

Hall effect in the dielectric regime of granular metal films

L. Friedman

General Telephone & Electronics Laboratories, 40 Sylvan Road, Waltham, Massachusetts 02254

(Received 17 February 1981; revised manuscript received 9 November 1981)

The Hall effect is considered in the dielectric regime of granular metal films, where the charge-transport mechanism is quantum-mechanical tunneling between isolated metallic grains. The dominant temperature dependence of the Hall mobility is found to be $\mu_H \sim \exp[-(T/T_{0H})^{1/2}]$, where $T_{0H} \ll T_0$, the characteristic temperature in the exponent of the electrical conductivity. The sign of the Hall effect is found to alternate with the orbital-quantum number of the highest occupied level at the grain Fermi energy, giving rise to cancellation effects which reduce the magnitude of μ_H by a temperature-dependent prefactor. These arise from finite temperature effects and the inherent spread in grain diameters.

INTRODUCTION

The electrical transport properties of granular metal films have been extensively investigated in recent years and have been the subject of several review articles.^{1,2} Above the percolation threshold there is a continuous metallic path through the specimen. However, below the percolation threshold, the so-called dielectric regime, the electrical transport mechanism is that of quantum-mechanical tunneling between isolated metallic particles in which the carrier is thermally activated to a level sufficient to overcome the grain charging energy. The tunneling rates and electrical conductivity for this case have been discussed and derived.

The Hall effect in the dielectric regime of granular metals is of particular interest because the conduction mechanism here is well defined as charging-energy-limited transport between isolated grains. In contrast, in the case of the Hall effect in amorphous semiconductors^{3,4} or narrow band materials, it is still uncertain whether transport is due to extended or localized (small polaron) states, whether or not the basic electronic states are atomlike or more extended,⁴ etc. In the present communication, we address the question of the Hall effect due to charging-energy-limited transport and the applicability of already existing theories of the Hall effect to this problem.

The existing theories of the Hall effect describe higher-order phonon-assisted hopping or tunneling processes between atomic or molecularlike states in which the charge carrier is localized because of either small polaron formation^{5,6} or Anderson localization.⁷ This has been the subject of general re-

views⁴ and, specifically, of reviews which focus on the question of the sign^{3,8} of the Hall effect in hopping conduction. In the microscopic theory, tunneling occurs between single nondegenerate ground-state atomic or molecular wave functions centered on adjacent sites. In the case of metallic grains, on the other hand, the electron occupies a (quasi)continuum of closely spaced levels within each grain and transport may be described by quantum-mechanical (WKB) tunneling methods. Thus, even though the grains are macroscopic, the tunneling events are entirely quantum mechanical, as in the microscopic theories. While lowest-order tunneling events suffice to yield the electrical conductivity,¹ higher-order tunneling events involving a minimum of three sites are needed to establish a Hall effect.^{5,6}

TEMPERATURE DEPENDENCE OF THE HALL MOBILITY

On the basis of these assumptions and those commonly made in computing the hopping conductivity of these systems, we may deduce the temperature dependence of the Hall effect as follows: We consider a region of the granular metal containing grains of about the same grain diameter d . Since it is empirically observed from electron micrographs that the composition averaged over several surface diffusion lengths is uniform,^{1,2} it follows that one may consider triangles of three grains of diameter d and separation s within such regions. It also follows that the ratio s/d is constant within each region, and that sE_c^0 is constant,

where $E_c^0 \simeq (e^2/d)$, the grain charging energy, is the energy required to generate a pair of fully dissociated positively and negatively charged grains.

We separate the charge generation process from the transport process by first taking a pair of negatively and positively charged grains to be thermally created, and then focusing on the motion of the excess electron (and hole) among the three grains involved in the Hall effect. The excess electron may then tunnel among the three grains at fixed energy. The number density of such carriers is proportional to the Boltzmann factor^{1,2} $\exp(-E_c^0/2kT)$.

Neglecting for the moment the question of sign (discussed in the next section), the three-site interference probability is proportional to

$$\left[\frac{eHA}{\hbar c} \right] \exp(-3\chi s),$$

where $A = s^2\sqrt{3}/4$ is the area of the triangle formed by the three grains, $\chi = (2m\phi/\hbar^2)^{1/2}$ is the tunneling constant with ϕ the effective barrier height, and $s = \text{const}/E_c$. Thus the off-diagonal conductivity (for a given s) is proportional to

$$\sigma_{xy}(s) \sim \frac{eH}{\hbar c} s^2 \frac{\sqrt{3}}{4} \exp(-3\chi s - E_c^0/2kT). \quad (1)$$

As for the case of the usual diagonal conductivity $\sigma_{xx} = \sigma_L$, we find the optimal value of $s = s_m^{xy}$ which maximizes

$$f_{xy}(s) = -3\chi s - (C/2\chi s kT),$$

where

$$C \equiv \chi s E_c^0.$$

This is easily found to be

$$s_m^{xy} = \left(\frac{2}{3}\right)^{1/2} s_m,$$

where

$$s_m = (2\chi)^{-1} (C/kT)^{1/2}$$

is the value of s which maximizes σ_{xx} . It also follows that

$$f_{xy}(s_m^{xy}) = \left(\frac{3}{2}\right)^{1/2} f(s_m), \quad (2)$$

where

$$f(s_m) = -2(C/kT)^{1/2} \equiv -(T_0/T)^{1/2}. \quad (3)$$

The Hall angle θ_H and Hall mobility are given by

$$\theta_H \equiv \frac{\mu_H H}{c} = \frac{\sigma_{xy}(s_m^{xy})}{\sigma_{xx}(s_m)}, \quad (4)$$

where $\sigma_{xx}(s_m) \equiv \sigma_L$ has already been calculated by Abeles and co-workers^{1,2} and is given by

$$\sigma_L \propto \exp[f(s_m)]. \quad (5)$$

Combining (2), (3), (4), and (5), we find that

$$\mu_H \propto \left[\frac{e(s_m^{xy})^2}{\hbar} \right] \exp\left\{ \left[\left(\frac{3}{2}\right)^{1/2} - 1 \right] f(s_m) \right\} \\ \propto \frac{e}{\hbar} \frac{2}{3} \frac{1}{(2\chi)^2} \frac{C}{kT} \exp\left\{ 0.2247 \left[-2 \left[\frac{C}{kT} \right]^{1/2} \right] \right\}$$

Thus the Hall mobility μ_H , like the drift mobility μ_D , varies as $\exp[-(T_{0H}/T)^{1/2}]$, but with $T_{0H} < T_0$, where $T_0 = (4C/k)$, defined by Eq. (3), is the characteristic slope of σ_L (or μ_D). Specifically,

$$T_{0H} = (0.2247)^2 T_0 \simeq 0.05 T_0. \quad (6)$$

Thus, when plotted as a function of $T^{-1/2}$, $\ln \mu_H$ is predicted to be considerably less temperature dependent than $\ln \sigma_L$. There is an additional temperature-dependent prefactor which arises in connection with the sign of the Hall effect discussed in the following section.

SIGN OF THE HALL EFFECT IN THE DIELECTRIC REGIME

The sign^{3,8} of the Hall effect is decided by: (a) the number of sites n making a closed path, and (b) the sign of the transfer integral J . In the present case of randomly dispersed metallic grains, we would expect the dominant contribution to the Hall effect to arise from three-site closed paths, $n = 3$. As for item (b), the sign of J depends on the relative signs (phases) of the electronic wave functions in the region in which they overlap. The thermally generated hole will also yield a Hall effect by the same mechanism presented here for the electron; the hole will tunnel among three grains, two of which are neutral. For the three-site ($n = 3$) case applicable to the present case, the sign of the Hall effect for the hole will be the same as that of the electron,⁸ which has yet to be determined. It then follows that the sign of the Hall effect in the dielectric regime should always be that of the electron.

We first present an approximate evaluation of the phase θ_J of the intergrain transfer integral J . Our approach is to evaluate θ_J over that portion of configuration space which makes the dominant contribution to J . We then give a more complete

evaluation of the required overlap integral in which the conclusion concerning the sign is corroborated.

Consider two spherical grains 1 and 2 centered at the origin and at \vec{b} , respectively, shown in Fig. 1. At these points let there be two parallel cartesian coordinate systems (x_1, y_1, z_1) , (x_2, y_2, z_2) and associated spherical polar systems (r_1, θ_1, ϕ_1) , (r_2, θ_2, ϕ_2) as shown. Let $\psi(\vec{r})$ and $\psi(\vec{r}-\vec{b})$ be the eigenfunctions of two spherical potential wells of radius $r=a$ and depth V_0 centered at $\vec{r}=0$ and $\vec{r}=\vec{b}$.

Now it has been argued at some length³ in the atomic case, that if the phases of the two wave functions are the same over the part of configuration space that make the dominant contribution to the wave-function overlap $S(\vec{r})=\psi^*(\vec{r})\psi(\vec{r}-\vec{b})$, then J is negative ($\theta_J=\pi$) and the sign of the electronic Hall effect is negative. This is true for s -like wave functions. On the other hand, if they are opposite, J is positive ($\theta_J=0$), as for p -like or anti-bonding orbitals, and the sign of the electronic Hall effect is positive. This follows from the fact that the one-electron potential $-|U_0|$, which enters into the definition of J , is intrinsically negative. Referring to Figs. 19 and 24 of Ref. 2, we take the one-electron potential in the intergrain region to be $-|U_0|$ with respect to vacuum; the potential of the spherical well referred to above is $-V_0$ with respect to the intergrain potential.

The eigenfunctions of the central spherical potential wells are⁹

$$\psi(r_i, \theta_i, \phi_i) = R(r_i) Y_{lm}(\theta_i, \phi_i) \quad \text{for } i=1, 2,$$

where

$$Y_{lm}(\theta_L, \phi_L) = e^{im\phi_L} P_{lm}(\cos\theta_L) \quad (7)$$

are the spherical harmonics, with $P_{lm}(\cos\theta_L)$ an associated Legendre polynomial and $-l \leq m \leq l$. The physically admissible exterior ($r > a$) solutions are spherical Hankel functions of the first kind which asymptotically take the form indicated,

$$R(r_i) = h_l^{(1)}(i\beta r_i) \xrightarrow{\beta r_i \rightarrow \infty} \frac{e^{-i(\pi/2)(l+2)} e^{-\beta r_i}}{\beta r_i}. \quad (8)$$

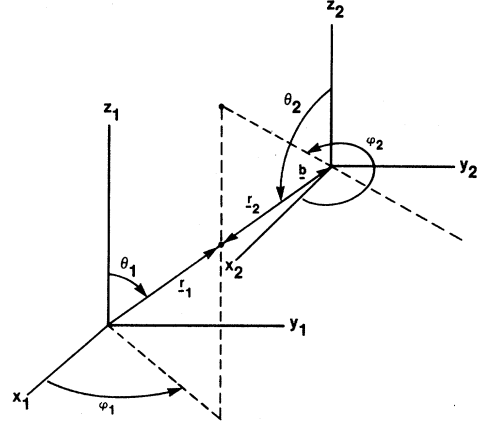


FIG. 1. Coordinate geometry for two-grain system.

The corresponding single-particle energy eigenvalues for a given value of $V_0 a^2$ are occupied sequentially according to the orbital quantum number l up to the limiting Fermi energy of the grain ($l=I_F$) at $T=0$. In the absence of a magnetic field, taking account of the $(2l+1)$ -fold degeneracy for a given l allows $2(I_F-1)^2$ electrons to be accommodated. The presence of a magnetic field is discussed briefly at the end of this section.

The approximate evaluation of the phase of $S(\vec{r})$ is based on the fact that in the dielectric regime in the limit of distantly separated grains, the dominant contribution to $S(\vec{r})$ is along the intergrain axis \vec{b} , i.e., at points (\vec{r}_1, \vec{r}_2) such that $\vec{r}_1 - \vec{r}_2 = \vec{b}$, or $|\vec{r}_1| + |\vec{r}_2| = b$. This follows from the rapid exponential decay of $R(r)$ as (\vec{r}_1, \vec{r}_2) moves off the axis. We first evaluate the phase of $S(\vec{r})$ on the axis and then investigate its behavior off the axis.

Referring to Fig. 1, we note that for \vec{r}_1 and \vec{r}_2 directed along \vec{b} , that

$$\theta_2 = \pi - \theta_1,$$

$$\phi_2 = \pi + \phi_1,$$

i.e., \vec{r}_1 and \vec{r}_2 are related by the inversion operation. It then follows that for this particular choice of (\vec{r}_1, \vec{r}_2) ,

$$Y_{lm}(\theta_2, \phi_2) = (-1)^l Y_{lm}(\theta_1, \phi_1),$$

as is well known. Thus,

$$S(\vec{r}_1, \vec{r}_2; r_1+r_2=b) = R^*(r_1) Y_{lm}(\theta_1, \phi_1) R(r_2) Y_{lm}(\theta_2, \phi_2) = (-1)^l \frac{e^{-\beta r_1}}{\beta r_1} \frac{e^{-\beta r_2}}{\beta r_2} [Y_{lm}(\theta_1, \phi_1)]^2. \quad (9)$$

We therefore see that S oscillates in sign and is positive or negative according to whether l is even or odd.

We now investigate $S(\vec{r})$ off the intergrain axis b . We consider the plane normal to b at the point (\vec{r}_1, \vec{r}_2) and take small displacements \vec{r} in this plane in the ϕ direction at constant θ and in the θ direction at constant ϕ . Since $\rho \ll r_i$, $r_i \rightarrow r_i + \rho^2/2r_i$. Very briefly, the essence of the argument is that since $\beta r_i \gg 1$, we may choose

$$\Delta\phi_i \sin\theta_i = (2/\beta r_i)^{1/2} \ll 1$$

and

$$\Delta\theta_i = (2/\beta r_i)^{1/2} \ll 1$$

for each of the above two cases, respectively. It then can be shown that: (a) the radial part of $S(\vec{r})$ is decreased by the factor e^{-2} , and (b) the additional terms in $Y_{lm}(\theta, \phi)$, which may yield a different phase $(-1)^l$, can be made negligibly small. Hence, we believe that the conclusion about the phase along \vec{b} , given by Eq. (9), applies with sufficient accuracy to the integral of $S(\vec{r})$ over all space.

An alternative, more complete evaluation of S is facilitated by recognizing that

$$S = \int d^3r \psi^*(\vec{r})\psi(\vec{r} - \vec{b}) \quad (10)$$

is of the form of a convolution integral, and may be evaluated by writing $\psi(\vec{r})$ as a three-dimensional Fourier transform, giving

$$S = \int d^3k e^{i\vec{k}\cdot\vec{b}} |\psi_{\vec{k}}|^2, \quad (11)$$

where

$$\psi_{\vec{k}} = \int d^3r e^{i\vec{k}\cdot\vec{r}} \psi(r). \quad (12)$$

Expanding $e^{i\vec{k}\cdot\vec{r}}$ in spherical harmonics with \vec{k} taken as the polar axis,

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{l=-\infty}^{\infty} (2l+1)i^l j_l(kr) P_l(\cos\theta), \quad (13)$$

substituting (7) for $\psi(\vec{r})$ and using the orthonormality of the spherical harmonics, we get

$$\begin{aligned} \psi_{\vec{k}} &= (2l+1)i^l \int dr r^2 j_l(kr) R_l(r) \\ &\equiv f_l(k). \end{aligned} \quad (14)$$

Substituting (14) back into (11), taking the polar axis along b and performing the angular integrations in k space, we are left with

$$S = 4\pi(2l+1)^2 \int_0^\infty dk k^2 \frac{\sin kb}{kb} |f_l(k)|^2. \quad (15)$$

In evaluating $f_l(k)$ given by Eq. (14), we employ the exterior radial solution

$$R_l(r) \simeq h_l^{(1)}(i\beta r),$$

where

$$\beta^2 = (2m/\hbar^2)(|E| + U_0).$$

Since $b \gg a$, the exterior solution will make the dominant contribution to S . The radial integration may be carried out,¹⁰ with the result

$$f_l(k) \simeq (k\beta)^{-1/2} (\beta^2 + k^2)^{-1} [(\beta a) J_{l+(1/2)}(ka) J_{l+(3/2)}(\beta a) - (ka) J_{l+(3/2)}(ka) K_{l+(1/2)}(\beta a)], \quad (16)$$

where

$$j_l(z) = (\pi/2z)^{1/2} J_{l+(1/2)}(z), \quad h_l^{(1)}(z) = (\pi/2z)^{1/2} H_{l+(1/2)}(z),$$

and $K_l(z) = (\pi i/2) e^{(\pi/2)l} H_l^{(1)}(iz)$ is a Hankel function of the first kind of imaginary argument.

In substituting (16) back into (15), noting that $l \gg 1$, we neglect the distinction between l , $(l + \frac{1}{2})$, and $(l + \frac{3}{2})$ as indices in the Bessel functions of large argument.¹¹ After some algebraic manipulation, we find that (15) can be written

$$S \simeq 4\pi(2l+1)^2 K_l^2(\beta a) \frac{a^2}{(\beta b)} \int_0^\infty dk \sin(kb) J_l^2(ka) \left[\frac{1}{(\beta+k)^2} \left[1 - \frac{4\beta^2 k^2}{(\beta^2 + k^2)^2} \right] \right]. \quad (17)$$

The integral is not easily carried out, but an upper bound on S can be found by replacing the slowly varying algebraic factor in the square bracket by $1/\beta^2$, noting that $b^{-1} \ll a^{-1} < \beta$. The integral is then readily performed,¹⁰ with the result

$$\begin{aligned} S &< 4\pi(2l+1)^2 K_l^2(\beta a) \frac{a}{(\beta b)\beta^2} \\ &\times \frac{1}{\pi} \cos(l\pi) Q_l \left[\frac{b^2}{2a^2} \right], \end{aligned} \quad (18)$$

where $Q_l(z)$ is a Legendre function of the second kind. The factor $\cos(l\pi) = (-1)^l$ explicitly displays the alternation in sign previously obtained by looking only at points along the intergrain axis.

Our result makes it difficult to arrive at any definite conclusion about the sign of the Hall effect in the dielectric regime. Consider metallic grains of diameter d and grain volume $G = (\pi/6)d^3$. For a typical conduction-electron density of $6 \times 10^{22} \text{ cm}^{-3}$ and Fermi energy $E_F = 5 \text{ eV}$, we calculate $g(E_F) = 1.8 \times 10^{22} \text{ eV}^{-1} \text{ cm}^{-3}$ and an energy-level spacing $\delta = [Gg(E_F)]^{-1} = 0.014 \text{ eV}$ ($\sim 160 \text{ K}$) for $d = 20 \text{ \AA}$ and $\delta \simeq 1.4 \times 10^{-5} \text{ eV}$ (0.16 K) for $d = 200 \text{ \AA}$. For $k_B T \lesssim \delta$ in each case, we would have to conclude that the sign of the Hall effect would be negative or positive according to whether the limiting orbital $l = l_F$ at μ corresponds to l even or odd, respectively, assuming a definite value of d . On the other hand, for $k_B T > \delta$, tunneling of the already thermally activated electron and hole will occur between the grain one-electron levels within an energy spread of $k_B T$ about μ . This tunneling is at fixed energy and for the electron, is proportional to the probability that the initial grain is occupied and the intermediate and final grains are unoccupied:

$$f(\epsilon)[1-f(\epsilon)][1-f(\epsilon)] = e^{\epsilon/2} \frac{1}{8} \text{sech}^3 \left[\frac{\epsilon}{2} \right],$$

$$\epsilon = \frac{\epsilon - \mu}{k_B T}. \quad (19)$$

For the hole, we obtain

$$[1-f(\epsilon)]f(\epsilon)f(\epsilon) = e^{-\epsilon/2} \frac{1}{8} \text{sech}^3(\epsilon/2). \quad (20)$$

Since the values of l involved are large ($l_F \gtrsim 10$), we have again assumed that the magnitude of the overlap is sensibly constant¹¹ for the fraction of levels of interest (of order $k_B T/\mu$). Also, as already pointed out, the electron and hole contributions have the same sign for $n = 3$. Thus, the above two contributions may be added, giving $\frac{1}{4} \text{sech}^2(\epsilon/2)$, which turns out to be the two-grain population factor, $f(\epsilon)[1-f(\epsilon)]$. In view of the alternating signs of adjacent levels, the overall temperature dependence of μ_H garnets the additional factor

$$\frac{1}{2} \left(\frac{1}{2} - \text{sech}^2 \bar{\delta} + \text{sech}^2 2\bar{\delta} - \dots \right) \equiv h(\bar{\delta}), \quad (21)$$

where

$$\bar{\delta} = \delta(E_F)/2k_B T.$$

It is found that, to a good approximation, $h(\bar{\delta})$ can be written

$$h(\bar{\delta}) = \begin{cases} (\bar{\delta})^2/12, & \bar{\delta} \lesssim 1.5 \\ \frac{1}{4} - \frac{2}{1+e^{\bar{\delta}}}, & \bar{\delta} > 1.5. \end{cases} \quad (22)$$

The smaller range would be expected to apply except at the lowest temperatures and largest grain sizes implying that the prefactor acquires the additional temperature-dependent factor $\frac{1}{12}(\bar{\delta})^2 = \frac{1}{12}(\delta/2k_B T)^2$.

In the preceding argument, we have calculated the cancellation effects which arise as a result of the thermal occupation of levels of alternating sign in the energy range $k_B T$ about μ , assuming a definite value of the grain diameter d . However, it is known^{1,2} that as a result of the competition between the changing energy and intergrain overlap, there is an inherent spread in grain diameters Δd corresponding to the spread in grain separations Δs about the optimal $s = s_m$ at temperature T [cf. just before Eq. (2)]. Thus, even if $k_B T < \delta$ so that only a single quantum level is involved in the transport, one must ask whether the above spread in diameters nevertheless washes out the Hall effect. According to the argument presented immediately below, it is shown that in most cases of physical interest this does not occur, i.e., that the condition $k_B T < \delta$ is sufficient to preclude cancellation effects.

The spread in grain separations Δs is obtained² by expanding

$$f(s) = -2\chi s - C/2\chi s k_B T$$

in a Taylor series to second order about s_m giving a Gaussian width

$$\Delta s = \frac{1}{8^{1/2}\chi} \left[\frac{C}{k_B T} \right]^{1/4}.$$

Then using the empirical rule^{1,2} that $s/d = \text{const}$, we immediately deduce that

$$\frac{\Delta d}{d_m} = \frac{\Delta s}{s_m} = \frac{1}{\sqrt{2}} \left[\frac{k_B T}{C} \right]^{1/4}. \quad (23)$$

The number of energy levels in the range $k_B T$ about μ is

$$R = \frac{k_B T}{\delta} = (k_B T)\rho(E_F)\frac{\pi}{6}d^3. \quad (24)$$

The change ΔR corresponding to a change Δd is

found. Setting $\Delta R = 1$ as the condition that the level at μ changes by one, we easily find that

$$\left[\frac{\Delta d}{d} \right]_1 = \frac{\delta}{3k_B T}. \quad (25)$$

Then taking the ratio of Eq. (23) to Eq. (25),

$$\frac{(\Delta d/d_m)}{(\Delta d/d)_1} = \frac{3}{\sqrt{2}} \frac{k_B T}{\delta} \left[\frac{k_B T}{C} \right]^{1/4}. \quad (26)$$

Now except for exceptional cases (corresponding to metal fraction $x \sim 0.5$),² $(k_B T/C) < 1$. Thus, if $k_B T < \delta$, the right-hand side of Eq. (26) will generally be less than unity, and the inherent spread in grain diameters will be less than that required to change the level at μ by one. In this case, the condition $k_B T < \delta$ will be sufficient to preclude cancellation of the Hall effect, as claimed. However, the ratio $(k_B T/C)$ must be carefully checked for each case of interest.

In the case of the Hall effect, there is of course an applied magnetic field \vec{B} which we take along the z (z_1 or z_2) axis (cf. Fig. 1). However, it is well known that to terms linear in B , the eigenfunctions given by Eq. (7) remain eigenfunctions of the $B \neq 0$ Schrödinger equation,¹² the sole effect of the magnetic field being to remove the m degeneracy and to shift all levels by the Zeeman energy $-(e\hbar/2m_e c)Bm$, $-l \leq m \leq l$. Hence, the previous calculation of the intergrain transfer integral remains valid to first order in B . However, one could envisage a situation where the Zeeman splitting becomes comparable with the grain energy-level spacing δ . It would then follow that the level $l = l_F$ which coincides with the Fermi level could shift from one l value to an adjacent one, implying a magnetic-field-induced alternation in the sign of the Hall effect. This possibility has not been studied.

SUMMARY AND CONCLUSION

In summary, the three-site interference mechanism responsible for the Hall effect due to hopping or tunneling transitions between atomic or molecularlike states has been generalized to the case of tunneling between macroscopic metallic grains according to the charging-energy-limited model. The Hall mobility is found to have the same temperature dependence as the low-field conductivity, $\mu_H \sim \exp(-T^{-1/2})$, but with a much smaller slope $T_{0H} \approx 0.05T_0$. Concerning the sign of the Hall effect, we find that the sign of the intergrain transfer

integral alternates with the orbital quantum number l in the vicinity of the grain Fermi energy, implying a similar alternation in the sign of the three-site Hall effect. The occupation of odd and even l values due to thermal effects or to the spread in grain sizes leads to cancellation effects, and makes the observation of the Hall effect problematic except at the lowest temperatures and for ideal specimens.

This is to be contrasted with the situation in the amorphous semiconductors^{3,4} where only a *single* lowest orbital partakes in the transport. For the chalcogenide glasses, J is negative, $n = 3$, and the sign of the Hall effect for holes is negative. In the case of electron transport between the antibonding orbitals of tetrahedrally coordinated amorphous semiconductors (e.g., *a*-Si), J is positive and the sign of the Hall effect is positive. Of course, the charge-transport mechanism in the amorphous semiconductors is not charging-energy limited, but rather is either diffusive transport at the mobility edge or small polaron hopping^{3,4}; nevertheless, the sign of the Hall effect has a common explanation.

The only experimental results for granular metal films in or approaching the dielectric regime are those of Sichel and Gittleman on Au-SiO₂ and W-Al₂O₃ cermets.¹³ All measurements were done at fixed temperature (room temperature). In the former material, R_H could only be measured in the metallic regime, and was found always to be negative in sign, no sign change being apparent as the percolation threshold to the dielectric regime was closely approached. For the W-Al₂O₃ system, R_H could be measured in the dielectric regime. It is positive in sign for pure W metal and metal-rich regimes, vanishes at the percolation threshold, and becomes negative in sign in the dielectric regime. These findings suggest only a negatively signed Hall effect in the dielectric regime. However, from our previous considerations, we can offer no explanation at the present time. More experimental work remains to be done, in particular the measurement of the temperature dependence of μ_H would be of considerable interest, as would be further measurements of the sign of the Hall effect to see if these conform to the predictions of the present paper.

ACKNOWLEDGMENTS

The author wishes to thank Dr. T. Holstein, Dr. E. Sichel, Dr. W. Bloss, Dr. G. Cooperman, and Dr. P. Sheng for discussion and assistance.

- ¹B. Abeles, Ping Sheng, M. D. Coutts, and Y. Arie, *Adv. Phys.* **24**, 407 (1975).
- ²B. Abeles, *Appl. Solid State Sci.* **6**, 1 (1976).
- ³D. Emin, in *Amorphous and Liquid Semiconductors*, Proceedings of the Seventh International Conference on Amorphous and Liquid Semiconductors, edited by W. E. Spear (Centre for Industrial Consultancy and Liaison, University of Edinburgh, 1977), p. 249.
- ⁴L. Friedman, *Philos. Mag.* **38**, 467 (1978).
- ⁵L. Friedman and T. Holstein, *Ann. Phys. (N.Y.)* **21**, 494 (1963).
- ⁶T. Holstein and L. Friedman, *Phys. Rev.* **165**, 1019 (1968).
- ⁷L. Friedman, *J. Non-Cryst. Solids* **6**, 329 (1971).
- ⁸T. Holstein, *Philos. Mag.* **27**, 225 (1973).
- ⁹E. Merzbacher, *Quantum Mechanics*, 2nd ed. (Wiley, New York, 1970), p. 194 ff.
- ¹⁰I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series and Products* (Academic, New York, 1980).
- ¹¹This may be verified by differentiating with respect to ν the large index approximation $J_\nu(z = \nu \operatorname{sech} \alpha) \sim (2\pi\nu \tanh \alpha)^{-1/2} \exp(\nu \tanh \alpha - \nu)$, $z < \nu$, given in Ref. (10), and the alternative large index approximation in which $z > \nu$.
- ¹²Reference 9, p. 180.
- ¹³E. K. Sichel and J. I. Gittleman, *Solid State Commun.* (in press).