

Theory of the Effect of Spin-Orbit Coupling on Magnetic Resonance in Some Semiconductors*

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The effect of spin-orbit coupling on the usual band theory of electrons in a lattice is considered. Particular attention is given to the bands in impurity semiconductors with diamond-type structure. g -values are calculated for electron states typical of various possible cases and it is found that different values are obtained according as to whether the Fermi level is near or distant from a band degeneracy. The spin-lattice relaxation time is calculated so that the effect of spin-orbit coupling on the wave functions is included, and times in fair agreement with those observed in silicon and alkali metals are obtained.

I. INTRODUCTION

THERE have recently been reported a number of observations of magnetic resonance in impurity semiconductors,¹ and it is found that the g -values and line-width vary with the material and the impurity concentration. In order to understand these effects a theory is developed here which takes particular account of the effects of spin-orbit coupling. We treat the case in which the electrons can be considered to move through the crystal (and are not trapped at the impurities), and make the usual assumptions of band theory. In another paper (to be referred to as A)² we have treated the effect of including spin in band theory from the group theoretical aspect and have shown that one of its main effects is the splitting of otherwise degenerate bands. In this paper it is shown that the properties of the resonance are rather different if the Fermi level is near or far away from a band degeneracy and in this way useful information can be obtained about the bands from the resonances.

The effect of the orbital angular momentum, as measured by the difference of g from the free electron value of 2.0023, is much larger for electrons in states near a degeneracy. This is calculated for particular kinds of states which are of interest in semiconductors but the resulting expressions should give the correct order of magnitude for all similar cases. Other calculations of such a spin-orbit effect have been carried out by Yafet³ for sodium metal where resonance has also been observed from the conduction electrons.⁴ The observed line-width in semiconductors appears to arise from a spin-lattice relaxation time in most cases, and it is the shortness of this time which may account for the absence of resonance in germanium. Because this time

is the measure of the interaction between the spins and the lattice, and because the interaction between the lattice and the orbital motion of the electron will be large we expect this effect to be greatly influenced by the spin-orbit interaction. The relaxation times due to the interaction with lattice vibrations and impurity centers will be discussed and it is found that the line widths predicted are usually within an order of magnitude of those observed. Calculations are also made for alkali metals and it is found that the mechanism involving spin-orbit coupling produces shorter times than those calculated by Overhauser⁵ on a free-electron model.

II. SPIN-ORBIT COUPLING AND BAND THEORY

The problem of an electron in a solid is usually treated as if it is moving in a perfect rigid lattice under a periodic potential. The Schroedinger equation is

$$[(\mathbf{p}^2/2m) + V]\Psi = E\Psi, \quad (1)$$

where V has both the point and translational symmetry of the lattice. The resulting wave functions are of course the well-known Bloch functions

$$u_k e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (2)$$

where u_k has the translational symmetry of the lattice. In order to introduce the appropriate spin-orbit interaction into (1) we start with the four-component Dirac equation and reduce it to two components in the usual way.⁶ The resulting power series in $(mc)^{-2}$ is to first order

$$\left[\frac{\mathbf{p}^2}{2m} + V - \frac{\mathbf{p}^4}{8m^3c^2} + \frac{\hbar}{4im^2c^2}(\nabla V \cdot \mathbf{p}) + \frac{\hbar}{4m^2c^2}(\nabla V \times \mathbf{p}) \cdot \boldsymbol{\sigma} \right] \Psi = E\Psi. \quad (3)$$

The third term gives the first-order relativistic correction, and will be neglected. The fourth term gives a

* A. W. Overhauser, Phys. Rev. **89**, 689 (1953).

† E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935), p. 129.

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¹ Honig, Portis, Kip, Kittel, and Morin (to be published). Portis, Kip, Kittel, and Brattain, Phys. Rev. **90**, 988 (1953). N. Bloembergen and F. K. Willenbrock, Phys. Rev. **91**, 1281 (1953).

² R. J. Elliott, following paper, Phys. Rev. **95**, 280 (1954).

³ Y. Yafet, Phys. Rev. **85**, 478 (1952).

⁴ G. Feher (to be published); Griswold, Kip, and Kittel, Phys. Rev. **88**, 951 (1951).

small contribution to the energy of states whose eigenfunctions are nonzero at singularities of V . It has the same symmetry properties as V and does not change the form of the Hamiltonian in (1) and can therefore be neglected. The last term is the spin-orbit coupling. (It reduces to the well-known form $\zeta(r)\mathbf{l}\cdot\mathbf{s}$ when V is spherically symmetric.) For the moment we simply note that this term has the same symmetry properties as V . Because there is a term in the spin operator in our Hamiltonian, the resulting eigenfunctions will now be linear combinations of different spin functions and will in general be written

$$[a_k|+\rangle + b_k|-\rangle]e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (4)$$

where $|+\rangle, |-\rangle$ are the two spin states with component of angular momentum $\pm\frac{1}{2}$ along some chosen direction. Considering the components of the matrix equation (3), it is clear that a_k and b_k have the symmetry of the lattice, like u_k in (2).

The symmetry properties of these wave functions are discussed in A, for some interesting lattices. In particular, it is shown that as a consequence of time-reversal symmetry, there is always a twofold degeneracy provided there is inversion in the symmetry group (as there is in the cases of interest here). By operating with the inversion operation on (4) we get a function

$$[a_{-k}|+\rangle + b_{-k}|-\rangle]e^{-i\mathbf{k}\cdot\mathbf{r}}, \quad (5)$$

where a_{-k}, b_{-k} are suitably defined. Inversion has no effect on the spin functions. This has the same energy as (4); and so has the function obtained by reversing the time axis of (5) which is by Kramers' theorem⁷

$$[a_{-k}^*|-\rangle - b_{-k}^*|+\rangle]e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (6)$$

Thus we obtain two functions with the same \mathbf{k} [(4) and (6)] and the same energy. At some points of high symmetry in the Brillouin zone we see in A that time reversal does not give any extra degeneracy. In this case there is still a function like (6) degenerate with (4), but it can be obtained from (4) by an operation with a symmetry group element.

III. APPROXIMATIONS

In order to be able to find the energy level splittings and the actual admixtures of the wave functions caused by the spin-orbit coupling we must find the matrix elements of the term in (3). In general these can only be obtained by complicated calculations of V and the wave functions. Approximate forms can be obtained by using a cellular method like that of Wigner-Seitz⁸ (see Yafet's calculation³). If the tight-binding approximation⁹ is

⁷ H. A. Kramers, Proc. Acad. Sci. Amsterdam **33**, 959 (1930).

⁸ E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).

⁹ See for example F. Seitz, *Modern, Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

valid it can be shown that the spin-orbit coupling effect is rather similar to that in atomic theory.

Now Wannier¹⁰ has shown that the wave function in a periodic lattice can be written in terms of functions centered about each lattice point—the so-called Wannier functions, w . In terms of these the eigenfunctions are

$$\Psi = \frac{1}{\sqrt{N}} \sum_{\mathbf{d}} w_k^s(\mathbf{r}-\mathbf{d}) \exp(i\mathbf{k}\cdot\mathbf{d}), \quad (7)$$

where \mathbf{d} denotes the vector coordinate of a lattice point. The w centered about different points are orthogonal, but they do overlap by a considerable amount. If we reduce all \mathbf{k} into the first zone, each band must be designated by a number s .

If we draw polyhedra about each lattice point made up of the planes perpendicularly bisecting the lines to nearby lattice points, the potential V will be the same in each cell and have a center of symmetry at the lattice point. That is,

$$V = \sum_{\mathbf{d}} V(\mathbf{r}-\mathbf{d}), \quad (8)$$

where $V(\mathbf{r}-\mathbf{d})$ is defined in the polyhedron about \mathbf{d} and is zero elsewhere. Then the spin-orbit coupling can be written

$$\frac{\hbar}{4m^2c^2} \sum_{\mathbf{d}} (\nabla V(\mathbf{r}-\mathbf{d}) \times \mathbf{p}) \cdot \boldsymbol{\sigma} = C. \quad (9)$$

Within the cell about \mathbf{d} , the expression can be written in the usual form,

$$\frac{\hbar^2}{4m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r} \mathbf{l} \cdot \mathbf{s},$$

if \mathbf{d} is the center of the coordinates and V has spherical symmetry. Because of the surrounding atoms, however, V will in fact have a symmetry lower than spherical and this expression must be modified.¹¹ Nevertheless since almost all the spin-orbit interaction arises when the electron is close to the nucleus and since the external field then has little effect, this expression remains a reasonable approximation.

We approximate by putting

$$\begin{aligned} \langle \Psi_s(\mathbf{k}) | C | \Psi_t(\mathbf{k}') \rangle &= \frac{1}{N} \sum_{\mathbf{d}} \exp[i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{d}] \langle w_k^s(\mathbf{r}-\mathbf{d}) | C | w_{k'}^t(\mathbf{r}-\mathbf{d}) \rangle \\ &= \delta_{kk'} \langle w_k^s(\mathbf{r}) | \zeta(r) \mathbf{l} \cdot \mathbf{s} | w_{k'}^t(\mathbf{r}) \rangle \\ &= \delta_{kk'} \lambda \langle w_k^s(\mathbf{r}) | \mathbf{l} \cdot \mathbf{s} | w_{k'}^t(\mathbf{r}) \rangle. \end{aligned} \quad (10)$$

¹⁰ G. H. Wannier, Phys. Rev. **53**, 671 (1938).

¹¹ K. W. H. Stevens (private communication). I am indebted to Dr. Stevens for instructive discussions on the effect of symmetry and the magnitude of λ .

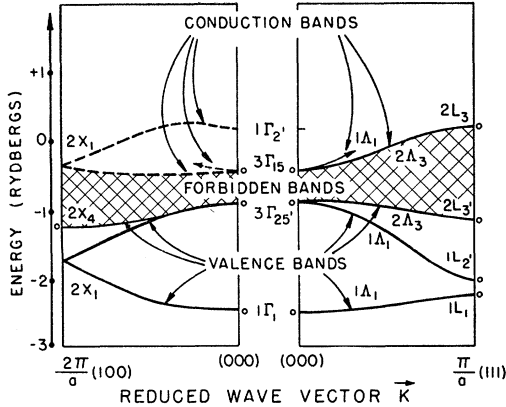


FIG. 1. Energy bands of diamond (after Herman, see reference 12). Slope of energy contour is zero at points marked "0."

That is to say, we neglect that part of w which spills over into other cells, and all overlap effects. Similarly for the matrix elements of the orbital angular momentum, $-i(\mathbf{r} \times \mathbf{p}) = \mathbf{l}$, we make the same approximation and write

$$\begin{aligned} \langle \Psi_s(\mathbf{k}) | \mathbf{l} | \Psi_t(\mathbf{k}') \rangle &= \frac{1}{N} \sum_{\mathbf{d}} \exp[i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{d}] \langle w_{k^s}(\mathbf{r} - \mathbf{d}) | \mathbf{l} | w_{k'^t}(\mathbf{r} - \mathbf{d}) \rangle \\ &= \delta_{k^s k'^t} \langle w_{k^s}(\mathbf{r}) | \mathbf{l} | w_{k'^t}(\mathbf{r}) \rangle. \end{aligned} \quad (11)$$

Various effects can now be calculated if it is further assumed that the angular dependence of the w is just that of the atomic functions used in the tight-binding method. The radial integration over ζ will remain an arbitrary parameter λ in our theory although if the tight-binding method gives a reasonable approximation we expect it to be somewhat like the spin-orbit coupling parameter for the appropriate atomic electrons.

IV. ENERGY BANDS IN DIAMOND TYPE CRYSTALS

A very extensive investigation of the energy bands in these crystals is being conducted by Herman. The calculated bands for diamond¹² are shown in Fig. 1, and preliminary results show that germanium has a some-

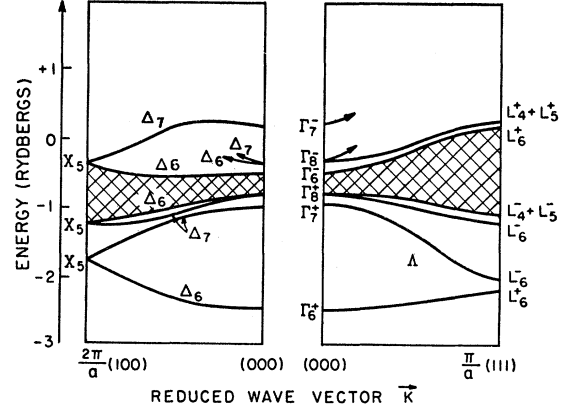


FIG. 2. Schematic representation of the energy bands of diamond including spin-orbit coupling effects. (Based on Herman's calculation, see Fig. 1).

what similar band structure¹³ from a symmetry point of view. In Fig. 2 we show schematically what the band structure is like when we include spin-orbit effects.

From the character tables 1, 2, 5, 7, 9 of A , we have found the degeneracies of the new irreducible representations and the way in which the old representations are split by adding spin (multiplying by $D_{1/2}$). There is further splitting of Γ_{15} , $\Gamma_{25'}$, Δ_5 , Δ_5' , Δ_3 , L_3 , L_3' , but not of X_1 and X_4 . Because of time reversal each of the bands is doubly degenerate in Fig. 2 as it was in Fig. 1 because of the spin orientations. In the figure we have not attempted to draw the new bands accurately or the splittings to scale. Away from the places where there are extra splittings the energies have been left unchanged. In fact there will be a slight admixture of wave functions from other bands which now have the same transformation properties, and a second-order change in energy.

The details of the band structure are greatly affected near these degeneracies which are now split; like Γ_{15} , $\Gamma_{25'}$. Herman investigated these points in some detail by means of a perturbation procedure, and it is therefore convenient to take them as a detailed example of the effects we are considering. For small values of \mathbf{k} the original triplet is split and Herman obtains the energies from a secular determinant of the form:

$$\begin{vmatrix} Ak^2 + (B-A)k_x^2 - E & Dk_x k_y & Dk_x k_z \\ Dk_x k_y & Ak^2 + (B-A)k_y^2 - E & Dk_y k_z \\ Dk_x k_z & Dk_y k_z & Ak^2 + (B-A)k_z^2 - E \end{vmatrix} = 0 \quad (12)$$

(where A , B , and D are constants obtained by numerical computation). An effective mass can be defined for the three bands in the usual way,

$$E = \hbar^2 k^2 / 2m^*, \quad (13)$$

although m^* varies in a complicated way with angle. With the inclusion of spin-orbit coupling, however, the

energy E may not be proportional to k^2 over a sufficient range of k to make the concept of effective mass useful. Possible results have been sketched diagrammatically in Figs. 3 to 6. In Fig. 3 we have drawn typical curves of energy versus \mathbf{k} for an arbitrary direction in \mathbf{k} space and for small values of \mathbf{k} in Herman's picture. The

¹² F. Herman, Phys. Rev. 88, 1210 (1952); thesis, Columbia University, 1953 (unpublished).

¹³ F. Herman and J. Calloway, Phys. Rev. 89, 518 (1953). Dr. Herman has informed me that more accurate calculations are now being made.

curves are the parabolic solutions (13) of the secular determinant (12). Figure 4 shows a possible effect of the introduction of spin-orbit coupling; for large \mathbf{k} the curves are similar to those in Fig. 3, but for smaller \mathbf{k} the splitting makes the picture very different. Thus if we have an electron system in which the Fermi level is F_2 in the figures, the effective mass and general properties of the electrons at the top of the distribution would not be greatly altered by the spin-orbit effects. This would also be true at high temperatures where the electrons have thermal energies and obey Boltzmann statistics rather than Fermi-Dirac. On the other hand, if we have an electron system with a Fermi level F_1 , it is clear that Herman's calculations will not be applicable. Figures 5 and 6 show a different kind of splitting and display how complicated the addition of the spin-orbit coupling may make the band forms.

We can make more explicit calculations of these effects by making the approximations discussed in Sec. III. That is, we calculate the matrix elements of the spin-orbit coupling by assuming that the tight-binding wave functions give a representation of the actual wave functions with the correct symmetry properties. The tight-binding approximation for the diamond crystal has been solved by Morita.¹⁴ His band structure did not agree with Herman's in that his bands occurred in a different order but he did have bands with the same symmetry properties which he built up from $2s$ and $2p$ atomic wave functions. We label the atomic wave functions of the s -type ϕ_s and the three p -types ϕ_x , ϕ_y , and ϕ_z . The symmetry properties of the tight-binding functions will be the same whatever the principal quantum number n , and the results will apply to diamond $n=2$, silicon $n=3$, germanium $n=4$, and grey tin, $n=5$. To obtain the wave functions, we note that the diamond lattice is built up from two interpenetrating face-centered cubic lattices, with principal vectors $\frac{1}{2}a(0,1,1)$; $\frac{1}{2}a(1,0,1)$; $\frac{1}{2}a(1,1,0)$; and so we define functions

$$\chi_j(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{d}} \exp(i\mathbf{k} \cdot \mathbf{d}) \phi_j(\mathbf{r} - \mathbf{d}), \quad (14)$$

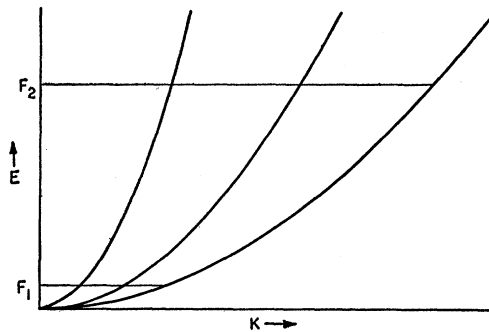


FIG. 3. Typical curves of energy vs k near a band degeneracy without spin-orbit coupling. F_1 and F_2 are Fermi levels (see text).

¹⁴ A. Morita, Science Repts. Tôhoku Univ. 33, 92 (1949).

where \mathbf{d} are the lattice points of such an f.c.c. structure and j can be s , x , y , or z . Now one of the lattices is obtained from the other by a translation $\mathbf{t} = \frac{1}{4}a(1,1,1)$, and the general tight-binding wave function built from these functions can be written

$$\Psi = \sum_j [a_j \chi_j(\mathbf{r}) + \alpha_j \exp(i\mathbf{k} \cdot \mathbf{t}) \chi_j(\mathbf{r} + \mathbf{t})], \quad (15)$$

where, since the two lattices are equivalent, $|a_j|^2 = |\alpha_j|^2$. In particular Morita finds that at $\mathbf{k} = (0,0,0)$ the eight eigenfunctions are

$$\Psi_j = \frac{1}{(2N)^{1/2}} \sum_{\mathbf{d}} [\phi_j(\mathbf{r} - \mathbf{d}) \pm \phi_j(\mathbf{r} - \mathbf{d} + \mathbf{t})]. \quad (16)$$

For the irreducible representations in which we are interested, the appropriate forms of (16) are,

$$\begin{aligned} \text{for } \Gamma_1, & \quad \frac{1}{(2N)^{1/2}} \sum_{\mathbf{d}} [\phi_s(\mathbf{r} + \mathbf{d}) + \phi_s(\mathbf{r} + \mathbf{d} - \mathbf{t})], \\ \text{for } \Gamma_2', & \quad \frac{1}{(2N)^{1/2}} \sum_{\mathbf{d}} [\phi_s(\mathbf{r} + \mathbf{d}) - \phi_s(\mathbf{r} + \mathbf{d} - \mathbf{t})], \\ \text{for } \Gamma_{25}', & \quad \frac{1}{(2N)^{1/2}} \sum_{\mathbf{d}} [\phi_j(\mathbf{r} + \mathbf{d}) - \phi_j(\mathbf{r} + \mathbf{d} - \mathbf{t})] \\ & \quad \text{where } j = x, y, z, \\ \text{for } \Gamma_{15}, & \quad \frac{1}{(2N)^{1/2}} \sum_{\mathbf{d}} [\phi_j(\mathbf{r} + \mathbf{d}) + \phi_j(\mathbf{r} + \mathbf{d} - \mathbf{t})]. \end{aligned} \quad (17)$$

Since we are assuming that spin-orbit coupling is small, the wave functions of the representations formed from these when we include the spin will just be linear combinations of (17). By inspection we see that just as in an atom when spin and spin-orbit effects are included, the component ϕ 's are the same in the s -states but in the p -states they are those corresponding to a total

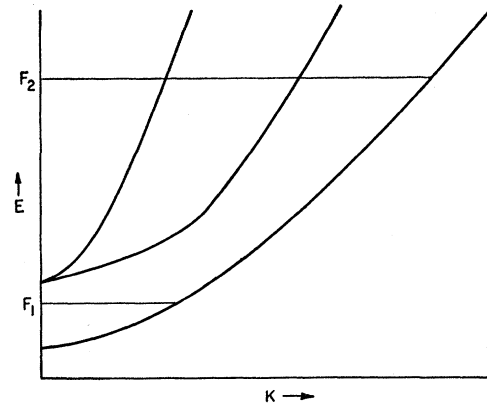


FIG. 4. Effect of inclusion of spin-orbit coupling on the curves shown in Fig. 3.

angular momentum J of $\frac{1}{2}$ in the twofold representation and $\frac{3}{2}$ in the fourfold. Then we have,

for Γ_6^+ ,

$$\frac{1}{(2N)^{\frac{1}{2}}} \sum_{\mathbf{d}} [\phi_s(\mathbf{r}-\mathbf{d}) + \phi_s(\mathbf{r}-\mathbf{d}+\mathbf{t})] |\pm\rangle,$$

for Γ_7^- ,

$$\frac{1}{(2N)^{\frac{1}{2}}} \sum_{\mathbf{d}} [\phi_s(\mathbf{r}-\mathbf{d}) - \phi_s(\mathbf{r}-\mathbf{d}+\mathbf{t})] |\pm\rangle,$$

for Γ_7^+ ,

$$\frac{1}{(2N)^{\frac{1}{2}}} \sum_{\mathbf{d}} [\phi_{\frac{1}{2}}(\mathbf{r}-\mathbf{d}) - \phi_{\frac{1}{2}}(\mathbf{r}-\mathbf{d}+\mathbf{t})],$$

for Γ_6^- ,

$$\frac{1}{(2N)^{\frac{1}{2}}} \sum_{\mathbf{d}} [\phi_{\frac{1}{2}}(\mathbf{r}-\mathbf{d}) + \phi_{\frac{1}{2}}(\mathbf{r}-\mathbf{d}+\mathbf{t})],$$

for Γ_8^+ ,

$$\frac{1}{(2N)^{\frac{1}{2}}} \sum_{\mathbf{d}} [\phi_{\frac{3}{2}}(\mathbf{r}-\mathbf{d}) - \phi_{\frac{3}{2}}(\mathbf{r}-\mathbf{d}+\mathbf{t})],$$

for Γ_8^- ,

$$\frac{1}{(2N)^{\frac{1}{2}}} \sum_{\mathbf{d}} [\phi_{\frac{3}{2}}(\mathbf{r}-\mathbf{d}) + \phi_{\frac{3}{2}}(\mathbf{r}-\mathbf{d}+\mathbf{t})],$$

where $\phi_{\frac{1}{2}}$ are the functions:

$$\frac{1}{\sqrt{2}}(\phi_x + i\phi_y) |+\rangle, \frac{1}{\sqrt{6}}[(\phi_x + i\phi_y) |-\rangle - 2\phi_z |+\rangle],$$

$$\frac{1}{\sqrt{6}}[(\phi_x - i\phi_y) |+\rangle + 2\phi_z |-\rangle], \frac{1}{\sqrt{2}}(\phi_x - i\phi_y) |-\rangle;$$

and $\phi_{\frac{3}{2}}$ are the functions:

$$\frac{1}{\sqrt{3}}[(\phi_x + i\phi_y) |-\rangle + \phi_z |+\rangle],$$

$$\frac{1}{\sqrt{3}}[(\phi_x - i\phi_y) |+\rangle - \phi_z |-\rangle].$$

Using the functions (19) as basic functions and calculating the spin-orbit matrix elements by means of (10), we can now construct the secular determinant which gives the energies of the bands near $\mathbf{k} = (0,0,0)$ analogous to (12). Since we know the matrix elements of the potential more accurately from Herman's calculation than from a tight-binding approximation like the above, we have used his calculation and written these elements in terms of the constants A , B , and D . The determinant is:

$$\begin{vmatrix} \frac{1}{2}\lambda + \frac{1}{2}P - E & \frac{1}{\sqrt{3}}R & \frac{1}{2\sqrt{3}}S & 0 & \frac{1}{\sqrt{6}}R & -\frac{1}{\sqrt{6}}S \\ \frac{1}{\sqrt{3}}\bar{R} & \frac{1}{2}\lambda + \frac{1}{6}(P+4Q) - E & 0 & -\frac{1}{2\sqrt{3}}S & -\frac{1}{3\sqrt{2}}(P-2Q) & -\frac{1}{\sqrt{2}}R \\ \frac{1}{2\sqrt{3}}\bar{S} & 0 & \frac{1}{2}\lambda + \frac{1}{6}(P+4Q) - E & \frac{1}{\sqrt{3}}R & \frac{1}{\sqrt{2}}\bar{R} & -\frac{1}{3\sqrt{2}}(P-2Q) \\ 0 & -\frac{1}{2\sqrt{3}}\bar{S} & \frac{1}{\sqrt{3}}\bar{R} & \frac{1}{2}\lambda + \frac{1}{2}P - E & \frac{1}{\sqrt{6}}\bar{S} & \frac{1}{\sqrt{6}}\bar{R} \\ \frac{1}{\sqrt{6}}\bar{R} & -\frac{1}{3\sqrt{2}}(P-2Q) & \frac{1}{\sqrt{2}}R & \frac{1}{\sqrt{6}}S & -\frac{1}{4}\lambda + \frac{1}{3}(P+Q) - E & 0 \\ -\frac{1}{\sqrt{6}}\bar{S} & -\frac{1}{\sqrt{2}}\bar{R} & -\frac{1}{3\sqrt{2}}(P-2Q) & \frac{1}{\sqrt{6}}R & 0 & -\frac{1}{4}\lambda + \frac{1}{3}(P+Q) - E \end{vmatrix} = 0, \quad (20)$$

where

$$P = 2Ak^2 + (B-A)(k_x^2 + k_y^2),$$

$$R = Dk_z(k_x + ik_y),$$

$$Q = Ak^2 + (B-A)k_z^2,$$

$$S = (B-A)(k_x^2 - k_y^2) + 2iDk_xk_y.$$

[A , B , and D are as defined by Eq. (12).] The roots of this determinant are equal in pairs, which can be readily checked since it can be transformed into a skew-symmetric form. The roots are, however, complicated

solutions of a cubic equation. We can obtain effective masses when the spin-orbit coupling is large and we are interested in electrons with kinetic energies much smaller than λ . For the $\frac{3}{2}$ (Γ_8) levels,

$$E = \frac{1}{6}\{2(P+Q) \pm [(P-2Q)^2 + 3(4|R|^2 + |S|^2)]^{\frac{1}{2}}\}$$

$$= Bk^2 \pm \frac{1}{3}\{(B-A)^2k^4$$

$$[D^2 - 3(B-A)^2](k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)\}^{\frac{1}{2}}. \quad (21)$$

For the $\frac{1}{2}$ (Γ_7) levels,

$$E = \frac{1}{3}(P+Q) = Bk^2. \quad (22)$$

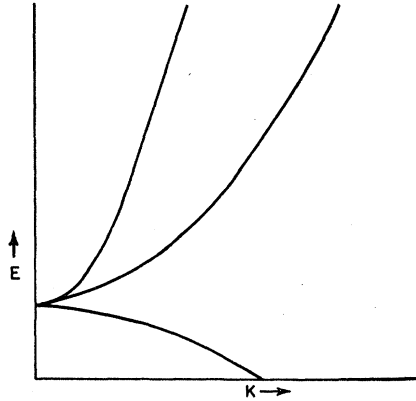


FIG. 5. Another possible form of band degeneracy. The curves shown are parabolas, so the curves can be described in terms of an effective mass.

In fact spin-orbit coupling has such a profound effect on bands near a degeneracy that any attempt to explain observations of the effective mass, magnetoresistance, etc. of electrons occupying such bands should be made with the above methods.

V. g -VALUES

The Hamiltonian of the interaction between a magnetic field and an electron is $\beta\mathbf{H} \cdot (\mathbf{l} + 2\mathbf{s})$. This lifts the remaining twofold degeneracy of the electron states and causes a splitting which we call $g\beta H$, thus defining g as the matrix element of $2(\mathbf{l} + 2\mathbf{s})$ in the direction of the field. In general g will depend on the direction of H and on \mathbf{k} . However, in a metal, collisions of the electron with lattice waves and impurity centers take place so often (every 10^{-13} second or less) that the measurement sees only an average effect. We shall compute the average value of g in three cases which seem to cover the possible band forms which can occur in these substances.

A. Electrons in a Nondegenerate Band

In the absence of spin-orbit coupling the wave functions for any vector \mathbf{k} are simply products of orbital and spin functions $\Psi|+\rangle$ and $\Psi|-\rangle$. In all singlet states the orbital magnetic moment is "quenched" and thus all such states have exactly the free-electron g value.¹⁵ Spin-orbit coupling causes admixtures of states corresponding to the same \mathbf{k} in all bands with the same transformation properties. In the general case, we saw in Sec. IV that the wave functions of all bands belong to the same irreducible representation; this means that

¹⁵ This will be true if the component of angular momentum in an arbitrary direction z is zero. This is the quantity $\int \Psi^* L_z \Psi d\tau$, where $L_z = -i(\mathbf{r} \times \nabla)_z$. Writing Ψ as a Bloch function $u_k e^{i\mathbf{k} \cdot \mathbf{r}}$ we require $\int u_k^* L_z u_k d\tau$. If (as is the case here) the crystal has inversion symmetry $u_k^* = au_{-k}$, where $aa^* = 1$, then

$$\int u_k^* L_z u_k = \int u_{-k} L_z u_{-k}^* = \int u_k L_z u_k^* = -\left(\int u_k^* L_z u_k\right)^* = 0,$$

since it must be real.

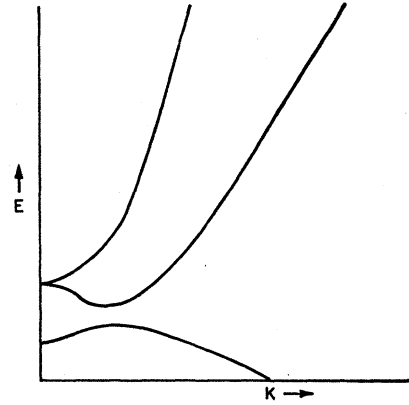


FIG. 6. Possible effect of spin-orbit coupling on the curves shown in Fig. 5. The curves are now more complicated in form and cannot be described in terms of an effective mass.

wave functions from all bands will be admixed. Since the matrix elements of spin-orbit coupling are small compared to the separation between bands, we can write the wave functions by perturbation theory in the form (15); and if $\chi_0, \chi_1, \dots, \chi_n$, were the original localized functions, the new localized function will be

$$\chi_0|+\rangle + \frac{1}{2} \sum_n \frac{1}{E_0(\mathbf{k}) - E_n(\mathbf{k})} [\langle \chi_n | \zeta l_z | \chi_0 \rangle \chi_n | + \rangle + \langle \chi_n | \zeta (l_x + il_y) | \chi_0 \rangle \chi_n | - \rangle]. \quad (23)$$

The matrix element of l_z is, to first order (using 11),

$$\sum_n \frac{\langle \chi_0 | \zeta l_z | \chi_n \rangle \langle \chi_n | l_z | \chi_0 \rangle}{E_0(\mathbf{k}) - E_n(\mathbf{k})}. \quad (24)$$

The average value of the matrix element of l for any direction will be of the same order of magnitude and so we expect that in this case the change in g from the free-electron value to be of the order

$$\Delta g \sim \lambda / \Delta E, \quad (25)$$

where λ is the spin-orbit coupling constant and ΔE the separation to the nearest band with the same transformation properties. This effect is very small, and because of the uncertainty in the value of λ it is hardly worth calculating the exact equality to replace the approximation (25). The more accurate calculation of Yafet for sodium gives a resulting Δg of the order expected from (25), with a value of λ somewhat smaller than in the free atom.

B. Electrons with Kinetic Energies Large Compared to the Spin-Orbit Coupling Energy Occupying States with Energies Near a Point Where Bands are Degenerate

An example of this would be that of the electron system with Fermi energy F_2 in Fig. 4. The electrons at the Fermi surface are in states which are determined

almost entirely by the lattice potential. The states around each lattice point are linear combinations of ϕ_x , ϕ_y , and ϕ_z which are completely determined as is their energy by a secular determinant like (12). Without spin-orbit coupling the wave function at \mathbf{k} in one band r , say, is in the form (15) where at each lattice point the wave function is

$$|r_0\rangle = a_r\phi_x + b_r\phi_y + c_r\phi_z. \quad (26)$$

Regarding spin-orbit as a perturbation to first order, we get, by using (10),

$$|r, +\rangle = |r_0, +\rangle + \frac{1}{2} \sum_{s \neq r} \frac{\lambda}{E_r(\mathbf{k}) - E_s(\mathbf{k})} \{ \langle s_0 | l_z | r_0 \rangle |s_0, +\rangle + \langle s_0 | l_x + il_y | r_0 \rangle |s_0, -\rangle \}. \quad (27)$$

From (11),

$$\Delta g_z = 2 \sum_{s \neq r} \frac{\lambda}{E_r(\mathbf{k}) - E_s(\mathbf{k})} |\langle r_0 | l_z | s_0 \rangle|^2. \quad (28)$$

Using the functions (26) and noting that

$$l_z\phi_x = i\phi_y, \quad l_z\phi_y = -i\phi_x, \quad l_z\phi_z = 0, \\ \text{we find} \quad \langle r_0 | l_z | s_0 \rangle = a_r^* b_s - a_s b_r^*. \quad (29)$$

Now we need the average value, which we will define for simplicity as

$$\Delta g = \frac{1}{3} (\Delta g_x + \Delta g_y + \Delta g_z). \quad (30)$$

By symmetry, from (29),

$$\Delta g = \frac{2}{3} \sum_{s \neq r} \frac{\lambda}{E_r(\mathbf{k}) - E_s(\mathbf{k})} \left[\sum_{abc} (a_r^* b_s - a_s b_r^*) (a_r b_s^* - a_s^* b_r) \right] \\ = \frac{2}{3} \sum_{s \neq r} \frac{\lambda}{E_r(\mathbf{k}) - E_s(\mathbf{k})} \left[\left(\sum_a a_r a_r^* \right) \left(\sum_a a_s a_s^* \right) \right. \\ \left. - \left(\sum_a a_r^* a_s \right) \left(\sum_a a_r a_s^* \right) \right],$$

and since the wave functions (26) are normalized and orthogonal this is just

$$\Delta g = \frac{2}{3} \sum_{s \neq r} \frac{\lambda}{E_r(\mathbf{k}) - E_s(\mathbf{k})}. \quad (31)$$

Besides averaging over the direction of \mathbf{H} we require the average over all directions and all those values of \mathbf{k} in all three bands which have energies equal to the Fermi energy; $E(\mathbf{k}) = W_F$. Now in a given direction in space we define an effective mass for each surface by means of (13). The number of electron states within a solid angle $d\Omega$ of \mathbf{k} and with wave vectors of magnitude between \mathbf{k} and $\mathbf{k} + \Delta \mathbf{k}$ are

$$V k^2 \Delta k d\Omega / (2\pi)^3.$$

The energy spread of such states is, from (13), $\hbar^2 k \Delta k / 2m^*$ so that the number of energy states per

unit energy range is $V m^* k d\Omega / \hbar^2 (2\pi)^3$ and the density at the Fermi surface is then

$$\rho = (2m^*)^{\frac{3}{2}} V W_F^{\frac{1}{2}} d\Omega / 2\hbar^3 (2\pi)^3. \quad (32)$$

The average Δg value is just

$$\int_0^{4\pi} \sum_r \rho_r \Delta g_r d\Omega / \int_0^{4\pi} \sum_r \rho_r d\Omega. \quad (33)$$

Assuming that the spin-orbit coupling has little effect on the energies $E_r(\mathbf{k})$, we have

$$E_r(\mathbf{k}) - E_s(\mathbf{k}) = \frac{\hbar^2 k^2 (m_s^* - m_r^*)}{2m_r^* m_s^*} = \frac{W_F (m_s^* - m_r^*)}{m_s^*}, \quad (34)$$

when \mathbf{k} is such that the electron in the r th band is at the Fermi surface. After some manipulation from (34), (32), and (30), Eq. (33) becomes:¹⁶

$$\Delta g = \frac{2\lambda}{3W_F} \int \sum_{r \neq s} \frac{m_r^* m_s^*}{\sqrt{m_r^*} + \sqrt{m_s^*}} d\Omega / \int \sum_r (m_r^*)^{\frac{3}{2}} d\Omega. \quad (35)$$

The Fermi temperature depends on the number n of conduction electrons,

$$n = \sum_r \int_0^{k_0} \int_0^{4\pi} \frac{V}{(2\pi)^3} k^2 dk d\Omega \\ = \frac{2\sqrt{2} V W_F^{\frac{3}{2}}}{3(2\pi)^3 \hbar^3} \int_0^{4\pi} \sum_r (m_r^*)^{\frac{3}{2}} d\Omega, \quad (36)$$

so

$$\Delta g = \frac{\lambda V^{\frac{1}{2}}}{\pi^3 (3n)^{\frac{3}{2}} \hbar^2} \int_0^{4\pi} \sum_{r \neq s} \frac{m_r^* m_s^*}{\sqrt{m_r^*} + \sqrt{m_s^*}} d\Omega / \left[\sum_r \int_0^{4\pi} (m_r^*)^{\frac{3}{2}} d\Omega \right]^{\frac{1}{2}}. \quad (37)$$

In our approximation the m^* are determined completely by the secular determinant (12), but the averages in (35) and (37) are found to depend in a very complicated way on the constants A , B , and D .

Another useful result which can be calculated on this approximation is the expression for Δg at high temperatures when the electrons obey Boltzmann statistics. Then

$$\Delta g = \int \int \sum_r n_r(\mathbf{k}) \Delta g_r(k) k^2 dk d\Omega / \int \int \sum_r n_r(\mathbf{k}) k^2 dk d\Omega, \quad (38)$$

¹⁶ I am indebted to Professor C. Kittel for first pointing out that one might expect $\Delta g \sim \lambda / W_F$ in this case.

where $n_r(\mathbf{k})$, the number of electrons in the r th band with \mathbf{k} , is

$$A \exp(-\hbar^2 k^2 / 2m_r^* kT). \quad (39)$$

After manipulation, and writing the expression (35) as $(\Delta g)_F$,

$$\Delta g = (W_F / kT) (\Delta g)_F. \quad (40)$$

Thus Δg will decrease with increasing temperature once we get above the Fermi temperature.

C. Electrons in a Degenerate Band with Energies Small Compared to the Spin-Orbit Coupling

An example of this would be the electron system in Fig. 4 with Fermi level F_1 . In this case the electrons at the Fermi surface would have wave functions given in first order by (18). Thus they would have the Landé g factor for these J states which is $\frac{2}{3}$ for the single $J = \frac{1}{2}$ band, and $4/3$ for the double $J = \frac{3}{2}$ band. In any practical case the states will be considerably perturbed and g can be expected to have a wide range of possible values. Explicit calculations unfortunately require the solution of the determinant (20) and hence must be numerical. Some idea of the possibilities can be obtained by considering a simple model where the energy depends only on $|\mathbf{k}|$ and the interaction is independent of direction. For a general value of \mathbf{k} the three p bands will have wave functions around each nucleus like

$$\begin{aligned} & \frac{1}{\sqrt{2}}(\phi_x + i\phi_y)|+\rangle, \\ & \frac{1}{\sqrt{2}}(\phi_x + i\phi_y)|-\rangle + \cos\theta\phi_z|+\rangle, \\ & \frac{1}{\sqrt{2}}(\phi_x + i\phi_y)|-\rangle - \sin\theta\phi_z|+\rangle, \end{aligned} \quad (41)$$

and their Kramers' conjugates. The first two, which have $g_{11}=4$, $g_{\perp}=0$, and $g_{11}=2\cos^2\theta$, $g_{\perp}=2\cos^2\theta + 2\sqrt{2}\sin\theta\cos\theta$, respectively, are degenerate when $k=0$. The other has $g_{11}=2\sin^2\theta$, $g_{\perp}=2\sin^2\theta - 2\sqrt{2}\sin\theta\cos\theta$ and arises from the $J = \frac{1}{2}$ band. In the case of large λ , when only one or two of these bands are occupied, it is clear that g may have a wide range of values, and the actual result will depend in a complicated way on the electron-lattice interaction.

Δg will have the same order of magnitude as that calculated in case B for any degeneracy which is lifted by the spin-orbit coupling. For any such degeneracy and case C the g will in general differ widely from 2 but its actual value will depend on the actual wave functions. If there is a degeneracy which is not affected by the introduction of spin-orbit coupling, case A will apply.

VI. REVIEW OF EXPERIMENTAL DATA

In an impurity semiconductor the extra electrons (or holes) have two kinds of energy states. There are

those which represent the electron trapped around the impurity centers, and others in which the electrons move freely (and occupy states in the bands). At high enough impurity concentrations there are no trapped states and the electrons are in the conduction band even at very low temperatures. The experiments¹ seem to indicate that this is the case in some of the specimens studied. Assuming then that the impurities have little effect on the actual band structure we can compare the experimental values with the g 's calculated for the band states in the last section.

The actual form of the bands in silicon and germanium is of considerable interest at the present time. Herring¹⁷ and others have deduced something about their form from magnetoresistance, and measurements of cyclotron resonance¹⁸ also throw some light on the problem. Since in n silicon the g -values are very close to 2, we can conclude that case A holds, and that the lowest point of the conduction band is not near a band degeneracy. Herman's calculation for diamond gave the minima in the conduction bands at six points along the (1,0,0), (0,1,0), and (0,0,1) directions. This is also likely to be true in Si and would certainly fit the observed g values. Δg seems to be about 3×10^{-3} , which, if λ is about 100 cm^{-1} as discussed below, gives $\Delta E \sim 4 \text{ ev}$, which is quite reasonable for the separation to the nearest Δ_7 band.

It is of some interest to consider briefly what values one might expect for λ in general. Now λ for $3p$ electrons on a Si atom¹⁹ with configuration $3s^2 3p^2$ is 150 cm^{-1} and on Si^+ with $3s^2 p^2$ is 190 cm^{-1} , i.e., somewhat larger. In silicon metal the ground state with completely filled valence bands is roughly equivalent to a $3s3p^3$ configuration for each atom so that the extra electrons in n Si make a $3p^4$ configuration and the holes in p Si a $3p^2$. There are no measurements of λ on atomic Si with these configurations but atomic S has $\lambda = 175 \text{ cm}^{-1}$ and 300 cm^{-1} in similar configurations. Thus if the electron wave functions in the metal are just linear combinations of the atomic wave functions around each lattice point we might expect λ to be very roughly about 100 cm^{-1} for electrons in n -type Si and 200 cm^{-1} for holes in p -type. The overlap of the atomic wave functions with those of neighboring atoms has a profound effect, however. The largest contribution to λ is made when the electron is very near the nucleus, so that the overlap region is not important from this point of view, but this overlap gives a contribution to the normalizing factor so that in effect the electron spends less of its time near a nucleus than it would do in an atom. Even in the general case when the tight-binding approximation is bad, one might expect the electron to behave rather like an atomic electron near the nucleus

¹⁷ C. Herring (private communication).

¹⁸ Dresselhaus, Kip, and Kittel, Phys. Rev. **92**, 827 (1953).

¹⁹ This and other numerical values quoted here are calculated from spectral measurements given by C. E. Moore, National Bureau of Standards Circular No. 467, 1949 (unpublished).

(where the field comes overwhelmingly from the nuclear charge) and hence λ to be still that of a free atom reduced by the fact that it spends less time there.

In the case of germanium λ will be very much larger, and only for high concentrations can we expect W_F to be larger than the splitting. In atomic Ge, with configuration $4s^2 4p^2 \ ^3P$, λ is about 1150 cm^{-1} . Se has $\lambda = 1090 \text{ cm}^{-1}$ for $4p^4$ and 5400 for $4p^2$ so that, following our argument for Si, we might expect λ to be, say, 500 cm^{-1} for electrons and 1500 cm^{-1} for holes in Ge. Even though the actual λ for the solid may be several times smaller as we have seen, the splitting will still be considerable. A similar situation will arise in grey tin.

VII. SPIN LATTICE RELAXATION AND RESONANCE LINE WIDTHS

The widths of the resonance lines observed from conduction electrons vary a great deal from substance to substance and with frequency and temperature in a given case. This width arises from a variety of causes. Because of the motion of the electrons there is a "diffusive broadening"²⁰ which, however, becomes very small for particles much smaller than a skin depth. A width remains which increases rapidly with increasing temperature^{1,4} and is therefore probably due to a spin lattice relaxation time. The width which occurs in paramagnetic resonance of salts and arises because electrons in different states have different g values and see differing magnetic fields from the other electrons and nuclei is negligible in this case because of motional narrowing. It has been shown for similar problems²¹ that, if the expected energy spread is $\hbar\omega$ but the electrons change states in a time τ_c because of interactions with the lattice, the actual spread is $\hbar\omega^2\tau_c$. Since τ_c is very short (10^{-12} sec or less) this line width is never appreciable except possibly in case C.

Overhauser⁵ has studied spin-lattice relaxation on a free-electron picture, but he finds that the times obtained from various mechanisms are somewhat longer than those observed in alkali metals.⁴ If his formulas are naively extended to the semiconductor results, the agreement is much worse. We shall discuss below an effect involving the spin-orbit coupling which gives fair agreement with experiment, and some of the discrepancies are possibly due to the crudity of the approximations involved.

The relaxation time τ can be conveniently defined^{5,22} in terms of the number N_+ of electrons with spins parallel to the applied magnetic field and the number N_- antiparallel. If the population difference $D = N_+ - N_-$ is denoted by D_0 at equilibrium, we have

$$D_0 - D/\tau_S = dD/dt = W_{+\rightarrow-} - W_{-\rightarrow+}, \quad (42)$$

²⁰ E. Abrahams and C. Kittel, Phys. Rev. **92**, 544 (1953). F. Dyson (unpublished). See also reference 4.

²¹ P. W. Anderson and P. R. Weiss, Revs. Modern Phys. **25**, 269 (1953).

²² Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

where $W_{+\rightarrow-}$ is the rate of transitions of electrons from the (+) to the (−) states. These W are proportional to the square of the matrix elements of an interaction between the electron and the lattice which causes a spin flip.

It was shown in Sec. II that when spin-orbit interaction is considered, the two classes of electrons which make up each band no longer differ just by the spin orientation but are described by wave functions of mixed character like Eqs. (4) and (6). Except when we are near a degeneracy point, the wave function can usually be written in a form where the function is overwhelmingly one of spin type with just a small admixture of the other orientation. In other words $a \gg b$. For convenience we shall continue to refer to these states simply as the (+) and (−) types. Now let us suppose that there is some interaction which scatters an electron from \mathbf{k} to \mathbf{k}' without changing the spin. The matrix element in the process will contain in first order the integral

$$\int a_{k'}^* \mathcal{H}_{\text{int}} a_k e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} d\tau. \quad (43)$$

Then the same interaction will cause transitions from one kind of spin state to the other but the matrix element (43) must be replaced by

$$\int (a_{-k'} \mathcal{H}_{\text{int}} b_k - b_{-k'} \mathcal{H}_{\text{int}} a_k) e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} d\tau. \quad (44)$$

In a number of cases we shall show in detail below that the matrix elements (43) and (44) are in the ratio b_k/a_k ($=c$, say). Then the probability of an electron making a transition from $|\mathbf{k}, +\rangle$ to $|\mathbf{k}', -\rangle$ is c^2 times the probability of it making the transition $|\mathbf{k}, +\rangle$ to $|\mathbf{k}', +\rangle$. Now, except for an angular factor which discriminates against forward scattering, the matrix element $\langle \mathbf{k}, + | \mathcal{H}_{\text{int}} | \mathbf{k}', + \rangle$ enters into the expression for the relaxation time τ_R characteristic of electrical resistivity,²³ in exactly the same way in which $\langle \mathbf{k}, + | \mathcal{H}_{\text{int}} | \mathbf{k}', - \rangle$ enters into τ_S as obtained by (42). Thus we expect $c^2\tau_S = \tau_R$. Further in Secs. V (A) and (B) we showed that $c \sim \lambda/\Delta E$ which is also of the same order as Δg . Thus we have

$$\tau_S \sim \tau_R (g-2)^2. \quad (45)$$

In order to completely satisfy ourselves of the applicability of this relation we shall consider in detail below the expressions pertaining to lattice scattering in alkali metals, and to lattice and impurity scattering in semiconductors. The formula is not expected to apply to the case when the spin-orbit coupling is large and g is not nearly 2 as in Sec. V (C), but this must be considered separately.

²³ See for example A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1936) or F. Bloch's original paper, Z. Physik **52**, 555 (1928).

VIII. RELAXATION BY LATTICE SCATTERING IN ALKALI METALS

In an alkali metal the wave functions of the partially occupied band can be written to a good approximation by Bardeen's method²⁴ in the form

$$\frac{1}{\sqrt{N}} \left[\sum_{\mathbf{d}} u_0(\mathbf{r}-\mathbf{d}) + i(\mathbf{k} \cdot \mathbf{r}-\mathbf{d}) u_1(\mathbf{r}-\mathbf{d}) \right] e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (46)$$

where u_0 and u_1 are spherically symmetric. Yafet incorporated spin-orbit coupling into Bardeen's method and obtained wave functions of the same form except around each lattice point the expression in square brackets had the form

$$[u_0(r) + i(\mathbf{k} \cdot \mathbf{r})u_1(r) + c(\mathbf{k} \times \mathbf{r})_Z u_2(r)]|+\rangle + c'(\mathbf{k} \times \mathbf{r})_{X+Y} u_3(r)|-\rangle. \quad (47)$$

The subscripts X , Y , Z refer to the components of these vectors along axes chosen so that the Z axis is the axis of the applied magnetic field \mathbf{H} , which is also chosen as the axis of quantization for the spin. u_2 and u_3 are spherically symmetric wave functions, and c and c' are constants, which Yafet obtains by numerical computation. If first-order perturbation theory had been used, the same form would have resulted with

$$c = c' \sim \lambda / \Delta E = (g-2), \quad (48)$$

and

$$u_1(r) = u_2(r) = u_3(r).$$

We write the interaction Hamiltonian arising from the distortion of the lattice by the phonons as

$$\mathcal{H}_{\text{int}} = \frac{1}{\sqrt{M}} \sum_{\mathbf{q}} a(\mathbf{q}) \mathbf{t}_{\mathbf{q}} \cdot \mathbf{A} e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (49)$$

where M is the mass of the crystal, \mathbf{q} the wave vector, $a(\mathbf{q})$ the amplitude and $\mathbf{t}_{\mathbf{q}}$ the polarization vector of a phonon and the summation is carried over all allowed phonons. In calculations of resistivity an explicit expression has to be taken for \mathbf{A} , but we need only assume its transformation properties since we wish only to compare our τ_S with τ_R (for which we can take the experimental value). We assume that \mathbf{A} transforms as a vector, in common with some other resistivity calculations.^{23,25} This simplifies the algebra considerably but gives the same order of magnitude as a more general interaction. We first outline the simple perturbation method of calculating τ_R using the Hamiltonian (49). Bloch²³ finds that, assuming the effective mass concept is adequate [i.e., $E(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m^*$],

$$\frac{1}{\tau_R} = \left(\frac{m^* K V}{\hbar^3 \pi} \right) \int \Pi(k, k') (1 - \cos \theta) d(\cos \theta), \quad (50)$$

²⁴ J. Bardeen, J. Chem. Phys. 6, 367 (1938).

²⁵ The best calculation for alkali metals is that of J. Bardeen, Phys. Rev. 52, 688 (1937).

where $\Pi(\mathbf{k}, \mathbf{k}')$ is the probability that an electron in state \mathbf{k} is scattered into state \mathbf{k}' and θ is the angle between \mathbf{k} and \mathbf{k}' . By using perturbation theory, Π is proportional to the square of the matrix element,

$$\begin{aligned} \langle P, \mathbf{k}, + | \mathcal{H}_{\text{int}} | Q, \mathbf{k}', + \rangle \\ = \langle P | \sum_{\mathbf{q}} \frac{1}{N \sqrt{M}} \sum_{\mathbf{d}} \exp[i(\mathbf{k}' - \mathbf{k} + \mathbf{q}) \cdot \mathbf{d}] \\ \times \int_{\text{cell}} u_0(r) (\mathbf{t}_{\mathbf{q}} \cdot \mathbf{A}) [(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}] u_1(r) a(\mathbf{q}) \\ \times \exp[i(\mathbf{k}' - \mathbf{k} + \mathbf{q}) \cdot \mathbf{r}] d\mathbf{r} | Q \rangle \end{aligned} \quad (51)$$

[using state (47)]. Here P and Q are states of the lattice, and Π is an average over all such possible states. Now

$$\sum_{\mathbf{d}} \exp[i(\mathbf{k}' - \mathbf{k} + \mathbf{d}) \cdot \mathbf{r}] = N \delta(\mathbf{k}' - \mathbf{k} + \mathbf{d} - \mathbf{K}_n),$$

where \mathbf{K}_n is a vector in the reciprocal lattice. If we make the further simplifying assumption that $\mathbf{K}_n = 0$ (i.e., if we neglect the "Umklappprozesse"), Eq. (51) can be written

$$\frac{B}{\sqrt{M}} \langle P | \sum_{\mathbf{q}} (\mathbf{t}_{\mathbf{q}} \cdot (\mathbf{k}' - \mathbf{k}) a(\mathbf{q}) \delta(\mathbf{k}' - \mathbf{k} + \mathbf{q}) | Q \rangle,$$

where

$$B = \int_{\text{cell}} u_0(r) (\mathbf{A} \cdot \mathbf{r}) u_1(r) d\mathbf{r}. \quad (52)$$

Then, following the usual calculation, one gets at high temperatures, where $T \gg \theta_D$ (the Debye temperature),

$$\frac{1}{\tau_R} = \left(\frac{2mk_0 V k T}{\pi \hbar^3 M S^2} \right) B^2 \int (1 - \cos \theta) \sin \theta d\theta, \quad (53)$$

where k_0 is the value of k at the top of the Fermi distribution and S is the velocity of sound. If we assume the simple Debye theory, the maximum possible value of q

$$q_{\text{max}} = 2^{\frac{1}{2}} k_0. \quad (54)$$

Thus, with $\mathbf{K}_n = 0$, the limits of the integral in (53) are 0 and $\theta = 2 \sin^{-1}(2^{-\frac{1}{2}})$ and the value of the integral becomes $2^{-8/3}$. With these approximations then

$$1/\tau_R = m^* k_0 V k T B^2 / 2^{\frac{1}{2}} \hbar^3 M S^2 2\pi. \quad (55)$$

τ_S , the spin-relaxation time, can be readily calculated using Overhauser's method.⁵ It is simply necessary to substitute the matrix element of (44) into his formula for W_{+-} and carry out the appropriate averages. In

this case the element required is

$$\begin{aligned}
 \langle P, \mathbf{k}, + | \mathcal{H}_{\text{int}} | Q, \mathbf{k}', - \rangle \\
 = \langle P | \sum_{\mathbf{q}} \frac{1}{N\sqrt{M}} \sum_{\mathbf{d}} \exp[i(\mathbf{k}' - \mathbf{k} + \mathbf{q}) \cdot \mathbf{d}] \\
 \times \int_{\text{cell}} u_0(r) (\mathbf{t}_q \cdot \mathbf{A}) [(\mathbf{k} + \mathbf{k}') \times \mathbf{r}]_{x+iY} \\
 \times u_3(r) a(\mathbf{q}) \exp[i(\mathbf{k}' - \mathbf{k} + \mathbf{q}) \cdot \mathbf{r}] d\tau | Q \rangle \\
 = \langle P | \sum_{\mathbf{q}} [(\mathbf{t}_q \times (\mathbf{k}' + \mathbf{k}))]_{x+iY} \\
 \times a(\mathbf{q}) \delta(\mathbf{k}' - \mathbf{k} + \mathbf{q}) | Q \rangle B(g-2), \quad (56)
 \end{aligned}$$

if we use (48), and put $\mathbf{K}_n = 0$ as before. We can follow the argument in Sec. II of Overhauser's paper. The square of the matrix element (56) when averaged over all polarizations of \mathbf{q} is

$$B^2(g-2)^2(n_q+1)\hbar|\mathbf{k}+\mathbf{k}'|^2/MSq$$

(where q is written for his k). With this we obtain, instead of his expression, on p. 692

$$\begin{aligned}
 \frac{dD}{dt} = \frac{VB^2(g-2)^2}{\pi MSkT} \int [ff_q'(n_q+1) + ff_{-q}'n_q] \\
 \times |\mathbf{k}+\mathbf{k}'|^2 k dk dq. \quad (D-D_0). \quad (57)
 \end{aligned}$$

At high temperature $T \gg \Theta_D$, this gives

$$\frac{1}{\tau_S} = \frac{mk_0 V k T B^2 (g-2)^2}{2\pi \hbar^3 M S^2} \left(2 \log \frac{q_{\max}}{q_{\min}} - 2^{-\frac{2}{3}} \right), \quad (58)$$

where q_{\max} is given by (54) and q_{\min} depends on the particle size (see Overhauser). In fact q_{\max}/q_{\min} is approximately equal to the particle diameter divided by the atomic diameter. For the small particles used in resonance the log may be expected to be of the order of 10.

With the above approximations we have

$$\tau_S = \frac{\tau_R}{2^{5/3}(g-2)^2 \log(q_{\max}/q_{\min})} = \frac{\tau_R}{30(g-2)^2}. \quad (59)$$

The numerical factor arises partly from the different values for the averages of $(\mathbf{t}_q \cdot \mathbf{q})^2$ and $[(\mathbf{t}_q \times (\mathbf{k} + \mathbf{k}'))_{x+iY}]^2$ over the directions of polarization of the phonons. Another numerical factor arises from the $(1 - \cos\theta)$ term which is present in resistivity calculations to discriminate against forward scattering but does not appear in the relaxation calculation. Because our treatment used a B independent of θ , neglected the "Umklappprozesse," and assumed the simple Debye theory for the lattice waves, the above calculation cannot be very accurate. Nevertheless we can expect $\tau_S = \alpha \tau_R / (g-2)^2$, where α is a numerical factor some-

what smaller than unity, at high temperatures. At low temperatures however the $(1 - \cos\theta)$ term has a much more profound effect. Since only long wavelength phonons are present only small angle collisions can occur (the maximum value of θ is $kT/\hbar S k_0$ if $T \ll \Theta_D$). The angular integral therefore varies as T^2 and since the number of phonons varies as T^3 , $1/\tau_R \propto T^5$. On the other hand, in the absence of the angular factor $1/\tau_R \propto T^3$. Bloch²⁶ showed that the ratio of τ_R at T_1 and T_2 if $T_1 \ll \Theta_D \ll T_2$ is

$$\tau_R(2)/\tau_R(1) = 497.6 (T_1/\Theta_D)^4 (T_1/T_2).$$

If we make the simple assumption that $1/\tau_S$ is proportional to the number of phonons we obtain from the Debye function a similar expression

$$\tau_S(2)/\tau_S(1) = 13.3 (T_1/\Theta_D)^2 (T_1/T_2).$$

Therefore, if $T \ll \Theta_D$,

$$\tau_S \sim (\tau_R / (g-2)^2) (T/\Theta_D)^2. \quad (60)$$

A more correct calculation would no doubt change the numerical factor, but if the conductivity obeys the usual T^{-5} law at low temperature as is the case in the alkali metals, we can expect τ_S to vary as T^{-3} and to be given roughly by (60) in the same region.

It may be pointed out that because of the factor $(\mathbf{t}_q \cdot \mathbf{q})$ occurring in (52), only longitudinal phonons contribute to the resistivity (as is well known), while the $[(\mathbf{t}_q \times (\mathbf{k} + \mathbf{k}'))]$ in (56) means both transverse and longitudinal phonons contribute to the spin relaxation.

In the alkali metals the relaxation time for resistivity is at room temperature approximately 1×10^{-14} , 3×10^{-14} , and 2×10^{-14} sec in Li, Na, and K, respectively. Unfortunately, the g values are so close to the free-electron value that there is as yet no reliable experimental value of Δg except that in Li and Na it is $\sim 10^{-3}$ or less. In view of the usual increase of spin-orbit coupling with increasing atomic number we might expect Δg to increase as we pass along the series. Yafet³ calculated Δg in Na to be 3×10^{-4} , which by our formula (45) leads to a spin-lattice time of about 3×10^{-8} sec, whereas the observed⁴ line width at room temperature corresponds to about 1×10^{-8} sec. The agreement is surprisingly good—in fact much better than our crude assumptions justify. The experimental value of Δg may of course make some difference. Overhauser⁵ obtained relaxation times of about this order, but somewhat longer, by his process, and it is not possible to rule this out because of the above agreement. It is, however, possible that more detailed experiments could decide between the two processes since Overhauser's shortest time varies slightly with H .

We expect that our mechanism will hold for most metals and it is of interest to consider briefly the order of relaxation time we may expect. In the noble metals

²⁶ F. Bloch, Z. Physik **59**, 208 (1930).

the resistivities are low and τ_R is again 10^{-14} sec, but it is believed from measurements on the transition metals that the band overlaps with bands made up largely from the atomic d electrons. Thus we would expect this band to have some d character and because of the nearness of the other band we expect $\lambda/\Delta E$ and hence Δg to be somewhat larger than in the alkalis. If Δg were $\sim 10^{-2}$, this would lead to $\tau_S \sim 10^{-10}$ sec and a very broad line at room temperature, which may prevent the observation of the resonance. However, it should be easier to see at helium temperatures where τ_R is 100 times longer. In other metals it is known that the bands overlap and here again this may lead to small ΔE and larger Δg with similar effects. In these metals the resistance is often larger than in the alkalis and τ_R may be less than 10^{-14} sec at room temperature.

IX. RELAXATION BY LATTICE SCATTERING IN SEMICONDUCTORS

In this case it is not as easy as it is in the alkali metals to write down wave functions which are a good approximation for calculating resistivity, and hence the argument for proving that (45) is a good approximation cannot be as precise. However, Bardeen and Shockley²⁷ have been able to relate the scattering of electrons by lattice waves to the elastic constants and so account for the resistivity observed at high temperatures in n and p -type silicon and germanium.

The interaction is very similar to the one discussed in the last section, although the details of the calculation are modified by the fact that the electrons involved have small \mathbf{k} vectors and can only interact with phonons with small \mathbf{q} (i.e., long wavelength); and the statistics are different. These modifications can be readily taken over into a calculation of τ_S which will go through in exactly the same way as in the last section with both kinds of phonons taking part. For a single band where the wave functions have the form (4) and the component of the wave function with reversed spin is of order $\lambda/\Delta E \sim (g-2)$ the matrix elements for a spin flip process are $(g-2)$ times those for resistivity as before, and $\tau_S \sim \tau_R/(g-2)^2$. If case (B) of Sec. V holds and the electrons occupy states near a band degeneracy the calculation is complicated by the fact that electrons can be scattered from states in one band to states in another. However a rough calculation shows that for every scattering there is an equivalent process which causes a spin flip and again the matrix elements are in the ratio $(g-2):1$ except for some angular factors which will on the average be of order unity. So the expression for τ_S still holds. In the other case (C) the situation is more complicated still. For example at sufficiently high temperatures there will be phonons present which could give electrons sufficient energy to jump from one band to another, but this will not be true at low temperatures. We shall not consider this case in detail here, but rough

²⁷ J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

calculations show that for electrons with kinetic energies comparable with the splitting of the degeneracy τ_S is of the same order as τ_R .

For n -type silicon²⁸ the resistivity at high temperatures appears to be independent of impurity content and

$$\tau_R \sim 10^{-9} T^{-\frac{1}{2}} \text{ sec},$$

where T is the temperature in $^{\circ}\text{K}$. The experiments indicate that $\Delta g \sim 3 \times 10^{-3}$ which gives

$$\tau_S \sim 10^{-9} \text{ sec at } 300^{\circ}\text{K},$$

and a line width of 50 gauss compared to an observed 30 gauss which can be considered good agreement in view of the uncertainties in the formulas and in Δg . In germanium the τ_R are some 5 times longer,²⁹ and the over-all absence of resonance can be accounted for only if Δg is large in both types. Certainly if we have the nearly degenerate bands this can be expected. Even if the bands were like those in silicon and case A could be applied, we would expect $\Delta g = \lambda/\Delta E$ to be greater since λ is greater by what could well be a factor of 20. Allowing for the longer τ_R would increase the line width by a factor of 10^2 and account for the failure to observe resonance at high temperatures.

X. RELAXATION BY IMPURITY SCATTERING IN SEMICONDUCTORS

In germanium and silicon semiconductors^{29,28} of relatively low impurity content it is found that τ_R , which we noted in the last section varies as $T^{-\frac{1}{2}}$ at high temperatures, passes through a maximum as the temperature is decreased and then decreases with decreasing temperature. This is caused by the interaction between the electrons and the impurity centers, an interaction which increases with decrease in velocity (and hence in temperature as long as we remain above the Fermi distribution). We expect that this mechanism will also give rise to a spin-lattice relaxation time, since the argument of Sec. VII would still seem to apply. However, if there is a similar proportionality factor we would expect the curve of line width against temperature to have exactly the form as the inverse of the mobility curves (see Fig. 9 of reference 28), but the resonance experiments do not show this.¹

Unfortunately it has not so far been possible to give an account of resistivity from this mechanism in terms of reasonably correct wave functions. Conwell and Weisskopf³⁰ calculated the effect by use of a free electron model and obtained curves which give quite good agreement with the form of the experimental results. We have calculated the relaxation time due to the spin-orbit effects caused by the impurity itself on a similar

²⁸ G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).

²⁹ J. R. Hayes and W. Shockley, Phys. Rev. **81**, 835 (1951). The experimental data have recently been reviewed by E. M. Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952).

³⁰ E. M. Conwell and V. F. Weisskopf, Phys. Rev. **71**, 388 (1950).

model but find that the times are far too long to give an observable effect. (See Appendix.)

We consider that the impurities cause an interaction which in a medium of dielectric constant κ is

$$\sum_{\mathbf{D}} \frac{e^2 \exp(-r/\rho)}{\kappa |\mathbf{r} - \mathbf{D}|},$$

where \mathbf{D} are a random selection of η of the lattice points and ρ is a screening radius which will be taken as the Debye length.

Fourier-analyzing this potential³¹

$$V = \int V_k \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{k}$$

we find

$$V_k = \left(\sum_{\mathbf{D}} \exp(i\mathbf{k} \cdot \mathbf{D}) \right) \frac{e^2}{\kappa} \frac{\rho^2}{k^2 \rho^2 + 1}. \quad (61)$$

The matrix element

$$\begin{aligned} \langle k' + |\mathcal{H}| k + \rangle &= \frac{e^2 \rho^2}{\kappa (q^2 \rho^2 + 1)} \left(\sum_{\mathbf{D}} \exp(i\mathbf{k} \cdot \mathbf{D}) \right) \\ &\times \int (a_{k'}^* a_k + b_{k'}^* b_k) d\tau, \quad (62) \end{aligned}$$

where $\mathbf{k} - \mathbf{k}' + \mathbf{q} = 0$. The matrix element required for τ_S is

$$\begin{aligned} \langle k' - |\mathcal{H}| k + \rangle &= \frac{e^2 \rho^2}{\kappa (q^2 \rho^2 + 1)} \left(\sum_{\mathbf{D}} \exp(i\mathbf{k} \cdot \mathbf{D}) \right) \\ &\times \int (a_{-k'} b_k - b_{-k'} a_k) d\tau. \quad (63) \end{aligned}$$

Thus, except for some small numerical factors arising from the angular dependences, τ_S/τ_R is proportional to the ratio of the squares of the integrals in (62) and (63).

Now in case (A) we saw by perturbation theory that $b_k \sim (\lambda/\Delta E) v_k$, where $v_k e^{i\mathbf{k} \cdot \mathbf{r}}$ is the wave function of another band in the absence of spin-orbit coupling. In a semiconductor where we are concerned with just a few electrons in a band, \mathbf{k} will not be very different from \mathbf{k}' , and all the wave vectors will be clustered around some value \mathbf{k}_1 which is not necessarily at the center of the zone (e.g., in the 6-valley model for n -Si). We may therefore use a perturbation procedure.³² To first order $a_k = a_{k'} = a_{k_1}$ and $v_k = v_{k'} = v_{k_1}$, so the integral in (63) is zero. To second order, each wave function

contains terms linear in $(k - k_1)$ and then (63) is seen to be of order of magnitude $\lambda k_{Av} R / \Delta E$ where k_{Av} is the average value of k measured relative to an origin at k_1 and R is a quantity of the dimension of length which represents the magnitude of these second-order terms. If the electron wave functions are tightly bound about the nuclei, R can be very roughly taken as the atomic radius. (It may be noted that the alkali metal wave functions (47) lead to an order of magnitude $ck_{Av}^2 R^2$ since b is zero to first order.) If we neglect the small numerical factor arising from the angular dependence, we obtain

$$\tau_S \sim \tau_R / (g-2)^2 R^2 k_{Av}^2. \quad (64)$$

Below the Fermi temperature the average value of k is k_0 , the value at the top of the Fermi distribution. If each impurity donates one electron, $k_0 = (3\pi^2 n/V)^{1/3}$, so that $Rk_0 = (3\pi n/4N)^{1/3}$. So if c is the concentration of impurities,

$$\tau_S \sim \tau_R / (g-2)^2 c^3. \quad (65)$$

Above the Fermi temperature $k_{Av}^2 \sim 2mkT/\hbar^2$, so

$$\tau_S \sim \tau_R [\hbar^2 / 2mkT (g-2)^2 a_0^2], \quad (66)$$

where a_0 is the atomic radius.

For case (B) of Sec. V, however, (63) is no longer small since the difference between a_k and $a_{k'}$ is a first-order effect in their angular dependence. And so, since $b \sim (g-2)a$ we again have $\tau_S \sim \tau_R / (g-2)^2$. If case (C) holds in the general case where the electrons have kinetic energies comparable with the band splitting b and a will be of the same order of magnitude and our crude argument gives $\tau_S \sim \tau_R$.

In n -type silicon, (65) is satisfactory in that the extra term c^{-3} not present in τ_S given by the phonon scattering ensures that τ_S is determined by the phonons to a much lower temperature and there is no maximum as there is in τ_R . The actual magnitude of τ_S given by (65) is a factor 10^2 too small to account for the line width at 4°K . This may partly be accounted for if the picture of six energy minima is correct. In this case the nearest excited band is relatively close and admixture of it may be somewhat larger than ka_0 . Further the scattering process in which the electrons change from states in one minimum to those in another gives a relaxation time related to the τ_R for this process given by (46) rather than (67). This τ_R is, however, much smaller than that observed.

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³¹ In accordance with a suggestion of C. Herring. See also H. Brooks, Phys. Rev. **83**, 879 (1951).

³² An appropriate perturbation theory has been discussed by W. Shockley, Phys. Rev. **78**, 173 (1950) and was used by Herman to obtain our Eq. (12). It is similar to Bardeen's method (see reference 24) which gave the wave function (46).

APPENDIX

If the spin-orbit effect is included, the equation describing the scattering of a free electron by a point charge $+|e|$ representing an impurity center in a medium of dielectric constant k is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{kr} + \frac{\hbar^2 e^2}{2km^2 c^2} \frac{1}{r^3} \mathbf{l} \cdot \mathbf{S}\right) \Psi = E\Psi. \quad (\text{A1})$$

The last term gives a probability that the electron will flip its spin in the process of scattering. We consider the electron as free so that its wave function is $(1/\sqrt{V})e^{i\mathbf{k}\cdot\mathbf{r}}$ when in a state $|\mathbf{k}\rangle$. From the Born approximation, the probability that an electron is scattered from \mathbf{k} to \mathbf{k}' and flips its spin is proportional to the square of the matrix element,

$$\begin{aligned} & \langle \mathbf{k}, + | \lambda \frac{1}{r^3} (\mathbf{l} \cdot \mathbf{S}) | \mathbf{k}', - \rangle \\ &= \frac{\lambda}{2V} \int e^{-i\mathbf{k}'\cdot\mathbf{r}} \frac{1}{r^3} (l_X + il_Y) e^{i\mathbf{k}\cdot\mathbf{r}} r^2 dr d(\cos\theta) d\phi, \quad (\text{A2}) \end{aligned}$$

where $\lambda = \hbar^2 e^2 / 2km^2 c^2$, and X, Y , are two axes chosen perpendicular to the axis of quantization Z of the spin. If there are n such impurity centers in the volume V , the total scattering probability will be n times the probability of scattering by a single center. It is convenient to assume that at any time the electron sees only the nearest center and that on the average it sees each center when it is within a distance R of it; where $4\pi R^3/3 = V/n$. The integral in (A2) is therefore taken over a sphere of radius R . If we put $\mathbf{k} - \mathbf{k}' = \mathbf{K}$, elementary integration gives the matrix element equal to

$$\frac{2i\pi\lambda}{VK^2} \left(\frac{\sin KR}{KR} - 1 \right) [(\mathbf{k} \times \mathbf{k}')_X + i(\mathbf{k} \times \mathbf{k}')_Y].$$

Because of energy conservation $|\mathbf{k}| = |\mathbf{k}'|$, so that if the angle between \mathbf{k} and \mathbf{k}' is α , $|\mathbf{K}| = 2k \sin(\alpha/2) = 2ks$. If we further call the angle between $(\mathbf{k} \times \mathbf{k})$ and Z , β (A2) becomes

$$I = i\pi \left(\frac{\sin 2kRS}{2kRS} - 1 \right) \cot \frac{\alpha}{2} \sin \beta. \quad (\text{A3})$$

Following Overhauser⁵ we let the electrons with spin parallel to Z form a Fermi distribution with Fermi energy ϵ_+ and those with spin antiparallel have Fermi energy ϵ_- . By writing the Fermi distribution function

$f(k, \epsilon)$ and substituting in (42),

$$\begin{aligned} \frac{dD}{dt} = & \mu \frac{2\pi}{\hbar} \int \int \{ f(k, \epsilon_+) [1 - f(k', \epsilon_-)] \\ & - f(k', \epsilon_-) [1 - f(k, \epsilon_+)] \} \delta[E(k) - E(k')] \\ & + 2\beta H |I|^2 \frac{4V^2}{(2\pi)^6} d\mathbf{k} d\mathbf{k}'. \quad (\text{A4}) \end{aligned}$$

But

$$\begin{aligned} f(k, \epsilon_+) - f(k', \epsilon_-) &= (\epsilon_+ - \epsilon_-) [\partial f(k, \epsilon) / \partial \epsilon]_{\epsilon=\epsilon_0} \\ &= (\epsilon_+ - \epsilon_-) \delta[(\hbar^2 k^2 / 2m) - \epsilon_0], \end{aligned}$$

where ϵ_0 is the Fermi energy. After some manipulation we obtain

$$\frac{1}{\tau} = \frac{32\pi\mu m k_0}{3V\hbar^3} \lambda^2 \int_0^1 \left(\frac{\sin 2k_0 SR}{2k_0 SR} \right)^2 \frac{(1-S^2)}{S} dS. \quad (\text{A5})$$

The integral in (A5) can be reduced by tedious but elementary manipulation to

$$\begin{aligned} & -\frac{1}{2} + \sin 2k_0 R - \frac{\cos 2k_0 R}{2k_0^2 R^2} - \frac{\sin 4k_0 R}{4k_0 R} \\ & - \frac{1}{16k_0^2 R^2} (1 - \cos 4k_0 R) + \left(1 - \frac{1}{8k_0^2 R^2} \right) \log 2\gamma k_0 R \\ & - \left(1 + \frac{1}{8k_0^2 R^2} \right) [\log 2 - Ci(4k_0 R)] - 2Ci(2k_0 R), \quad (\text{A6}) \end{aligned}$$

where

$$Ci(x) = \log \gamma x - \int_0^x \frac{1 - \cos t}{t} dt,$$

and is given in Jahnke and Emde³³ (γ is Euler's constant). If we apply a simple one band model and if each impurity has donated one electron to the semiconductor,

$$k_0 = (3\pi^2 \mu / V)^{1/3} = (1/R)(9\pi/4)^{1/3}. \quad (\text{A7})$$

Putting $kR = 2$ then, we find (A6) has the value 1.81. In a typical observation¹ n -Si was used where $\mu/V \sim 10^{18}/\text{cm}^3$ and $k \sim 10$. If we put these values in (A5) and (A7) we get $\sim 10^2$ sec. This is very much too long to give any observable line width. It is possible that the effect has been somewhat underestimated because (a) the fact that the electron will spend relatively more time near an impurity than the free model allows; and (b) the effective charge seen by the electron when near the impurity center will be greater than one and hence λ will be greater. Nevertheless it does not seem feasible to introduce the factor 10^{10} which would be required to make this mechanism effective, and we conclude that it can make no contribution to the line width.

³³ E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1945).