fig. 3. The search was carried out at temperatures between 1.18 and 1.22°K and in the highest available external field of 16 kG. From the data we conclude that the fractional peak-to-peak amplitude of any oscillations is less than 6×10^{-5}. Other high-frequency oscillations, labeled α and τ in Ref. 25, were searched for and were not seen. We did not expect to see these oscillations, for, using the estimates of Sec. IV they should be roughly 10^3 times smaller in amplitude than the β oscillations.

IV. DISCUSSION

A. Knight Shift

We will concern ourselves here entirely with the anisotropic Knight shift. The most recent discussion is given by Boon,[27] and we phrase our discussion in terms of his. The anisotropic Knight shift may be defined in terms of a second-rank tensor $\mathbf{K}$ by separating out the isotropic part:

$$K_{\mathrm{iso}}=\tfrac{1}{3}\,\mathrm{Tr}\mathbf{K}. \tag{8}$$

The remaining traceless component has, in the representation in which $\mathbf{K}$ is diagonal, the *xx*, *yy*, and *zz* elements $-\frac{1}{2}K_{\mathrm{an}}$, $-\frac{1}{2}K_{\mathrm{an}}$, and K_{an}, respectively. Mercury falls into the class of uniaxial systems for which

---

[25] B. Cognac and J. Brossel, Compt. Rend. **249**, 77 (1959).

[26] G. B. Brandt and J. A. Rayne, Phys. Letters **15**, 18 (1965); Phys. Rev. **148**, 644 (1966).

[27] M. H. Boon, Physica **30**, 1326 (1964).

Boon shows that

$$K(\theta)=K_{\mathrm{an}}P_2{}^0(\cos\theta),$$

where $P_2{}^0(\cos\theta)$ is an associated Legendre polynomial; θ is the angle between the applied field H_0 and the c axis (or rhombohedral axis) of the crystal. The constant K_{an} is given by the integral

$$K_{\mathrm{an}}=\int d^3r'\frac{F'(\mathbf{r}')}{r'^3}P_2{}^0(\cos\theta'). \tag{9}$$

$F'(\mathbf{r}')$ is demonstrated explicitly by Boon; he shows that it is a basis for the identity representation of the point group of the crystal. It is this fact which Boon uses to classify the angular dependences of the Knight shift for various crystal classes. $F'(\mathbf{r}')$ may be written in terms of eigenfunctions $\psi_p(r')$ of the electron Hamiltonian, which consists of the usual kinetic energy, potential energy, and Zeeman terms. Boon's $F'(\mathbf{r}')$ is thus

$$F'(\mathbf{r}')=g^2\mu_\theta{}^2\sum_p(\partial f/\partial\epsilon)_p|\psi_p(\mathbf{r}')|^2, \tag{10}$$

where g is the usual electron-magnetic moment, μ_0 is the Bohr magneton, and f is the Fermi function whose argument is the usual energy ϵ_p associated with $\psi_p(\mathbf{r}')$.

It has frequently been conventional to discuss the anisotropic Knight shift in terms of an expansion of $\psi_p(\mathbf{r}')$ in angular-momentum eigenfunctions of the Hamiltonian. It is clear from the orthogonality of the Legendre polynomials that the angular part of $F'(\mathbf{r}')$ must transform as $P_2{}^0(\cos\theta)$; otherwise the coefficient K_{an} vanishes. Early discussions[28,29] of the anisotropic Knight shift were couched entirely in terms of the cross term in $|\psi_p(\mathbf{r}')|^2$ which came from a product of $l=1$ functions. Limited to this one term, the anisotropic Knight shift, combined with knowledge of the fractional s character from the isotropic Knight shift, seemed to give satisfying information on the fractional p character of the conduction-electron wave functions. We merely wish to point out here that the s-d cross terms also transforms as $P_2{}^0(\cos\theta)$, and there is no reason to believe that the magnitude of the s-d term is negligible. This comment has also been made by Jones and Williams[2] with reference to tin. Indeed, an analysis in Ref. 9 which deliberately ignores the s-d cross term gives nonsensical results. Thus the two pieces of experimental information K_{iso} and K_{an} are insufficient to specify more of the coefficients of the wave-function expansion than does K_{iso} by itself in the usual way when considering mercury.

In addition, we show in the Appendix that anisotropy of the g tensor, and related anisotropy of the conduction-electron susceptibility, is also a mechanism for the anisotropic Knight shift. This point is implicit in the appendix of Boon,[27] where the effects of spin-orbit interaction are calculated. We note for completeness that Boon's appendix shows that if the spin-orbit interaction is included, higher harmonics than $P_2{}^0(\cos\theta)$ are to be expected in the angular dependence; indeed, he points out that in principle isotropy is not be to expected in the cubic system because of these terms. Our data are not accurate enough to warrant analysis in terms of harmonics higher than $P_2{}^0$ however.

B. Oscillatory Knight Shift

The possibility that the Knight shift might be field dependent in pure metals at low temperatures was first recognized in print by Das and Sondheimer.[30] Since their suggestion, the effect has been calculated on a free-electron model by several investigators, most completely by Stephen.[31] We wish to employ Stephen's formula for the field-dependent paramagnetic shift σ_p to estimate the size of the effect for β orbits in Hg with the external field in the $[2\bar{1}\bar{1}]$ direction. We also wish to compare the paramagnetic shift with the diamagnetic shift σ_d, which according to Stephen, is much larger. As we shall see, Stephen's estimate that $(\sigma_p/\sigma_d)\ll 1$ is somewhat in error, at least as we interpret it for Hg, and the inequality is probably reversed. We will show that Stephen's formula, modified slightly, does in fact predict oscillation amplitudes less than we could have seen experimentally for β orbits in mercury, and gives reasonable agreement with experiment for the recently observed Knight-shift oscillators in white tin.[5]

Stephen writes the following result for $(\sigma_p)_{\mathrm{osc}}$:

$$(\sigma_p)_{\mathrm{osc}}=\frac{4\pi^2N\mu_0{}^2}{V\zeta_0}kT\left(\frac{m}{m^*}\frac{1}{\mu_0H\zeta_0}\right)^{1/2}\sum_n(-1)^n\times\left\{\frac{\sin(n\pi m^*/m)\cos(n\pi\zeta_0/\mu_0{}^*H-\frac{1}{4}\pi)}{n^{1/2}\sinh(n\pi^2kT/\mu_0{}^*H)}\right\}. \tag{11}$$

To obtain a meaningful number for our particular circumstances it is necessary to interpret and modify this formula. The shielding constant $(\sigma_p)_{\mathrm{osc}}$ has been related to the oscillating part of the paramagnetic susceptibility by the equation

$$(\sigma_p)_{\mathrm{osc}}=\tfrac{1}{3}(8\pi)(\chi_p)_{\mathrm{osc}}. \tag{12}$$

This relationship is valid for a uniform electron density; use of the relationship in a real metal is, according to Das and Sondheimer,[30] and estimate only. In the spirit of that relation, Stephen has replaced the conduction electron density at the nucleus $\langle|\psi_{(0)}|^2\rangle_{E_F}=P_F$ by the factor $1/V$, where V is the atomic volume. As he recognizes, the use of $1/V$ in place of P_F substantially underestimates the size of the paramagnetic term. We arbitrarily modify his $(\sigma_p)_{\mathrm{osc}}$ by multiplying by P_FV. N/V is now the density of electrons participating in the

---

[28] N. Bloembergen and T. J. Rowland, Acta Met. 1, 731 (1953).

[29] Y. Masuda, J. Phys. Soc. Japan 12, 523 (1957).

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

[31] M. J. Stephen, Phys. Rev. 123, 126 (1961); see also S. Rodriquez, Phys. Letters 4, 306 (1963).

β orbits. We can estimate N/V by using the formulas derived by Shoenberg,[32] which relate de Haas–van Alphen frequencies to electron densities, and the results of Brandt and Rayne's de Haas–van Alphen experiments on Hg. ζ_0 is the Fermi energy for the β electrons and $\mu_0^* = (m/m^*)\mu_0$ is the Bohr magneton μ_0 multiplied by the inverse effective-mass ratio for the β electrons. The ratio ζ_0/μ_0^* is most usefully written as

$$\zeta_0/\mu_0^* = 2\nu_\beta(1/H)\,, \qquad (13)$$

where $\nu_\beta(1/H)$ is the frequency (in G) of the β de Haas–van Alphen oscillations, for which we use the experimental data. Keeping just the $n=1$ term in the sum, we can rewrite Eq. (11):

$$(\sigma_p)_{\text{osc}} = -4\pi^2 \frac{kT}{H^{1/2}} (P_F V)\left(\frac{N}{V}\right)\left(\frac{m^*}{m}\right)\left[2\nu_\beta\left(\frac{1}{H}\right)\right]^{-3/2} \times \frac{\sin(\pi m^*/m)\cos[(2\pi/H)\nu_\beta - \frac{1}{4}\pi]}{\sinh(\pi^2 kT/\mu_0^* H)}. \qquad (14)$$

The isotropic Knight shift, $K = \frac{1}{3}(8\pi)\chi_p P_F V$ allows one to estimate the electron probability density at the nucleus. A reasonable estimate of χ_p, obtained in a number of ways,[9] is $\chi_p = 1.5\times10^{-6}$ cgs volume units. Using this value of χ_p and the measured isotropic Knight shift we obtain $P_F V \simeq 2000$. Using $N/V = 0.10\times10^{20}/\text{cm}^3$, $T = 1.2°\text{K}$, $H = 16\,000$ G, $\nu_\beta(1/H) = 10.8\times10^5$ G, and $m^*/m = 0.23$, we obtain $(\sigma_p)_{\text{osc}} \sim 1.0\times10^{-5}$, i.e., the oscillatory shift in the resonance position at 16 kG should be roughly ±0.2 G. This estimate rests on the additional assumptions that the fractional s character of the β electrons is the same as the average s character over the entire Fermi surface and that T^*, the effective-scattering temperature,[33] is zero. From the field dependence[26] of the de Haas–van Alphen oscillation amplitude for β orbits in mercury samples very similar to the one we used in this work, T^* was found to be about 1°K. Since our experimental upper limit on the peak-to-peak amplitude ($\pm3\times10^{-5}$) of the Knight-shift oscillations is slightly more than the predicted oscillation amplitude for $T^* = 0$, a value of $T^* = 1°\text{K}$ would certainly not allow us to see the oscillations experimentally according to the above estimate. For $T^* = 1°\text{K}$, Eq. (14) yields $\sigma_p \sim 0.12\times10^{-5}$. The fractional s character of the β electrons cannot be calculated unless the Knight-shift oscillations are seen and an accurate value of T^* for the particular sample is known. All that can be said is that the theoretical estimate above is not a gross underestimate for the particular sample and oscillations that we searched for in mercury.

The conclusion is unchanged upon consideration of $(\sigma_d)_{\text{osc}}$. From Stephen, we can write the ratio of the amplitudes of the oscillating terms:

$$\frac{\sigma_p}{\sigma_d} = \frac{2}{3\pi I(1)}\left(\frac{H}{2\nu_\beta}\right)^{1/2} \frac{m^*}{m} \tan\left(\pi\frac{m^*}{m}\right) P_F V \approx 0.01 P_F V = 20 \qquad (15)$$

if previous numbers are used. In the above equation, $I(1) \approx 0.3$.[34] Thus, unless the fractional s character of the β electrons is less than 5% of the average, the diamagnetic shift is negligible.

Since oscillations in the Knight shift were recently seen[5] in white tin, we wish to use Stephen's equations, as we have used them above, in order to see if there is agreement between theory and experiment. The tin experiment was done at $T = 1.2°\text{K}$ in fields between 10 and 16 kG, directed along [001], on very pure samples. Because of the very high resistance ratio stated for the tin samples, T^* considerations will be ignored in what follows. The de Haas–van Alphen frequencies needed to calculate N/V for the 3δ orbits of tin can be found in the recently published work of Stafleu *et al.*[35] and m^*/m values can be found in the work of Good and Priestly.[36] $P_F V$ is calculated by using the published values of K_{iso} (Ref. 2) and χ_p (Ref. 19) for tin. Using $(N/V)_{3\delta} = 0.33\times10^{21}/\text{cm}^3$, $P_F V = 450$, $(m^*/m)_{3\delta_1} = 0.095$, and $(m^*/m)_{3\delta_2} = 0.15$, Eqs. (14) and (15) yield the results shown in the first four columns of Table I. The fifth column contains the experimental values.

Since $\sigma_p)_{\text{osc}} \sim \sigma_d)_{\text{osc}}$ for the 3δ orbits of tin in the field range between 10 and 16 kG, $\sigma)_{\text{osc}} = \sigma_p)_{\text{osc}} + \sigma_d)_{\text{osc}}$ is the quantity which should be compared to the experimentally observed $\sigma_e)_{\text{osc}}$. It should be emphasized that if the amplitudes of σ_p and σ_d are comparable, the different phases of the trigonometric factors they multiply must be considered in assessing the over-all field dependence of the oscillatory shift. In general, the field dependence under these circumstances will not be expressible terms in of a power of H. The agreement between theory and experiment expressed in Table I is quite good when it is realized that the average $P_F V$ was used and not $(P_F V)_{3\delta}$. The good agreement might suggest that $(P_F V)_{3\delta}$ is not too far from the average value. In fact, if a value $(P_F V)_{3\delta} \approx 4(P_F V)_{\text{av}}$ were used the agree-

TABLE I. A comparison of theoretical amplitudes and experimental amplitudes[a] $(\sigma_e)_{\text{osc}}$ for the oscillating Knight shift in Sn.

Orbit and field	$(\sigma_p)_{\text{osc}}\times10^5$	$(\sigma_d)_{\text{osc}}\times10^5$	$(\sigma)_{\text{osc}}\times10^5$	$(\sigma_e)_{\text{osc}}\times10^5$
$3\delta_1$ (10 kG)	1.6	3.2	1.3	3.5
$3\delta_1$ (16 kG)	2.7	4.3	1.0	1.5
$3\delta_2$ (10 kG)	0.6	0.6	0.3	2.5
$3\delta_2$ (16 kG)	1.2	1.0	0.9	4.0

[a] See Ref. 5

---

[32] D. Shoenberg, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1957), Vol II, p. 226.

[33] R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 500 (1952); **A211**, 517 (1952); **A212**, 38 (1952); **A212**, 47 (1952).

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

[35] M. D. Stafleu and A. R. de Vroomen, Phys. Status Solidi **23**, 675 (1967); **23**, 683 (1967).

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

PHYSICAL REVIEW VOLUME 172, NUMBER 3 15 AUGUST 1968

Theory of the Vibrations of Dilute Alloys with Short-Range Order*

W. M. HARTMANN
Argonne National Laboratory, Argonne, Illinois 60439

(Received 4 December 1967)

Using thermally averaged double-time Green's functions, we develop a theory to calculate the effect of a small concentration of nonrandom mass defects on the vibrational properties of a monatomic crystal. The low-concentration approximation used is shown to be equivalent to that used by Elliott and Taylor for the random-impurity case, correct to first order but only approximately correct to higher orders in the concentration. This simple theory is used to find a shift of the resonant or local-mode peak due to short-range order among defects, which might be seen by infrared absorption in imperfect insulators. The integrated absorption is shown to be independent of the ordering for charged defects, but not for uncharged defects which induce optical absorption through atomic deformations. The general expression derived for the inelastic coherent neutron scattering cross section includes a branch-mixing term which disappears for scattering vectors of high symmetry. Using the Debye approximation (for which the cross section can be written in a self-energy form) and the appropriate short-range order parameters from the linear theory of Clapp and Moss, we calculate the shifts and widths of the neutron scattering peaks for $Cu_{0.907}Au_{0.093}$. The agreement with the experimental results of Svensson, Brockhouse, and Rowe is not good. A small clustering of light mass defects, represented approximately by nearest-neighbor correlations, is shown to broaden a low-frequency impurity band but to have relatively little effect on a high-frequency local mode.

I. INTRODUCTION

WHEN defects are introduced into a crystal, striking changes in the vibrational properties of the crystal may occur. Vibrational modes may appear at frequencies above the band of perfect-crystal vibration frequencies, or the band itself may be altered. These effects have been observed experimentally in measurements of the infrared absorption coefficient and neutron scattering cross sections. Their thermodynamic consequences have been apparent in measurements of specific heat, thermal conductivity, and thermopower. On the whole, the theories of imperfect-crystal vibrations which have been developed are successful in explaining the general features of a wide variety of experiments when the defect atom concentration c is low and when the effect of a single defect extends only to the nearest or second-nearest neighbors. In the simplest approximation, a foreign substitutional atom is treated as an isolated mass defect with force constants unchanged.

The Green's-function theory provides a way to sum exactly all the phonon scatterings from a single defect. At finite defect concentrations, however, the interference between phonons scattered by different defects may become important. Since Dyson's[1] paper on the vibrations of a disordered harmonic chain, many authors have tried to account for these interference effects in one, two, and three dimensions.[2] Recently, Payton and Visscher[3] have performed extensive computer calculations for three-dimensional crystals, and Elliott and Taylor,[4] and Taylor[5] have derived approximate analytic theories for calculating the thermal averages of physical properties of realistic imperfect crystals.

So far as we know, no general theory has been given without the assumption that the defects are randomly distributed in the crystal, although correlations between nearest-neighbor defects have been included in a computation of the moments of the frequency spectrum of a linear chain[6] and in a calculation of the normal-mode frequencies of β-brass to second order in perturbations on a mean crystal.[7] At large concentrations of defects, of course, many alloys become ordered, and a proper theory would begin with the stoichiometric alloy rather than with the pure solvent crystal. Even at defect concentrations well below the ideal concentration, the defects may tend to order themselves to approximate the arrangement of an ordered phase close to the given concentration on the phase diagram.

The theory developed in this paper involves a low-concentration expansion, but allows for possible short-range order among the defects as can be measured by x-ray diffraction. The theory is useful then for those concentrations that are low enough for a low-concentration expansion to apply yet high enough for some ordering of the defects to occur over short ranges. The nonrandom defect distribution is introduced through a defect pair correlation function $\rho_{l_1 l_2}$, which depends only on unit cell indices. For presentation, we have taken the simplest such case, mass defects in a monatomic cubic crystal, but the theory is directly applicable to any problem in which the mass defects can be considered as segregated onto one particular site of the unit cell. Mass defects in alkali halides and III-IV compounds could thus be treated directly, whereas defects in diamond or anion defects in alkaline-earth halides would require a somewhat more complicated formalism with a site-dependent $\boldsymbol{\rho}$.

---

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] F. J. Dyson, Phys. Rev. **92**, 1331 (1953).

[2] See the review by A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 273 ff.

[3] D. N. Payton and W. M. Visscher, Phys. Rev. **154**, 802 (1967); **156**, 1032 (1967).

[4] R. J. Elliott and D. W. Taylor, Proc. Roy. Soc. (London) **296**, 161 (1967). This paper will be referred to as ET.

[5] D. W. Taylor, Phys. Rev. **156**, 1017 (1967).

[6] Y. Fukuda and K. Yoshida, J. Phys. Soc. Japan **17**, 920 (1962).

[7] P. J. Wojtowicz and J. G. Kirkwood, J. Chem. Phys. **33**, 1299 (1960).