Theory of the Hall Effect in Disordered Systems: Impurity-Band Conduction

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A general quantum-mechanical formula for the low-field Hall effect is derived in the density matrix approach, thus making it possible to treat this effect in disordered systems. With some assumptions about the one-electron matrix elements involved, the Hall and ordinary conductivities are correlated for the impurity-band conduction in the "metallic range." According to our results, the sign of the Hall effect depends on the degree of filling of the impurity band.

1. INTRODUCTION

THE theory of the Hall effect is an unclarified problem in disordered systems, such as impurity bands and amorphous semiconductors. In these systems the classical "scattering approach" to the transport problem fails, because in any approximation the electronic states can not be regarded as quasifree; consequently, such a basic concept as the effective mass can not be defined. But it is not clear what other parameter would then govern the sign of the Hall effect.

Some qualitative considerations, as yet unproved, can be found in a paper by Mott and Twose.[1] A rigorous basis for a future theoretical investigation of this problem is contained in R. Kubo's work[2] concerning the general theory of low-field Hall effect.

In this work, we derive the general formula for the low-field Hall conductivity in a manner different from that of Kubo, introducing adiabatically both the electric and magnetic fields (Sec. 2). Such an approach seems to be simpler. For a system of dynamically noninteracting electrons, using the second quantization formalism, we express the transverse conductivity in terms of products of certain one-electron matrix elements (involving momenta and the disordered potential), and Fermi distribution functions (Sec. 3).

The formula which has been obtained is applied to the case of high-concentration impurity-band conduction, where some simple assumptions about the matrix elements are possible (Sec. 4). According to our results, the sign of the Hall effect depends on the filling of the impurity band.

2. THE GENERAL FORMULA OF HALL CONDUCTIVITY

Let us consider the density-matrix equation

$$i\hbar d\rho/dt=[H+H'(t),\rho], \tag{1}$$

where H is the Hamiltonian of a dissipative system and $H'(t)$ is the adiabatically turned-on external-field Hamiltonian (electric and magnetic).

For a calculation of low-field Hall conductivity it is sufficient to consider the terms of the density matrix which are bilinear in the external electric and magnetic fields.

The second iterative solution of Eq. (1), with the initial condition

$$\rho|_{t=-\infty}=\rho_0(H)$$

[$\rho_0(H)$ = grand canonical equilibrium density matrix] is

$$\rho^{(2)}=-\frac{1}{\hbar^2}\int_{-\infty}^{0}dt\int_{-\infty}^{0}dt'e^{s(t+t')}e^{iHt/\hbar}[H',e^{iHt'/\hbar}[H',\rho_0]e^{-iHt'/\hbar}]e^{-iHt/\hbar};\quad(s\to+0). \tag{2}$$

As we had mentioned before

$$H'=H_M+H_E, \tag{3}$$

where, in the second quantization formalism,

$$H_M=\int d\mathbf{r}\,\psi^\dagger(\mathbf{r})\left(-\frac{e}{mc}\mathcal{H}x\hat{p}_y+\frac{e^2}{2mc^2}\mathcal{H}^2x^2\right)\psi(\mathbf{r})$$
$$H_E=\int d\mathbf{r}\,\psi^\dagger(\mathbf{r})(-e\mathcal{E}y)\psi(\mathbf{r}). \tag{3a}$$

[We have chosen the dc magnetic and electric fields along Oz and Oy axes, respectively, with the potentials $\varphi=-\mathcal{E}y$ and $\mathbf{A}=(0,\mathcal{H}x,0)$.]

[1] N. F. Mott and W. D. Twose, Advan. Phys. **10**, 107 (1961).
[2] R. Kubo, J. Phys. Soc. Japan **19**, 2127 (1964).

Thus the average current, in which we are interested is

$$\langle j_x\rangle_{\mathrm{av}}=-\frac{e^3}{\Omega\hbar^2m^2c}\mathcal{E}\mathcal{H}\int_{-\infty}^{0}dt\int_{-\infty}^{0}dt'e^{s(t+t')}\,\mathrm{Tr}\{[Y,[M(t'),\rho_0]]P_x(-t)+[M,[Y(t'),\rho_0]]P_x(-t)\}\,, \tag{4}$$

where

$$Y=\int d\mathbf{r}\,\psi^\dagger(\mathbf{r})y\psi(\mathbf{r});\quad M=\int d\mathbf{r}\,\psi^\dagger(\mathbf{r})x\hat{p}_y\psi(\mathbf{r});\quad P_x=\int d\mathbf{r}\,\psi^\dagger(\mathbf{r})\hat{p}_x\psi(\mathbf{r})$$

and Ω is the volume of the system considered.

A step-by-step resolution of the commutators, using the well-known identity

$$[F,e^{zH}]=-e^{zH}\int_0^{-z}d\lambda\,e^{\lambda H}[F,H]e^{-\lambda H}=-ihe^{zH}\int_0^{-z}d\lambda\,\dot{F}(-i\hbar\lambda)=i\hbar\int_0^{z}d\lambda\,\dot{F}(-i\hbar\lambda)e^{zH}\,,$$

gives for the transverse (Hall) conductivity

$$\sigma_H=-\frac{e^3}{\Omega\hbar m^2c}\mathcal{H}\int_{-\infty}^{0}dt\int_{-\infty}^{0}dt'e^{s(t+t')}\int_0^{\beta}d\lambda\Big\langle\Big\{i[\dot{M},Y]+i[\dot{Y},M]+\hbar\int_0^{-(it'/\hbar+\lambda)}d\eta(\dot{M}\dot{Y}(-i\hbar\eta)+\dot{Y}\dot{M}(-i\hbar\eta))$$
$$-\hbar\int_0^{-(it'/\hbar+\lambda-\beta)}d\eta(\dot{M}(-i\hbar\eta)\dot{Y}+\dot{Y}(-i\hbar\eta)\dot{M})\Big\}P_x(-t-t'+i\hbar\lambda)\Big\rangle_0\,, \tag{5}$$

where the symbol $\langle\cdots\rangle_0$ means the average over the grand canonical distribution, and $\beta=1/kT$.

3. ONE-ELECTRON APPROACH

In what follows we shall make some suppositions which, of course, will restrict the generality of our results. We shall consider that our system of electrons can be described by a Hamiltonian of following type:

$$H=\int d\mathbf{r}\,\psi^\dagger(\mathbf{r})\Big(-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\Big)\psi(\mathbf{r})=\sum_\mu\epsilon_\mu a_\mu^\dagger a_\mu\,, \tag{6}$$

(that is, the electrons are dynamically independent).

Then, it can be easily shown that

$$[Y,\dot{M}]=(\hbar/m)P_x;\quad[M,\dot{Y}]=0,$$
$$\dot{Y}=m^{-1}P_y=m^{-1}\textstyle\sum_{\mu,\nu}(\hat{p}_y)_{\mu\nu}a_\mu^\dagger a_\nu\,, \tag{7}$$
$$\dot{M}=\textstyle\sum_{\mu,\nu}(\hat{\kappa})_{\mu\nu}a_\mu^\dagger a_\nu;\quad\hat{\kappa}=m^{-1}(\hat{p}_x\hat{p}_y-x\partial V(\mathbf{r})/\partial_y)\,.$$

Putting (7) into Eq. (5) and solving integrals over η, λ, t, and t' we have

$$\sigma_H=-\frac{e^3}{\Omega m^3c}\mathcal{H}\sum_{\substack{\mu_1,\mu_2,\mu_3,\\ \nu_1,\nu_2,\nu_3}}\Big\{\delta_{\mu_2\mu_1}\delta_{\nu_2\nu_1}\Big(\frac{1}{(-i/\hbar)(\epsilon_{\mu_3}-\epsilon_{\nu_3})+s}\Big)^2\frac{1-e^{-\beta(\epsilon_{\mu_3}-\epsilon_{\nu_3})}}{\epsilon_{\mu_3}-\epsilon_{\nu_3}}(\hat{p}_x)_{\mu_1\nu_1}(\hat{p}_x)_{\mu_3\nu_3}\langle a_{\mu_1}^\dagger a_{\nu_1}a_{\mu_3}^\dagger a_{\nu_3}\rangle_0$$
$$+\frac{((\hat{\kappa})_{\mu_1\nu_1}(\hat{p}_y)_{\mu_2\nu_2}+(\hat{\kappa})_{\mu_2\nu_2}(\hat{p}_y)_{\mu_1\nu_1})(\hat{p}_x)_{\mu_3\nu_3}}{(-i/\hbar)(\epsilon_{\mu_3}-\epsilon_{\nu_3})+s}\Big[\frac{1}{\epsilon_{\mu_2}-\epsilon_{\nu_2}}\Big(\frac{1}{(-i/\hbar)(\epsilon_{\mu_2}-\epsilon_{\nu_2}+\epsilon_{\mu_3}-\epsilon_{\nu_3})+s}\frac{1-e^{-\beta(\epsilon_{\mu_2}-\epsilon_{\nu_2}+\epsilon_{\mu_3}-\epsilon_{\nu_3})}}{\epsilon_{\mu_2}-\epsilon_{\nu_2}+\epsilon_{\mu_3}-\epsilon_{\nu_3}}$$
$$-\frac{1}{(-i/\hbar)(\epsilon_{\mu_3}-\epsilon_{\nu_3})+s}\frac{1-e^{-\beta(\epsilon_{\mu_3}-\epsilon_{\nu_3})}}{\epsilon_{\mu_3}-\epsilon_{\nu_3}}\Big)-\frac{1}{\epsilon_{\mu_1}-\epsilon_{\nu_1}}\Big(\frac{e^{\beta(\epsilon_{\mu_1}-\epsilon_{\nu_1})}}{(-i/\hbar)(\epsilon_{\mu_1}-\epsilon_{\nu_1}+\epsilon_{\mu_3}-\epsilon_{\nu_3})+s}\frac{1-e^{-\beta(\epsilon_{\mu_1}-\epsilon_{\nu_1}+\epsilon_{\mu_3}-\epsilon_{\nu_3})}}{\epsilon_{\mu_1}-\epsilon_{\nu_1}+\epsilon_{\mu_3}-\epsilon_{\nu_3}}$$
$$-\frac{1}{(-i/\hbar)(\epsilon_{\mu_3}-\epsilon_{\nu_3})+s}\frac{1-e^{-\beta(\epsilon_{\mu_3}-\epsilon_{\nu_3})}}{\epsilon_{\mu_3}-\epsilon_{\nu_3}}\Big)\Big]\langle a_{\mu_1}^\dagger a_{\nu_1}a_{\mu_2}^\dagger a_{\nu_2}a_{\mu_3}^\dagger a_{\nu_3}\rangle_0\Big\}\,. \tag{8}$$

For the equilibrium average over the products of creation and annihilation operators we may use the formula

$$\langle a_{\mu_n}^\dagger\cdots a_{\mu_1}^\dagger a_{\nu_1}\cdots a_{\nu_n}\rangle_0=f(\epsilon_{\nu_1})\cdots f(\epsilon_{\nu_n})\det|\delta_{\mu_i\nu_k}|;\quad(i,k=1,\cdots,n)\,, \tag{9}$$

where $f(\epsilon)$ is the Fermi distribution function.

Taking into account that the equilibrium average of any of the involved one-electron operators $\hat{p}_x$, $\hat{p}_y$, $\hat{\kappa}$ vanishes, we need retain in Eq. (8) only the terms in which all the matrix indices are coupled. After a somewhat cumbersome regrouping of terms the calculation gives

$$\sigma_H=-\frac{e^3\hbar^2}{\Omega m^3 c}\mathfrak{IC}\sum_{\mu_1,\mu_2,\mu}\left\{\delta_{\mu_2\mu_1}\left(\frac{1}{\epsilon_{\mu_3}-\epsilon_{\mu_1}+i\hbar s}\right)^2\Delta f_{13}|(\hat{p}_x)_{\mu_1\mu_3}|^2\right.$$
$$+\frac{((\hat{\kappa})_{\mu_2\mu_3}(\hat{p}_y)_{\mu_1\mu_2}+(\hat{\kappa})_{\mu_1\mu_2}(p_y)_{\mu_2\mu_3})(p_x)_{\mu_3\mu_1}}{\epsilon_{\mu_3}-\epsilon_{\mu_1}+i\hbar s}\left[\frac{1}{\epsilon_{\mu_2}-\epsilon_{\mu_1}}\left(\frac{\Delta f_{32}}{\epsilon_{\mu_3}-\epsilon_{\mu_2}+i\hbar s}-\frac{\Delta f_{31}}{\epsilon_{\mu_3}-\epsilon_{\mu_1}+i\hbar s}\right)\right.$$
$$\left.\left.+\frac{1}{\epsilon_{\mu_2}-\epsilon_{\mu_3}}\left(\frac{\Delta f_{21}}{\epsilon_{\mu_2}-\epsilon_{\mu_1}+i\hbar s}-\frac{\Delta f_{31}}{\epsilon_{\mu_3}-\epsilon_{\mu_1}+i\hbar s}\right)\right]\right\},\quad(10)$$

where

$$\Delta f_{ij}=[f(\epsilon_{\mu_i})-f(\epsilon_{\mu_j})]/[\epsilon_{\mu_i}-\epsilon_{\mu_j}].$$

We mention that the same result may be obtained without the use of the second quantization formalism, by introducing into Eq. (4) a one-electron Hamiltonian and a Fermi-Dirac one-electron density matrix.

If we put into the Liouville equation (1) a term $i\hbar(\rho-\rho_0)/\tau$, which represents an ideal relaxation law, we obtain instead of Eq. (10) a similar expression, in which the adiabatic parameter s is changed to τ^{-1}. To verify our formula, it is easy to calculate σ_H for such an ideally relaxing free-electron system. Such a calculation gives the classical formula

$$\sigma_H=(Ne^3/\Omega m^2 c)\mathfrak{IC}\tau^2.\quad(11)$$

Returning to our Eq. (10) for infinitesimal $\epsilon=\hbar s$, and using the identity

$$\frac{1}{\epsilon_j-\epsilon_i}\left(\frac{\Delta f_{kj}}{\epsilon_k-\epsilon_j+i\epsilon}-\frac{\Delta f_{ki}}{\epsilon_k-\epsilon_i+i\epsilon}\right)=\frac{\Delta f_{ik}+\Delta f_{jk}-\Delta f_{ij}}{(\epsilon_k-\epsilon_j+i\epsilon)(\epsilon_k-\epsilon_i+i\epsilon)},$$

we have

$$\sigma_H=-\frac{e^3\hbar^2}{\Omega m^3 c}\mathfrak{IC}\sum_{\mu_1,\mu_2,\mu_3}\left(\frac{1}{\epsilon_{\mu_3}-\epsilon_{\mu_1}+i\epsilon}\right)^2\left\{\delta_{\mu_2\mu_1}|(\hat{p}_x)_{\mu_1\mu_3}|^2\Delta f_{13}\right.$$
$$\left.+((\hat{\kappa})_{\mu_1\mu_2}(\hat{p}_y)_{\mu_2\mu_3}+(\hat{\kappa})_{\mu_2\mu_3}(\hat{p}_y)_{\mu_1\mu_2})(\hat{p}_x)_{\mu_3\mu_1}\left[\frac{\Delta f_{13}+\Delta f_{23}-\Delta f_{12}}{\epsilon_{\mu_3}-\epsilon_{\mu_2}+i\epsilon}-\frac{\Delta f_{13}+\Delta f_{12}-\Delta f_{23}}{\epsilon_{\mu_2}-\epsilon_{\mu_1}+i\epsilon}\right]\right\}.\quad(12)$$

(By interchanging the indices 1 and 3, it may be seen that this expression is real.)

With the notations

$$n(\epsilon_1)n(\epsilon_2)A(\epsilon_1,\epsilon_2)=\sum_{\substack{\mu_1,\mu_2\\(\epsilon_{\mu_1}=\epsilon_1,\ \epsilon_{\mu_2}=\epsilon_2)}}|(\hat{p}_x)_{\mu_1\mu_2}|^2,\quad(13)$$
$$n(\epsilon_1)n(\epsilon_2)n(\epsilon_3)B(\epsilon_1,\epsilon_2,\epsilon_3)=\sum_{\substack{\mu_1,\mu_2,\mu_3\\(\epsilon_{\mu_1}=\epsilon_1,\ \epsilon_{\mu_2}=\epsilon_2,\ \epsilon_{\mu_3}=\epsilon_3)}}((\hat{\kappa})_{\mu_1\mu_2}(\hat{p}_y)_{\mu_2\mu_3}+(\hat{\kappa})_{\mu_2\mu_3}(\hat{p}_y)_{\mu_1\mu_2})(\hat{p}_x)_{\mu_3\mu_1},$$

and $n(\epsilon)$ for the density-of-states function, Eq. (12) reads

$$\sigma_H=-\frac{e^3\hbar^2}{\Omega m^3 c}\mathfrak{IC}\left\{\int d\epsilon_1\int d\epsilon_2\frac{d}{d\epsilon_1}\left(\frac{1}{\epsilon_2-\epsilon_1+i\epsilon}\right)n(\epsilon_1)n(\epsilon_2)\Delta f_{12}A(\epsilon_1,\epsilon_2)\right.$$
$$\left.+\int d\epsilon_1\int d\epsilon_2\int d\epsilon_3\frac{d}{d\epsilon_1}\left(\frac{1}{\epsilon_3-\epsilon_1+i\epsilon}\right)n(\epsilon_1)n(\epsilon_2)n(\epsilon_3)B(\epsilon_1,\epsilon_2,\epsilon_3)\left[\frac{\Delta f_{13}+\Delta f_{23}-\Delta f_{12}}{\epsilon_3-\epsilon_2+i\epsilon}-\frac{\Delta f_{13}+\Delta f_{12}-\Delta f_{23}}{\epsilon_2-\epsilon_1+i\epsilon}\right]\right\}.\quad(14)$$

4. IMPURITY CONDUCTION

In disordered systems, of course, this expression must be averaged also over all the possible arrangements of the atoms. In the following, we shall assume, as is usually done in such problems, that after averaging, in Eq. (14), $n(\epsilon)$, $A(\epsilon_1,\epsilon_2)$, and $B(\epsilon_1,\epsilon_2,\epsilon_3)$ will appear with their mean values.

If the energy dependence of the averaged A and B is sufficiently smooth, they may be taken outside the inte-

grals. Such a case probably occurs in impurity-band conduction, at least in the so-called "metallic range," as is shown in Kasuya's approach.[3] Thus, in the case considered, using the well-known identity

$$(x+i\epsilon)^{-1}=Px^{-1}-i\pi\delta(x), \quad \epsilon\to+0$$

we have

$$\sigma_H=-(e^3\hbar^2/\Omega m^3c)\mathfrak{C}[\bar{A}I+\bar{B}(J_0+J_1)], \tag{15}$$

where

$$I=\int d\epsilon_1\int d\epsilon_2\frac{d}{d\epsilon_1}\left(P\frac{1}{\epsilon_2-\epsilon_1}\right)n(\epsilon_1)n(\epsilon_2)\Delta f_{12},$$

$$J_0=2\pi^2\int d\epsilon\, n^2(\epsilon)\frac{dn(\epsilon)}{d\epsilon}\frac{df(\epsilon)}{d\epsilon}, \tag{15a}$$

$$J_1=\int d\epsilon_1\int d\epsilon_2\frac{d}{d\epsilon_1}\left(P\frac{1}{\epsilon_2-\epsilon_1}\right)n(\epsilon_1)n(\epsilon_2)\Delta f_{12}\int d\epsilon_3 n(\epsilon_3)\left(P\frac{1}{\epsilon_1-\epsilon_3}+P\frac{1}{\epsilon_2-\epsilon_3}\right).$$

Let us consider a density of states in the impurity band, of the type

$$n(\epsilon)=(N/\pi\Delta)[1+(\epsilon/\Delta)^2]^{-1}, \tag{16}$$

where N is the total number of impurity states. With such a resonance-type function, the integrals (15) can be easily solved in the complex plane. For the integrals involving the symbol $d(Px^{-1})/dx$ we used the artifice

$$\int dx\,\varphi(x)\frac{d}{dx}\left(P\frac{1}{x}\right)=\lim_{a\to0}\frac{d}{da}\int dx\,\varphi(x)P\frac{1}{x+a}.$$

The result is

$$\sigma_H=\frac{e^3\hbar^2}{\Omega m^3c}\mathfrak{C}\frac{N^2\bar{A}}{\pi\Delta^3}\int_{-\infty}^{\infty}dx\left[f(x)\frac{2x(3-x^2)}{(1+x^2)^4}+\gamma\frac{df(x)}{dx}\frac{x(7-x^2)}{(1+x^2)^4}\right] \tag{17}$$

with

$$\gamma=\bar{B}N/\bar{A}\Delta \text{ (dimensionless coefficient)}$$

and x being the energy in units of Δ.

If $kT\ll\Delta$, then $f(x)$ may be approximated by $\theta(\bar{\mu}-x)$ where $\bar{\mu}=\mu/\Delta$ ($\mu=$chemical potential). Then, in the "metallic range," for low temperatures, the Hall conductivity reads explicitly

$$\sigma_H=-\frac{e^3\hbar^2}{\Omega m^3c}\mathfrak{C}\frac{N^2\bar{A}}{\pi\Delta^3}\left[\frac{5-3\bar{\mu}^2}{6(1+\bar{\mu}^2)^3}+\gamma\frac{\bar{\mu}(7-\bar{\mu}^2)}{(1+\bar{\mu}^2)^4}\right]. \tag{18}$$

On the other hand, concerning γ, we can observe that

$$(\hat{\kappa})_{\mu_1\mu_2}(\hat{p}_y)_{\mu_2\mu_3}(\hat{p}_x)_{\mu_3\mu_1}=m^{-1}(\hat{p}_x\hat{p}_y)_{\mu_1\mu_2}(\hat{p}_y)_{\mu_2\mu_3}(\hat{p}_x)_{\mu_3\mu_1}-m^{-1}(x\partial V/\partial y)_{\mu_1\mu_2}(\hat{p}_y)_{\mu_2\mu_3}(\hat{p}_x)_{\mu_3\mu_1}$$
$$=m^{-1}|(\hat{p}_x)_{\mu_1\mu_3}|^2|(\hat{p}_y)_{\mu_2\mu_3}|^2+m^{-1}\sum_{\nu(\neq\mu_3)}(\hat{p}_x)_{\mu_1\nu}(\hat{p}_y)_{\nu\mu_2}(\hat{p}_y)_{\mu_2\mu_3}(\hat{p}_x)_{\mu_3\mu_1}$$
$$-m^{-1}(x\partial V/\partial y)_{\mu_1\mu_2}(\hat{p}_y)_{\mu_2\mu_3}(\hat{p}_x)_{\mu_3\mu_1}.$$

The first term of this expression is essentially real and positive, but the others have no definite sign. We may expect that their average value over a chaotic distribution of atoms will vanish. If this is correct, then

$$\bar{B}\approx2\bar{A}^2/m.$$

Thus

$$\gamma\approx2\bar{A}N/m\Delta. \tag{18a}$$

But we may easily show that the ordinary conductivity, with the same assumption about the averages, may be expressed also in terms of $\bar{A}$. Thus, according to the well-known quantum theory of electric conductivity,[4]

$$\sigma=-\frac{\pi e^2\hbar}{\Omega m^2}\sum_{\mu_1,\mu_2}\frac{df(\epsilon_{\mu_1})}{d\epsilon_{\mu_1}}|(\hat{p}_x)_{\mu_1\mu_2}|^2\delta(\epsilon_{\mu_1}-\epsilon_{\mu_2}). \tag{19}$$

After averaging over the impurities, we obtain

$$\sigma=-\frac{\pi e^2\hbar}{\Omega m^2}A\int d\epsilon\, n^2(\epsilon)\frac{df(\epsilon)}{d\epsilon}. \tag{20}$$

[3] T. Kasuya, J. Phys. Soc. Japan **13**, 1096 (1958).

[4] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

Introducing into Eq. (20) our density of states (16), we get the following formula which is valid in the "metallic range" for low temperatures:

$$\sigma=(e^2\hbar/\Omega m^2)(N^2\tilde{A}/\pi\Delta^2)(1+\bar{\mu}^2)^{-2}. \tag{20a}$$

We may observe that the Hall and ordinary conductivity are correlated in a simple manner, through the phenomenological parameter $\tilde{A}$:

$$\sigma_H=\frac{\hbar\omega_0}{\Delta}\left[\frac{5-3\bar{\mu}^2}{6(1+\bar{\mu}^2)}+\gamma\frac{\bar{\mu}(7-\bar{\mu}^2)}{(1+\bar{\mu}^2)^2}\right]\times\sigma;\quad \omega_0=\frac{|e|\mathfrak{H}}{mc}, \tag{21}$$

$$\gamma=(2\pi m/e^2\hbar)\Delta(1+\bar{\mu}^2)^2/(N/\Omega)\times\sigma. \tag{21a}$$

By inspection of Eq. (21) and by comparison of its sign with that of the classical formula (11), we can conclude that the first term in (21) always gives a positive-charge contribution to the Hall effect, while the second gives a negative one for $\bar{\mu}<0$ and a positive one for $\bar{\mu}>0$. Therefore, for $\bar{\mu}>0$, that is for hole conduction in the impurity band—at least in the "metallic range"—we must have a positive-charge Hall effect. For low electron concentration our formula shows that a negative-charge Hall effect is very plausible; this seems, indeed, to be true because an estimate of γ [through Eq. (21a), using the data of the experiments of Fritzsche and Cuevas[5]] gives $\gamma\gg1$. It is interesting that even so, there is a slight asymmetry in favor of the holes.

5. CONCLUSIONS

We have derived the general quantum-mechanical formula for low-field Hall conductivity. This is necessary for the discussion of the Hall effect in disordered systems, where such concepts as "effective mass" and "quasifree" approach are of doubtful value. Our formula was put in its one-electron form for a system of dynamically independent electrons. We think that such a formulation is possible for the majority of transport problems, particularly for disordered systems.

Assuming the constancy of certain matrix elements (averaged over all the possible arrangements of the atoms), we have correlated the Hall conductivity for an impurity band with its ordinary conductivity [Eqs. (17), (20)]. (Here we neglected the possible overlap of the impurity band with the nearest band of the host crystal, which occurs at too high impurity concentration.) Our assumption seems to be justified for the nonlocalized states, which are characteristic for the "metallic range" of impurity-band conduction. In this case, for low temperatures ($kT\ll\Delta$), according to our formula (18), both negative and positive Hall effects are possible (depending on the position of the Fermi level), in contradiction with Mott's arguments.[1] Nevertheless, the change of sign occurs when a symmetrical impurity band is less than half filled.

It seems that in the impurity-band case, as in the Bloch-band case, the sign of the Hall effect is governed by the sign of the first derivative of the density of states in the conduction region.

A thorough comparison of our results with the experiments could not be performed because only incomplete and uncertain experimental data are presently available.

We intend to apply our general formulas (5) or (14) to other interesting cases, such as the problem of the Hall conductivity of the amorphous semiconductors within the model used by one of the authors.[6]

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[5] H. Fritzsche and M. Cuevas, Phys. Rev. 119, 1238 (1960).

[6] L. Bányai, *Proceedings of the Seventh International Conference on the Physics of Semiconductors* (Dunod Cie, Paris, 1964), p. 417.