viously described in detail,[6] in which the sample serves as the core of an inductance in the tank circuit of an oscillator. Figures 1 and 2 show the change in oscillator frequency on the ordinate, plotted against temperature, as the susceptibility of the sample changes at the superconducting transition.

If one takes the Nb_3Sn compounds to be of mass 394.73 and 402.73, respectively, the value of p for $Nb_3Sn = -0.08 \pm 0.02$. This compares with values in the neighborhood of -0.5 reported for the soft superconducting metals. The difference in magnitude between the observed value of p for the compounds and that of the elemental tin isotopes is far outside any limits of error. Additional experiments are called for before any final conclusions as to the isotope effect in the transition elements can be drawn. It is hoped that in the near future this will be done.

[6] A. L. Schawlow and G. E. Devlin, Phys. Rev. **113**, 120 (1959).

ACKNOWLEDGMENTS

We take this opportunity to thank Dr. B. T. Matthias and Dr. A. L. Schawlow for much helpful discussion.

PHYSICAL REVIEW VOLUME 120, NUMBER 6 DECEMBER 15, 1960

Effective Mass in Gray Tin from Knight Shift Measurements

W. E. BLUMBERG AND J. EISINGER
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received July 25, 1960)

The nuclear magnetic resonance of Sn^{119} in gray tin was measured between 200°K and 300°K and the effective g factor was found to increase by about 4 parts in 10^5 over this temperature range. This increase in Knight shift is thought to arise from an increase in the number of conduction electrons. By combining this result with Busch and Mooser's measurements of the magnetic susceptibility over the same temperature range m_l, the single-valley effective mass of the lighter of the charge carriers, is found to be $(0.3 \pm 0.05)m$ if the electron g factor is 2. The experiment also allows one to determine the Knight shift without making a comparison with a diamagnetic substance. The Knight shift of intrinsic gray tin is found to be 6×10^{-5} at 300°K. The fact that the Knight shift is positive shows that the electron g factor is not negative as would be expected if the band structure of gray tin were similar to that of InSb.

SHIFTS in the nuclear magnetic resonance fields which arise from the hyperfine interaction between the nuclei and conduction electrons are generally known as Knight shifts (k) and have been observed in many metals.[1] Semiconductors are also expected to have Knight shifts but because of the greatly reduced number of conduction electrons at convenient temperatures, the shifts are small and have not previously been observed. In gray tin the forbidden gap is very narrow so that the Knight shift though still small compared to chemical shifts, is made observable by virtue of its temperature dependence. In this way we were able to measure k in gray tin and to use the result in gaining some information about its band structure.

I. THEORY

In intrinsic semiconductors the total number of charge carriers is given by

$$N = (1/2\pi^2)(2kTm/\hbar^2)^{\frac{3}{2}}(\bar{m}_e^* \bar{m}_h^*)^{\frac{3}{4}} F_{\frac{1}{2}}[(E_F - E_c)/kT], \quad (1)$$

where $\bar{m}_e^*$ and $\bar{m}_h^*$ are the average density of state masses for the electrons and holes divided by the free electron mass m and $F_{\frac{1}{2}}(\eta)$ is the Fermi-Dirac function $\int_0^\infty z^{\frac{1}{2}}[1+\exp(z-\eta)]^{-1} dz$. Values for $F_{\frac{1}{2}}(\eta)$ and its derivatives have been computed by McDougall and Stoner.[2] E_F and E_c are the Fermi level and the lower edge of the conduction band, respectively. For an intrinsic semiconductor E_F is completely determined by the gap, temperature, and $\bar{m}_e^*/\bar{m}_h^*$.

Among the experimental quantities which depend on the number of carriers are the magnetic susceptibility χ, the conductivity σ, and the Hall coefficient R. Since these parameters are proportional to $(\bar{m}_e^* \bar{m}_h^*)^{\frac{3}{4}}$ it might be thought that their measurement would yield information about the effective masses. However, one cannot hope to separate either mass from the product $\bar{m}_e^* \bar{m}_h^*$ by such experiments, and one is moreover dealing with an *average* density of state mass whose relation to the effective masses appropriate to each individual conduction band minimum (m_e^*, m_h^*) is complicated and unknown unless the band structure is well understood. The value of N and hence of χ, σ, and R at a particular temperature depends on the value of the energy gap ΔE at this temperature and the position of Fermi level in relation to the gap. For intrinsic semiconductors, $E_F = \Delta E/2 - \frac{3}{4}kT \ln(\bar{m}_e^*/\bar{m}_h^*)$ if E_F is measured from the top of the valence band. Therefore, if the temperature dependence of ΔE is

[1] W. D. Knight, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 2, p. 93.

[2] J. McDougall and E. C. Stoner, Phil. Trans. Roy. Soc. (London) **A237**, 67 (1938).

known, the variation of χ, σ, or R can be used to estimate $\bar{m}_e^*/\bar{m}_h^*$. This ratio can then be combined with $(\bar{m}_e^*\bar{m}_h^*)^{\frac{1}{2}}$ obtained by measuring the absolute value of any of these quantities to obtain $\bar{m}_e^*$ and $\bar{m}_h^*$ but the single-valley density of state masses remains unknown.

The interpretation of Knight shift measurements suffers from the same limitation as was pointed out above. We shall show, however, that by combining the measurement of k and χ an estimate of single valley effective mass m^* can be made.

Formulas for the Knight shift and relaxation time in semiconductors have been derived for both Fermi-Dirac (F-D) and Maxwell-Boltzmann (M-B) statistics by Bloembergen.[3] It is more convenient for our purposes to use the following formulation. We write

$$k=\frac{AM}{2g^*g_I\mu_0}(\chi_{ep}\zeta_e+\chi_{hp}\zeta_h), \tag{2}$$

where A = hyperfine interaction constant, g^* = effective g factor of the carrier divided by the free electron g factor, g_I = nuclear g factor = μ_I/I, M = nuclear mass, χ_{ep}, χ_{hp} = paramagnetic susceptibility per unit mass for electrons and holes, respectively, and ζ_e, ζ_h, = fractional s character of electron and hole wave functions.

Apart from the small temperature dependence due to the volume expansion (which is contained in the susceptibility *per atom* $M\chi_p$), the entire temperature dependence of k is contained in χ_p. For M-B statistics, therefore, k is proportional to $T^{\frac{1}{2}}\exp(-\Delta E/2kT)$ while k is to first order temperature independent for pure F-D statistics. If $E-E_c$ is comparable to kT (E is the highest occupied conduction band level), k is proportional to $1+aT^2$.

The total magnetic susceptibility is given by

$$\chi_{\text{total}}=\chi_{ep}+\chi_{ed}+\chi_{hp}+\chi_{hd}+\chi_i,$$

where the subscript d refers to the diamagnetic susceptibilities and χ_i is the susceptibility of the ion cores, which is temperature independent. Let us call χ the temperature dependent part of χ_{total}. For either charge carrier we have, for parabolic bands,[4]

$$\chi_p=Cg^{*2}, \tag{3}$$

$$\chi_d=C(-1/3m^{*2}), \tag{4}$$

with

$$C=(\mu_0^2/2\pi^2\rho)(2m/\hbar^2)^{\frac{3}{2}}(\bar{m}_e^*\bar{m}_h^*)^{\frac{1}{4}}(kT)^{\frac{1}{2}} \times F_{\frac{1}{2}}'[(E_F-E_c)/kT], \tag{5}$$

where the reduced effective mass m^* is assumed isotropic, ρ is the density and $F_{\frac{1}{2}}'(\eta)$ is the derivative of the Fermi-Dirac function[2] $dF_{\frac{1}{2}}(\eta)/d\eta$. If m^* is not isotropic but has ellipsoidal symmetry with reduced longitudinal and transverse masses m_l^* and m_t^* it is given by $(1/m^*)^2=(1/3m_t^{*2})+(2/3m_l^*m_t^*)$. It is seen from Eqs. (2) and (3) that the sign of k is determined by the sign of g^*. Since χ_p and χ_d have the same temperature dependence regardless of whether the Fermi level is below or above E_c, i.e., whether the statistics is "classical" or "degenerate," we have from (2), (3), and (4),

$$\frac{k}{\chi}=\frac{AM}{2g_I\mu_0}\frac{\zeta_eg_e^*+\zeta_hg_h^*}{g_e^{*2}-1/3m_e^{*2}+g_h^{*2}-1/3m_h^{*2}}. \tag{6}$$

Note that k/χ is independent of the average density of state masses ($\bar{m}^*$). A can usually be estimated with fair precision[1] and even a very crude model of the band structure allows one to make reasonable estimates of g^* and ζ, so that information about the single-valley effective masses (m^*) can be obtained from an experimental determination of k/χ. From (6)

$$(1/m_e^{*2})+(1/m_h^{*2})=3(g_e^{*2}+g_h^{*2}) -(3AM/2g_I\mu_0)(\zeta_eg_e^*+\zeta_hg_h^*)(\chi/k). \tag{7}$$

II. EXPERIMENT

Gray tin (α—Sn) is a semiconductor with the same crystal structure as Si and Ge, but with a gap of only 0.08 ev.[5] It was prepared by innoculating metallic tin (β—Sn) obtained from the United Mineral and Chemical Corporation, New York (impurities one part in 10^7) with gray tin and keeping it at dry ice temperature for a few days. The nuclear resonance of Sn^{119} was observed at a field of 10 000 gauss by means of a Varian wide-line spectrometer. The sample was coarse powder which had a thermocouple junction imbedded in it so that the temperature could be monitored continuously.

The resonance curve was Lorentzian in shape and had a width of 0.4œ at room temperature which is appreciably greater than the dipole-dipole root second moment of 0.07œ. This corresponds to a spin lattice relaxation time T_1 of 2.3×10^{-4} second which is in agreement with $T_1=3\times10^{-4}$ second obtained by observing the saturation of the line with increasing rf field at room temperature. At 195°K T_1 was found to be 9×10^{-4} second. At temperatures much below this, T_1 was too long to be measured by this method and the signal-to-noise ratio too low to allow the determination of the center of the resonance with precision.

The magnetic field was monitored by a Varian 4400 deuteron probe which was in a region of the field which differed from that at the α-Sn sample by a few parts per million. The deuteron and α-Sn resonances were displayed simultaneously by means of a two channel recorder while sweeping the magnetic field and keeping the Sn frequency constant. The deuteron

[3] N. Bloembergen, Physica **20**, 1130 (1954).
[4] W. Pauli, Z. Physik **41**, 81 (1927); L. Landau, Z. Physik **64**, 629 (1930). D. Geist, Z. Physik **157**, 335 (1959).
[5] E. E. Kohnke and A. W. Ewald, Phys. Rev. **102**, 1481 (1956); G. Busch and J. Wieland, Helv. Phys. Acta **26**, 697 (1953).

frequency was changed in increments of about 100 cps to obtain several field calibration points during each passage through the Sn line.

The sample was in a small Dewar containing acetone which was initially at its freezing point (178°K). It was allowed to warm up to room temperature slowly while the temperature and effective g factor of the Sn were measured repeatedly. The effective g factor was found to increase by about 4 parts in 10^5 between 200°K and 300°K.[6] These results are plotted for a series of runs in Fig. 1. In the same figure we have plotted Busch and Mooser's results[7] of their determination of χ. It is seen that both experiments can be fitted satisfactorily by a single curve. In this way we find

$$k/\chi = -1.2\times10^3 \text{ g cm}^{-3}. \quad (8)$$

The value of k for intrinsic $\alpha-$Sn was found to be 6×10^{-5} at 300°K. This represents the smallest Knight shift which has been observed and was moreover obtained without using a diamagnetic tin compound as a comparison material.

III. DISCUSSION

We are now in a position of estimating m^* by using Eq. (7) and making certain assumptions.

In speculating about the band structure of gray tin one can adopt one of two points of view: The first is to consider $\alpha-$Sn as an extrapolation of the series of Group IV semiconductors (C, Si, Ge). The other possibility is to consider $\alpha-$Sn to have a band structure similar to InSb which is the III–V semiconducting compound consisting of its neighbors in the periodic table.

The former approach leads one to expect a band structure similar to that of Ge and hence reduced effective masses of the order of a few tenths and an electron g factor near 2. The latter approach on the other hand, suggests that the conduction band minimum will occur at $\mathbf{k}=0$ as is the case for InSb. Roth, Lax, and Zwerdling[8] have calculated a relationship between g_e^* and m^* for such bands. For spin-orbit interactions which are large compared to ΔE (which undoubtedly applies to $\alpha-$Sn) one can write $2g_e^*=3-(1/m_e^*)$. Since m_e^* at $\mathbf{k}=0$ can be expected to be small (it is of the order of 0.013 [9] for InSb and should be smaller for $\alpha-$Sn which has a smaller gap) this leads to a large negative g factor (-50 for InSb [9]). Since g_h^* and m_h^* can be considered of order unity for such a band structure it can be seen from Eqs. (2) and (6) that k would be negative and k/χ positive. This is not in accord with our experimental result. We shall therefore analyze our result using the assumption that the band structure of $\alpha-$Sn is similar to that of Ge and that g_e and g_h are approximately 2.

Kendall[10] has shown a striking empirical relationship between ΔE and the lattice constants of a number of diamond-type semiconductors which includes $\alpha-$Sn. This again suggests that the band structure of $\alpha-$Sn will not be too different from that of Si and Ge and that interband perturbations[11] of the gap are not important.

Accordingly, we assume the wave functions of the electrons have predominantly s character near the nucleus and that the hole wave functions have negligible s character.[12] This corresponds to putting $\zeta_e=1$, $\zeta_h=0$. Furthermore, as was discussed above, we assume the g factors of the carriers to be the same as for free electrons, i.e., $g_e^*=g_h^*=1$.

The hyperfine interaction A can be estimated from Goudsmit's formula with appropriate corrections for the ionization state in the metal. This leads to a value[1] of $A=0.455$ cm^{-1}. It is encouraging that the measured values of k and χ for $\beta-$Sn together with a reasonable estimate of the ξ, the ratio of electron probability amplitudes at the nucleus in the metal and the free atom, yield a value of A similar to the one given above.[1] It has been found that the Knight shift is the same in cubic and hexagonal lanthanum[13] metal and even a transition from the solid to the liquid state does not change the Knight shift appreciably.[14] It seems justifiable therefore to use the A of $\beta-$Sn as an estimate for A of $\alpha-$Sn.

With these assumptions one finds from (7) and (8) that if $m_e^*\ll m_h^*$, $m_e^*=0.25$. If on the other hand $m_e^*=m_h^*$ one finds $m_e^*=0.35$, so for $m_e^*\leq m_h^*$, $m_e^*=0.3\pm0.05$. Similarly one finds that if $m_h^*\leq m_e^*$, $m_h^*=0.3\pm0.05$. In other words $m_l^*=0.3\pm0.05$ where m_l^* refers to the lighter carrier. This result is quite insensitive to the assumptions we made regarding ζ_e and ζ_h and g^*. If the electron g factor differs from 2 by 50%, this will change m_l^* by approximately 25%.

Note that this effective mass is of the same order of magnitude as is found for Si and Ge.[15] This may seem surprising in view of the much smaller gap for $\alpha-$Sn. The result is however not unreasonable if a displacement in k space between the valence band maximum and the conduction band minimum is postulated as has indeed been found to exist in Si and Ge.[15]

Without further information about the degeneracy and symmetry of the valence and conduction band it is

[6] Note that the temperature dependence of v_A would be in the opposite direction and considerably smaller. See reference 1, p. 126.
[7] G. Busch and E. Mooser, Helv. Phys. Acta **26**, 611 (1953).
[8] L. M. Roth, B. Lax, and S. Zwerdling, Phys. Rev. **114**, 90 (1959).
[9] G. Bemski, Phys. Rev. Letters 4, 62 (1960).
[10] J. T. Kendall, Phil. Mag. **45**, 141 (1954).
[11] See, for example, C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, New York, 1956), p. 288.
[12] Recent experiments by the authors on p-type and n-type gray tin have shown that the electrons are responsible for the observed Knight shift and that the hyperfine interaction between the Sn nucleus and holes is negligible. This justifies putting $\zeta_h=0$.
[13] W. E. Blumberg, J. Eisinger, V, Jaccarino, and B. T. Matthias, Phys. Rev. Letters **5**, 52 (1960).
[14] W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. **8**, 173 (1959).
[15] See, for example, *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Company, New York, 1959).

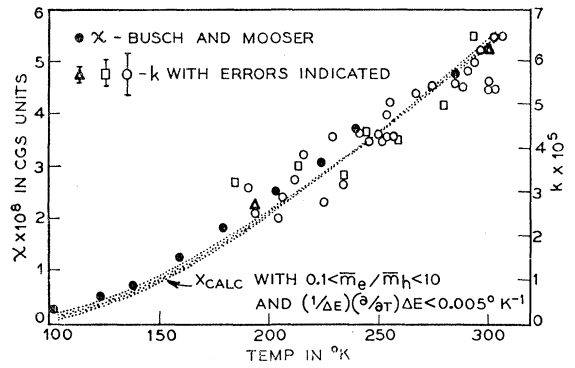

FIG. 1. Knight shift and susceptibility measurements in gray tin as a function of temperature. The various symbols denote experimental points. The stippled area represents the theoretical temperature dependence of k and χ obtained from Eq. (5) and normalized to the experimental points at $T=250°$K. The argument of $F_{\frac{1}{2}}'$ appearing in Eq. (5) depends on both $(\bar{m}_e^*/\bar{m}_h^*)$ and the temperature dependence of ΔE. The stippled area encompasses the mass ratios $0.1\leqslant(\bar{m}_e^*/\bar{m}_h^*)\leqslant 10$ and the gap temperature dependence range $0\leqslant(1/\Delta E)d\Delta E/dT\leqslant 0.005°\text{K}^{-1}$. It appears therefore that for $\alpha-$Sn the temperature dependence of χ and k is quite insensitive to wide variations in $\bar{m}_e^*/\bar{m}_h^*$.

not possible to calculate the effective mass of the heavier carriers.

Since $\bar{m}^*$ represent a mass averaged over all the valleys it must be greater than or equal to m^*. If the band structure contains a number of degenerate bands, the relationship $\bar{m}^*=\lambda^{\frac{2}{3}}m^*$ is expected to hold. If the degeneracy λ is 4 or 6, as is the case in Ge and Si, respectively, $\bar{m}_l^*$ for $\alpha-$Sn would be 0.8 approximately.

Values for $\bar{m}_e^*$ and $\bar{m}_h^*$ have been reported in the literature. Busch and Mooser[7] find that values of $\bar{m}_e^*=\frac{2}{3}$ and $\bar{m}_h^*=3$ are consistent with the observed temperature dependence of χ. These values are, of course, not comparable with the results for the single valley masses obtained above. This is moreover not a fruitful approach since this method yields a value for the product $\bar{m}_e^*\bar{m}_h^*$ but cannot give any information on the effective masses separately or their ratio. This is demonstrated in Fig. 1 which shows how insensitive the temperature dependence of χ for $\alpha-$Sn is to $\bar{m}_e^*/\bar{m}_h^*$. Kohnke and Ewald[5] report $\bar{m}_e^*=\bar{m}_h^*=0.68$ by analyzing conductivity and Hall measurements over a wide temperature range. The assumptions implicit in their results are the equality of $\bar{m}_e^*$ and $\bar{m}_h^*$ and a temperature dependence of the carrier mobilities similar to that found in Ge.

As has been pointed out by Busch and Mooser,[7] magnetic measurements (χ,k) which can be made with powdered samples are—to first order—not affected by carrier scattering by the lattice or impurity centers and can, therefore, be interpreted more easily than electrical measurements. Powder specimens of $\alpha-$Sn can moreover be obtained with greater purity than the bulk specimens which are needed for σ or R measurements.

It may be pointed out here that the Korringa relation for the relaxation time, as modified by Anderson,[16] gives a relaxation time 10^3 longer than that observed. Either this relation as stated does not hold in this case or a more important relaxation mechanism is operative.

IV. CONCLUSION

We have succeeded in measuring the Knight shift in semiconducting $\alpha-$Sn and by combining this measurement with the previously measured susceptibility we find that the reduced effective mass of the lighter charge-carrier is 0.3. While this result was obtained only after making a number of assumptions, it should be noted that the value is not very sensitive to several of these. It is not known if this value refers to holes or electrons. To answer this question similar experiments using $\alpha-$Sn doped with donors and acceptors are being undertaken.

The sign of the Knight shift together with the observation[12] that it is caused by electrons, not holes, excludes negative electron g values. From this one can conclude that in $\alpha-$Sn the conduction band minimum is not at $\mathbf{k}=0$ as had been found in InSb.

ACKNOWLEDGMENTS

We are particularly grateful to S. Meiboom who made his Varian apparatus available to us. We had stimulating discussions with W. Kohn, H. Suhl, and Y. Yafet and thank them for their help. G. Feher and V. Jaccarino loaned us several pieces of equipment, and L. Medford was helpful in the sample preparations.

[16] Quoted by R. G. Shulman and B. J. Wyluda, Phys. Rev. **103**, 1127 (1956).