$3d$ electrons are 5 to 10% more spread out than in the free ion and that the amount of $4s$ admixed into the $3d$ band is rather small, unless there is some new additional effect such as a negative polarization of the conduction band.[7]

Incidentally the calculations show that if iron were a paramagnetic metal it would have a negative Knight shift.[9] Thus there is no difficulty in principle of understanding the occurrence of negative Knight shifts in platinum[10] and manganese.[11]

We would like to thank Dr. W. Marshall for many valuable discussions.

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TOROIDAL ENERGY SURFACES IN CRYSTALS WITH WURTZITE SYMMETRY

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(Received September 6, 1960; revised manuscript received September 23, 1960)

This note describes the results of an investigation which demonstrates the possibility of toroidal energy surfaces in wurtzite-type solids. The model leads to an anisotropy in the Hall effect, which, in principle, can be made as large as one pleases by lowering the sample temperature.

Based on an earlier symmetry analysis,[1] the shapes of the constant-energy surfaces in the vicinity of the conduction and valence band extrema have been obtained for several crystals having the wurtzite symmetry. Analyses[1-6] of data on the optical absorption in hexagonal CdS, ZnS, ZnO, and CdSe indicate that for these materials the extrema lie at (or very close to) $\vec{k}=0$, where $\vec{k}$ is the electron wave vector. Therefore, the dispersion of the single-particle energy $E(\vec{k})$ has been investigated only in the neighborhood of the origin of the Brillouin zone. Study of the optical data also indicates that the conduction band wave functions at $\vec{k}=0$ transform according to the representation Γ_7 of the point group C_{6v} (including the effects of spin-orbit interaction), and that the corresponding wave functions associated with the upper and lower "split-off" valence bands belong to the representations Γ_9 and Γ_7, respectively. Expanding $E(\vec{k})$ about its value at $\vec{k}=0$ to second order in the wave vector components by means of the well-known $\vec{k}\cdot\vec{p}$ perturbation technique, where $\vec{p}$ is the electron momentum, the following results were obtained: (1) The constant-energy surfaces for the upper (Γ_9) valence band are doubly degenerate ellipsoids of revolution about the k_z axis ($z \parallel c$). (2) For the Γ_7 conduction and valence bands, the possibility of finite slopes[7] in $E(\vec{k})$ at $\vec{k}=0$ together with the existence of a single rotational axis in wurtzite-type materials (the c axis) allows the possibility of toroidal energy surfaces. Henceforth, we shall confine our attention to the toroidal surfaces and the physical properties of wurtzite-type crystals which one might expect to result therefrom.

For the Γ_7 bands $E(\vec{k})$ has two roots ($\mp$) of the form

$$E_{\mp}(\vec{k}) = E_0(0) \mp Lk_{\perp} + Ak_{\perp}^2 + Ck_z^2, \qquad (1)$$

where

$$k_{\perp} = (k_x^2 + k_y^2)^{1/2}, \quad L = m^{-1}|(1|\pi_y|2)|,$$

$$A = (2m)^{-1} + \textstyle\sum_i (m^2\omega_{0i})^{-1}|(1|\pi_x|i)|^2, \qquad (2)$$

and C is given by the right side of Eq. (2) with π_z substituted for π_x. In the above expressions, m is the free-electron mass, $\vec{\pi}$ is the generalized

form of $\vec{p}$ in the $\vec{k}\cdot\vec{p}$ perturbation scheme when spin-orbit coupling is included,[8] $|1)$ and $|2)$ are the states belonging to Γ_7 with energy $E_0(0)$, $|i)$ is an intermediate state with energy $E_i(0)$, and $\omega_{0i} = E_0(0) - E_i(0)$. We have set $\hbar = 1$, throughout. Letting $\beta = L/2A$ and choosing the zero of energy such that $E_0(0) = A\beta^2$, Eq. (1) becomes

$$E_{\mp}(\vec{k}) = A(k_{\perp} \mp \beta)^2 + Ck_z^2. \tag{3}$$

We assume that A and C are both positive for the conduction band and both negative for the valence band. For the purpose of illustration we shall discuss only electrons in the conduction band. Since, by definition, $k_{\perp} \geq 0$, the root E_+ does not exist for $E(\vec{k}) < A\beta^2$. In the range $0 < E(\vec{k}) \leq A\beta^2$, the equation $E_- =$ constant describes a toroidal surface with cylindrical symmetry about the k_z axis. The cross section of the surface with a plane containing the k_z axis consists of two ellipses. The minimal line, $E_- = 0$, is a circle in the plane $k_z = 0$. For $E(\vec{k}) \geq A\beta^2$ both roots must be taken into account.

We have investigated the consequences of toroidal energy surfaces for the following properties: (1) Density of states, dN/dE. For a crystal of unit volume,

$$(dN/dE) = (4\pi)^{-1}[\beta/(AC)^{1/2}] = \text{constant}, \tag{4}$$

for $A\beta^2 \geq E \geq 0$. For $E >> A\beta^2$, dN/dE is proportional to $E^{1/2}$. A closed-form expression for dN/dE in the intermediate energy range has been obtained, but is too unwieldy to merit presentation here. In terms of interband transitions, the effect on the optical absorption of the sharp leading edge of an otherwise essentially parabolic density-of-states curve might be expected to sharpen the absorption edge. The importance of the effect will depend upon the magnitude of $A\beta^2$ relative to the scale of photon energies in the absorption curves. The magnitude of $A\beta^2$ is discussed in a subsequent paragraph. What the effects of the toroidal surfaces are on the dynamical properties of excitons has not been ascertained. It must be noted, however, that Thomas and co-workers[5] have succeeded in giving an account of the dependence of the absorption coefficient on photon frequency at the absorption edge for CdS by assuming phonon-assisted excitonic transitions and spherical energy bands. (2) Cyclotron frequency, ω_C. With a magnetic field $\vec{H}$ applied parallel to the c axis, the tube mass[9] m^*, which is inversely proportional to ω_C, is given by the relation

$$m_{\mp}^* = (2A)^{-1} k_{\perp}(k_{\perp} \mp \beta)^{-1}. \tag{5}$$

Electrons in the band E_- with $k_{\perp} < \beta$ rotate in a sense opposite to that for electrons with $k_{\perp} > \beta$. For electrons in the band E_- with $k_{\perp} = \beta$, $\omega_C = 0$. These electrons have group velocities parallel to $\vec{H}$. Electrons in either band with $k_{\perp} >> \beta$ have masses which approach a constant value, $(2A)^{-1}$. This result is consistent with the fact that the energy surfaces resemble ellipsoids of revolution about the k_z axis for $E(\vec{k}) >> A\beta^2$, except in the immediate vicinity of the line $k_{\perp} = 0$. (3) Transport properties. The zero-field components, $\sigma_{xx}^{(0)}$ and $\sigma_{zz}^{(0)}$, of the conductivity tensor as well as the Hall coefficients, $R(H \perp c)$ and $R(H \parallel c)$, have been calculated using the Jones-Zener[10] weak-field expansion of the Boltzmann equation. Particularly simple results obtain under the conditions $\Lambda = (A\beta^2/k_B T) >> 1$ and $\tau =$ constant. In the foregoing, k_B is Boltzmann's constant, T is the absolute temperature, and τ is the relaxation time. Physically, the condition $\Lambda >> 1$ implies that most of the carriers are in the band E_-. In addition to introducing formal simplifications this condition justifies the neglect of interband scattering provided the predominant scattering mechanism is elastic. Because of the assumption of a constant relaxation time, our results are to be interpreted only as indicating a measure of the anisotropy introduced by the toroidal surfaces. Subject to the foregoing restrictions the results are

$$\sigma_{xx}^{(0)} = (Ne^2\tau)A = \sigma_{yy}^{(0)}, \quad \sigma_{zz}^{(0)} = (Ne^2\tau)(2C), \tag{6}$$

$$R(H \perp c) = -(Nec_L)^{-1},$$

$$R(H \parallel c) = -(Nec_L)^{-1}\{2(\Lambda/\pi)^{1/2} \exp(-\Lambda)\}. \tag{7}$$

In Eqs. (6) and (7), N is the number of electrons in the conduction band, e is the absolute value of the electronic charge, and c_L is the velocity of light. The expression for $\sigma_{zz}^{(0)}$ is equal to that which would obtain for an ellipsoid of revolution, as is to be expected by inspection of Eq. (3). The most striking feature of these results is the strong anisotropy exhibited by the Hall coefficients. Apart from a proportionality constant of order unity, the ratio $R(H \parallel c)/R(H \perp c)$ diminishes as $\Lambda^{1/2} \exp(-\Lambda)$ with decreasing temperature. It can be shown that the exponential factor in $R(H \parallel c)$ persists if τ is generalized such that τ^2 is any analytic function of E. Physically, the coefficient

$R(H \| c)$ is small because electrons with $k_\perp < \beta$ rotate in a sense opposite to that for electrons with $k_\perp > \beta$ and because ω_c tends to zero as $k_\perp$ approaches β.

For CdS Thomas et al.[5] have estimated an upper bound of the order of a few hundredths of an ev for the displacement of any energy minima below $E(0)$ in the conduction band. In the toroidal model this energy displacement equals $A\beta^2$. Setting $A\beta^2 = 0.04$ ev, one obtains $\Lambda \approx 6$ at $T = 77°K$. Thus, one might hope to observe a large anisotropy in the Hall effect, if the model is correct.

It should be emphasized that the model results from an approximation. Extension of the $\vec{k}\cdot\vec{p}$ perturbation calculation to higher orders will lower the symmetry of the surfaces to one of sixfold rather than continuous rotational invariance. Whether or not the corrections are important will depend upon the size of β and the proximity of other bands. For $A\beta^2 = 0.04$ ev and $A = (2m)^{-1}$, β is typically of the order of one-tenth the shortest distance in $\vec{k}$ space between the point $\vec{k} = 0$ and any of the reduced zone boundaries parallel to the k_z axis.

Added note. The toroidal model is a direct consequence of the spin-orbit interaction. The nature of $E(\vec{k})$ in the limit of zero spin-orbit coupling is described in the earlier work of Rashba,[11] who has recently given independent consideration to the effects of including the interaction.[12]

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NUCLEAR POLARIZATION IN He^3 GAS INDUCED BY OPTICAL PUMPING AND DIPOLAR EXCHANGE*

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Although almost complete polarization of alkali metal nuclei can be produced by optical pumping utilizing a buffer gas and a filter to remove the D_2 resonance light,[1,2] the number of atoms polarized is necessarily very small and is limited by optical opacity of the sample vapor. The usual range of pressure is 10^{-7} to 10^{-3} mm for successful detection and production of optical polarization. The Overhauser nuclear polarization effect[3] involving dipolar interactions[4-8] between such an optically polarized atom and the nucleus of a suitable buffer gas should provide a mechanism for the transfer of polarization to a gas at considerably higher pressure than that of the alkali vapor. In other words, the Overhauser effect should work not by the dipole-coupled relaxation of a saturated paramagnetic impurity toward a polarized equilibrium, but by the relaxation of an optically polarized impurity toward a nearly depolarized equilibrium. We have observed this effect in He^3 gas used as the buffer gas for the optical pumping of natural rubidium vapor.

The nuclear magnetic relaxation time in a liquid or a monatomic gas depends inversely on both the square of the magnetic moment of the nucleus and the square of the moment of other spins causing the relaxation. If He^3 is contaminated with "dissolved" Rb atoms having a moment 10^3 times as great as the He^3, a concentration of more than 1 part in 10^6 would dominate the relaxation. The dipole interaction terms in-