infinite as $T \rightarrow 0$. This reemphasizes the need to consider the tunnelling process at very low temperatures.

6. CONCLUSIONS

The principal purpose of this paper has been the derivation of a rate formula for defect motion in solids based on equilibrium quantum statistics. This was done by making use of an interpretation of the canonical density matrix for a harmonic oscillator as an ensemble of oscillators which are in minimum-uncertainty states. This interpretation leads to a probability distribution function defined on a phase space of quantum means of coordinates and momenta and bears a close resemblance to the classical picture.

The classical limit of the derived quantum rate formula has a frequency factor which does not agree with that of Vineyard. The difference is due to the assumptions regarding mode interaction on the hill of the potential surface. Vineyard's derivation[2] assumes sufficient interaction to maintain equilibrium there; the present derivation assumes no interaction. This may have some relevance for observed anomalous isotope effects (see Le Claire[5] and Glyde[1]), but this question has not been examined here.

The low-temperature behavior of the quantum rate formula has been examined for a Debye model. The analysis indicates that the frequency factor $\omega_e' \sim T$ for $T \ll \Theta$, with Θ the Debye temperature and that the apparent activation energy of the process becomes infinite as $T \rightarrow 0$. Tunnelling has not been included in the present derivation but it appears that it should be possible to do so within the same framework.

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Electrical Conduction in *n*-Type Cadmium Sulfide at Low Temperatures*

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Measurements of the Hall mobility and electrical conductivity of *n*-type CdS were made between 1.8 and 294°K. Both Ohmic and non-Ohmic regions were studied at low temperatures. In these undoped crystals, a donor level of 0.021 eV, believed due to excess Cd, was found. Below 22°K, charge transport by impurity conduction was observed. The electric field dependence of the conduction-band mobility was found to be caused by hot-electron effects and the acoustoelectric effect. Good agreement between hot-electron theory and experiment was obtained when ionized-impurity as well as acoustic-phonon scattering were included in the theory. To obtain satisfactory agreement between theory and experiment, electron-phonon interactions via deformation and piezoelectric potentials were included. In the impurity-conduction region, variations of the Hall mobility with electric field were shown to be caused by the hot-electron behavior of the conduction-band electrons.

I. INTRODUCTION

SEVERAL investigators[1–8] have made Hall-effect measurements on *n*-type CdS at low temperatures. Their results[1–6] indicate that with decreasing temperature, the mobility increases, reaches a maximum in the neighborhood of 30°K, and then decreases rapidly. The Hall constant increases with decreasing temperature until the temperature of the mobility maximum is reached. At lower temperatures the Hall constant saturates or decreases with decreasing temperature. The rapid decrease in mobility has been interpreted as being due to either ionized-impurity scattering or impurity conduction.[9]

Measurements of the Hall effect at high electric fields[3] have shown the existence of the acoustoelectric effect which limits the drift velocity of the electrons to the sound velocity. Thus, hot-electron effects[10] are not observable. Measurements of the electric field dependence of the electrical conductivity at low temperatures

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[1] F. A. Kroger, H. J. Vink, and J. Volger, Phillips Res. Rept. **10**, 39 (1955).
[2] W. W. Piper and R. E. Halsted, in *Proceedings of the International Conference on Semiconductor Physics, 1960* (Czechoslovak Academy of Sciences, Prague, 1961), p. 1046.
[3] A. R. Moore and R. W. Smith, Phys. Rev. **138**, A1250 (1965).
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[5] B. A. Kulp, K. A. Gale, and R. G. Schulze, Phys. Rev. **140**, A252 (1965).
[6] H. Shenker, J. Phys. Chem. Solids **19**, 1 (1961).
[7] H. Fujita, K. Kobayashi, T. Kamai, and K. Shiga, J. Phys. Soc. Japan **20**, 109 (1965).
[8] M. Onuki and K. Shiga, J. Phys. Soc. Japan Suppl. **21**, 427 (1966).
[9] N. F. Mott and W. D. Twose, Advan. Phys. **10**, 107 (1961).
[10] J. B. Gunn, in *Progress in Semiconductors*, edited by A. F. Gibson and R. E. Burgess (John Wiley & Sons, Inc., New York, 1957), Vol. 2.

by Moore and Smith[3] and Shenker[6] showed non-Ohmic behavior which they attributed to impact ionization of shallow donors.

In this paper we shall discuss Hall-effect measurements on CdS as a function of electric field, between room temperature and 1.8°K. The low-temperature non-Ohmic conductivity is interpreted as being due to changes in the carrier mobility and concentration due to electron heating. The field dependence of the mobility is found to be in good agreement with theory when all the scattering mechanisms are taken into account. The non-Ohmic behavior of the Hall effect is shown to be proof of impurity conduction.

II. EQUIPMENT AND PROCEDURE

Undoped single-crystal boules were grown from the vapor phase by slow motion through a sharp temperature gradient.[11] Hall bars of standard shape, 6 mm×2 mm, were cut from 1 mm slices. Indium electrodes were ultrasonically affixed to the ends and four side arms of the crystals. These contacts were Ohmic at all temperatures. The crystals were oriented with the c axis along the direction of current flow.

Measurements were made in a glass liquid-helium Dewar. The crystal was mounted on a sapphire slab fastened to a copper sample holder containing a carbon resistance thermometer and heater. The sample holder was mounted on the end of a stainless-steel tube in an evacuable copper chamber immersed in liquid helium. Thermal contact between sample holder and chamber walls was established by means of helium exchange gas.

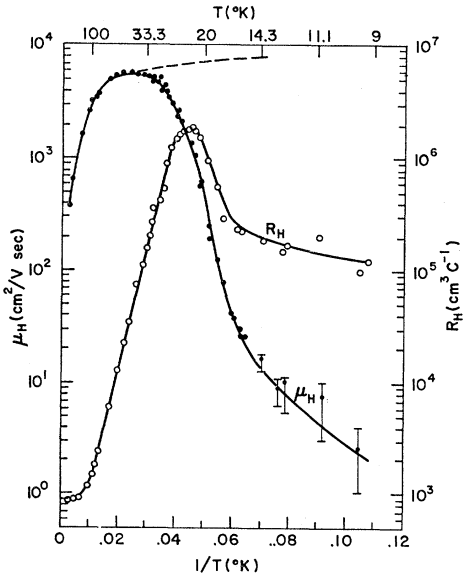

FIG. 1. The Hall mobility μ_H and the Hall constant R_H as a function of temperature in sample 1. (○) R_H; (●) μ_H; dashed line: μ_c calculated from Eq. (A1).

[11] A. Dreeben, J. Electrochem. Soc. **111**, 174 (1964).

Temperatures below 4.2°K were obtained by lowering the vapor pressure of liquid helium. Temperatures above 4.2°K were determined by the heat input from the heater and loss via the exchange gas.

The low-field Hall data were obtained by conventional dc methods using a high-impedance electrometer to measure Hall voltage, potential drop in the crystal, and current. For the high-field measurements, pulsed current techniques were used to avoid sample heating. The Hall voltage, potential drop in the crystal, and current were displayed on an oscilloscope using a differential preamplifier. The magnetic field was 700 Oe.

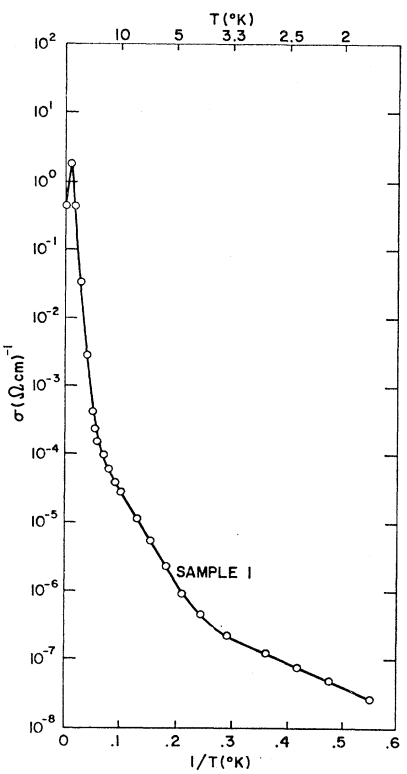

FIG. 2. The electrical conductivity σ as a function of temperature.

III. EXPERIMENTAL RESULTS

Measurements on n-type, single-crystal CdS are discussed below. Sample 1 has a room temperature carrier concentration of 6.9×10^{15} cm^{-3}.

In Fig. 1 we show the results of dc Hall-effect measurements on sample 1 between room temperature and 9.5°K. The Hall mobility μ_H increases with decreasing temperature, reaches a maximum at about 40°K, and then decreases rapidly with decreasing temperature. Below 15°K the uncertainty in the measurements increases markedly because of the small Hall signals. As we shall explain below, low electric fields should be used to avoid hot-electron effects. The Hall constant R_H increases with decreasing temperature, reaches a

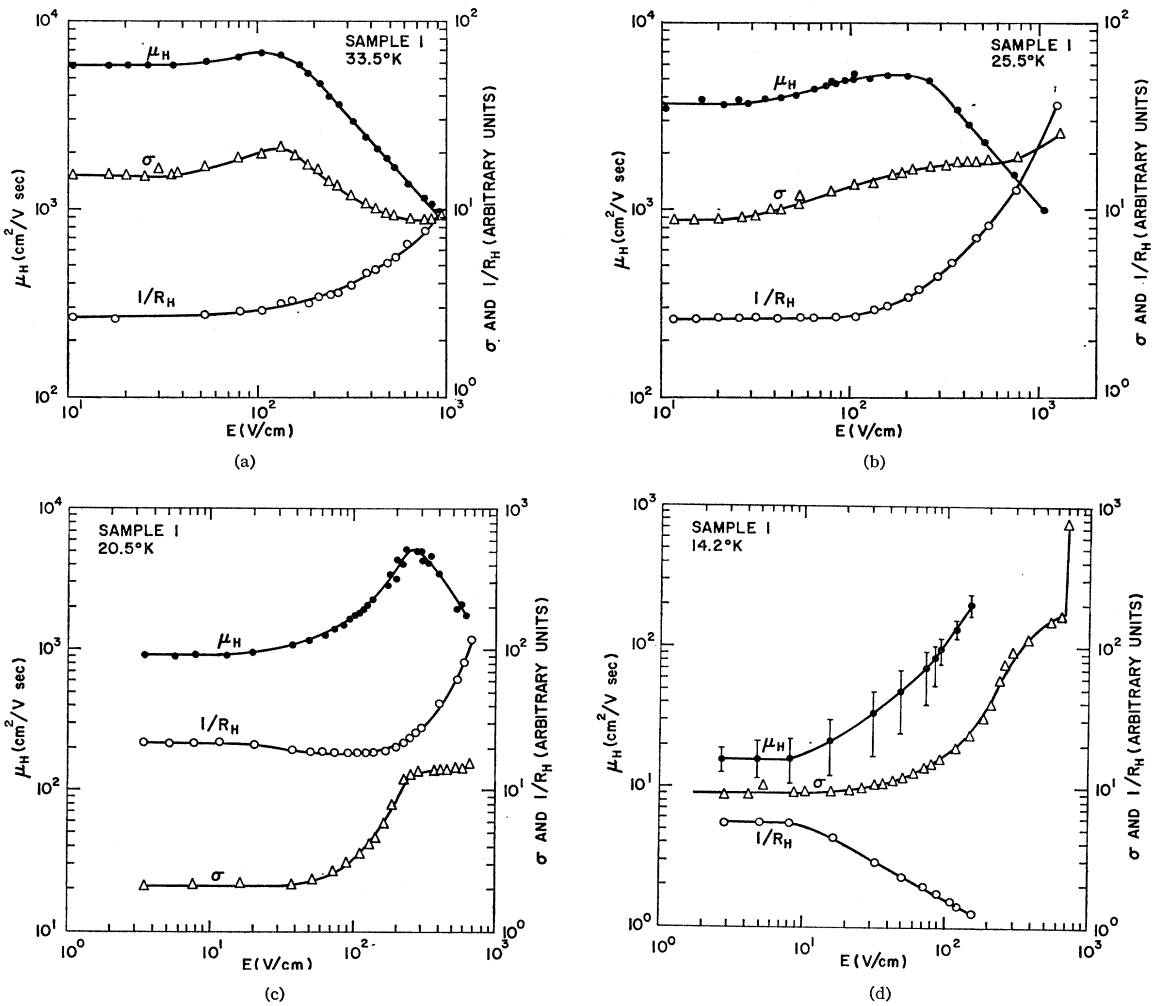

FIG. 3. (a) Hall mobility, Hall constant, and electrical conducting of sample 1 versus electric field at 33.5°K. $\mu_c(0)=5.8\times10^3$ cm²/V sec. (●) μ_H; (△) σ; (○) $1/R_H$. (b) Hall mobility, Hall constant, and electrical conductivity of sample 1 versus electric field at 25.5°K. $\mu_c(0)=7.4\times10^3$ cm²/V sec. (●) μ_H; (△) σ; (○) $1/R_H$. (c) Hall mobility, Hall constant, and electrical conductivity of sample 1 versus electric field at 20.5°K, $\mu_c(0)=8\times10^3$ cm²/V sec. (●) μ_H; (△) σ; (○) $1/R_H$. (d) Hall mobility, Hall constant, and electrical conductivity of sample 1 versus electric field at 14.2°K. $\mu_c(0)=8.3\times10^3$ cm²/V sec. (●) μ_H; (△) σ; (○) $1/R_H$.

maximum at 22°K, and decreases sharply between 22 and 16°K, below which it remains nearly constant.

In Fig. 2 we show the dc electrical conductivity σ between room temperature and 1.8°K. Below 22°K the conductivity of sample 1 can be expressed by

$$\sigma=[7.5\times10^{-4}\exp(-32/T)+2.1\times10^{-7}\times\exp(-7.9/T)](\Omega\text{ cm})^{-1}. \quad (1)$$

In other words, the conductivity is an activation energy process with activation energies of 0.0026 and 0.00066 eV.

The results of Hall-effect versus electric-field measurements on sample 1 are shown in Fig. 3(a)–(d). Direct-current measurements were made at low fields, whereas, at high fields 10–100 μsec current pulses were used to avoid heating effects. On the graphs we show σ, μ_H, and $1/R_H$ for clarity even though the relation $R_H\sigma=\mu_H$ holds. Figures 3(a) and (b) show data obtained above 22°K (the Hall-constant maximum), whereas Figs. 3(c) and (d) show data for lower temperatures. The significant features of the data are: (1) The Hall mobility increases with increasing electric field, reaches a maximum, and decreases as the reciprocal of the electric field. (2) $1/R_H$, which is proportional to the carrier density, increases with electric field indicating an increase in carrier density (as we show in the next section, the decrease in $1/R_H$ does not indicate a carrier decrease). (3) Below 21°K the Hall mobility begins to increase at a field where the conductivity is field-independent. (4) At 14.2°K and below, the current increases very rapidly above 650 V/cm. At 14.2°K, Hall-effect measurements are not reliable above 150 V/cm because of a nonuniform potential distribution in the crystal.

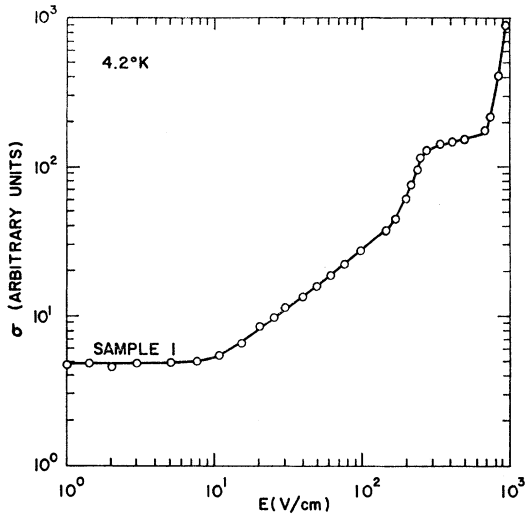

FIG. 4. Electrical conductivity versus electric field at 4.2°K.

Below 4.2°K, the Hall effect was not detected in sample 1. Therefore, the mobility is less than 0.5 cm²/V sec below 4.2°K. The conductivity versus electric field measurements at 4.2°K shown in Fig. 4 were made using pulses 0.05–100 μsec in duration. No heating effects were observed.

IV. DISCUSSION

A. Low-Field Results

Above 25°K the Hall-effect measurements have a straightforward interpretation. The temperature dependence of the Hall constant expresses the recombination of conduction-band electrons with ionized donors, presumably excess cadmium atoms.[11] If we assume there is one donor level and a single-valley conduction band, the following expression[12] can be used to determine the N_D donors, N_A acceptors, and binding energy ϵ_D of the donors:

$$\frac{n_c(n_c+N_A)}{N_D-N_A-n_c}=\left(\frac{2\pi}{h^2}m^*kT\right)^{3/2}\exp(-\epsilon_D/kT). \quad (2)$$

At high temperatures the donors are ionized and the density of conduction-band electrons n_c is equal to N_D-N_A. At lower temperature, where n_c is less than N_A, Eq. (2) was fitted to the data in Fig. 1 to determine that $\epsilon_D=0.021$ eV, $N_A=7.1\times10^{15}$ cm^{-3}, and $N_D=1.4\times10^{16}$ cm^{-3}. A value of $0.16m_0$ was used for the density of states mass[13] m^*. R_H was taken equal to $1/n_ce$. The error involved in this assumption[14] is the order of the experimental error.

[12] E. G. S. Paige, in *Progress in Semiconductors*, edited by A. F. Gibson and R. E. Burgess (John Wiley & Sons, Inc., New York, 1964), Vol. 8, p. 47.
[13] J. Zook, Phys. Rev. **136**, A869 (1964).
[14] A. Beer, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 4, p. 130.

We now show that below 26°K the above interpretation of the Hall effect is incorrect because impurity conduction is a competing mode of charge transport. Impurity conduction is electron transport between an ionized and unionized donor. A model of impurity conduction applicable to the low-donor density in this crystal is the "hopping" model of Mott and Conwell.[15] An electron makes a transition from a filled donor to an empty donor without entering the conduction band. The activation energy for this process is the decrease in the donor energy due to the repulsive Coulomb field of the acceptor located near the empty donor.

Assuming two noninteracting conduction mechanisms, we may write the conductivity, Hall mobility, and Hall constant as[9]

$$\sigma=\sigma_c+\sigma_i=e(n_c\mu_c+n_i\mu_i), \quad (3a)$$

$$\mu_H=(\mu_c{}^H\sigma_c+\mu_i{}^H\sigma_i)/\sigma, \quad (3b)$$

and

$$R_H=\mu_H/\sigma. \quad (3c)$$

The conduction-band conductivity is σ_c, the conduction-band conductivity mobility is μ_c, and the conduction-band Hall mobility is $\mu_c{}^H$; similar symbols apply to the impurity-conduction mechanism. In this crystal, conduction by conduction-band electrons dominates above 26°K. Thus, the Hall effect measures parameters of the conduction-band electrons above 26°K.

If we neglect the variation with temperature of the mobilities, the Hall-constant maximum occurs when $\sigma_i=\sigma_c$. Since the donors are nearly deionized, $n_i=N_D-N_A$. Thus, we may estimate the impurity-conduction mobility at the temperature of the Hall-constant maximum: μ_i (22°K)=1 cm²/V sec. Because n_i is larger than n_c, the conduction-band mobility is larger than the impurity-conduction mobility. Thus, $\mu_c{}^H\sigma_c\gg\mu_i{}^H\sigma_i$. Therefore the Hall mobility above about 10°K can be approximated by

$$\mu_H\cong\mu_c{}^H(\sigma_c/\sigma). \quad (3d)$$

From expression (3d) we see that the measured Hall mobility is less than or equal to the conduction-band Hall mobility. Thus, in the domain of impurity conduction where $\sigma>\sigma_c$, the conduction-band mobility can not be determined. We can, however, use the calculated value of the conduction-band mobility as a guide to what we would expect in the absence of impurity conduction. The dotted line in Fig. 1 is μ_c calculated from Eq. (A1) of the Appendix with $P_c=0$. In calculating μ_c we used the following zero-field-mobility values:

$$\mu^D(0)=8.7\times10^4(33.5/T)^{3/2}\text{ cm}^2/\text{V sec} \quad (4a)$$

and

$$\mu_c{}^P(0)=1.6\times10^4(33.5/T)^{1/2}\text{ cm}^2/\text{V sec}. \quad (4b)$$

[15] N. F. Mott, Progr. Metal. Phys. **3**, 76 (1956); E. M. Conwell Phys. Rev. **103**, 51 (1956).

The mobility due to acoustic-phonon scattering via the deformation potential[16] is $\mu^D(0)$; via the piezoelectric potential[13] $\mu_c{}^P(0)$. The choice of these magnitudes is explained in a later section of this paper. The ionized-impurity-scattering mobility is given by the Conwell-Weisskopf expression,[17] with 7×10^{15} cm^{-3} scatterers, an effective mass m^* of $0.16m_0$, and a dielectric constant of 11.[1] At these low temperatures, optical-phonon scattering does not contribute to the low-field mobility.[7,8] Two effects cause the calculated mobility to increase slightly with decreasing temperature. The lattice mobility, Eqs. (4a) and (4b), increases with decreasing temperature. The logarithmic term, Eq. (A4), weakens the temperature dependence of ionized-impurity scattering.

Below 22°K the conductivity is due to impurity conduction whose temperature dependence is shown in Fig. 2. The temperature-dependence of the conduction-band conductivity is much the same as above 22°K. Since the conduction-band mobility increases with decreasing temperature, the strong temperature dependence of σ_c is caused by donor deionization. σ_c decreases faster than does σ below 22°K; therefore, the Hall mobility Eq. (3d) decreases rapidly with decreasing temperature.

We expect the Hall mobility and Hall constant to decrease with decreasing temperature until $\mu_c{}^H\sigma_c \simeq \mu_i{}^H\sigma_i$. At this temperature and below the Hall effect measures the parameters of the impurity-conduction mechanism. In Fig. 1 the Hall constant has little temperature dependence below 15°K. Our results are similar to those found in n-type germanium.[9,18,19] In the so-called "intermediate concentration range"[19] there are two activation energies associated with impurity conduction. The lower energy ϵ_3 is associated with hopping conduction. The role of the higher activation energy ϵ_2 is uncertain at present. We may thus ascribe the ϵ_2 activation energy to the conduction between 22 and 3°K in CdS. Below 3°K impurity conduction is presumably via the hopping mode.

B. High Field Results

Because of the high conduction-band mobility in CdS at low temperatures,[7,8] it is possible to observe non-Ohmic transport at moderate electric fields. Since the free-electron density is small, the acoustoelectric effect should not preclude non-Ohmic transport due to hot-electron effects. Hot-electron effects are normally observed when the drift velocity exceeds the sound velocity.[10] If the electron drift velocity is less than the velocity of sound, the fractional increase in electron energy is very small; the order of the square of the ratio of drift to sound velocity.[10] When the drift velocity exceeds the sound velocity the average energy increases rapidly with electric field. For most scattering mechanisms the mobility depends on electron energy. Thus, when the average energy increases, the mobility changes.

At the temperatures of interest in this experiment, the important scattering mechanisms and the energy dependence of their relaxation times are: (1) Ionized impurity,[17] $\tau_I \propto \epsilon^{3/2}/L(\epsilon)$; $L(\epsilon)$ is defined in Eq. (A4); (2) acoustic phonons interacting via the deformation potential,[16] $\tau_D \propto \epsilon^{-1/2}$; (3) acoustic phonons interacting via the piezoelectric potential,[13] $\tau_{pp} \propto \epsilon^{1/2}$. The mobility relaxation is due to these three mechanisms, whereas energy loss is to acoustic phonons. Three other electron energy loss mechanisms which can be important under special circumstances are: (1) Electrons with an energy of 0.037 eV[7] can emit polar optical phonons.[10] (2) At electron densities greater than about 5×10^{12} cm^{-3},[20] acoustoelectric saturation[3] retards electron heating. If the electron drift velocity is greater than the sound velocity, most of the energy supplied to the electrons is used for sound wave amplification. (3) Because there are deionized donors located at 0.021 eV, these can be impact ionized by high-energy conduction-band electrons.[21]

A complication in the interpretation of hot-electron processes is impurity conduction which tends to mask the non-Ohmic transport in the conduction band. The mobility in the impurity conduction mode is too low for impurity conduction hot-electron effects to occur at the low fields in these experiments.

The electric field dependence of the Hall effect at 33.5°K is shown in Fig. 3(a). At this temperature there is an insignificant contribution from impurity conduction. Ionized impurities and acoustic phonons interacting via the deformation potential contribute about equally to electron scattering. The strength of both these scattering mechanisms decreases as the electron energy increases. Thus, the mobility will increase with increasing electric field. There is significant electron heating when the electron drift velocity is of the order of sound velocity.[10] The average sound velocity in CdS is about 3×10^5 cm/sec. Thus, for a mobility of 5800 cm^2/V sec, the drift velocity is equal to the sound velocity at an electric field of 53 V/cm. As we see in Fig. 3(a) the mobility has increased at this field.

The strength of the deformation potential interaction between electrons and acoustic phonons increases whereas the piezoelectric potential interaction and the interaction with ionized impurities decreases as the electron energy increases. As the electric field increases electron heating, more electrons are concentrated in the high-energy tail of the electron distribution. Thus, there will be a stronger interaction via the deformation

[16] Reference 12, p. 67.
[17] Reference 12, p. 75; E. M. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950).
[18] Reference 12, p. 147.
[19] E. A. Davis and W. D. Compton, Phys. Rev. **140**, A2183 (1965).
[20] A. R. Moore (private communication).
[21] S. H. Koenig, R. D. Brown, III, and W. Schillinger, Phys. Rev. **128**, 1668 (1962).

potential. When the current is mainly due to these high-energy electrons, the mobility will decrease with increasing electric field. The deformation-potential interaction, however, does not dominate the current until the electron energy is greater than an optical-phonon energy. But electrons of this energy will emit optical phonons at a much faster rate than acoustic phonons. Thus, the optical-phonon interaction, not the deformation-potential interaction determines the current for these high-energy electrons. This strong optical-phonon scattering limits the increase in mobility with increasing electric field and can even cause a saturation of the drift velocity.[10] The observation of this effect is complicated by the onset of acoustoelectric saturation[3] at roughly the same field that the optical phonon becomes important. The decrease of the mobility with increasing electric field in Fig. 3(a) is caused by acoustoelectric saturation.[3]

The drift velocity saturates at 1×10^6 cm/sec. This result is to be compared with the room-temperature acoustoelectric saturation[3] at the sound velocity. The electron-trapping effect noted by Moore and Smith[3] is probably responsible for the higher-saturation velocity at low temperature.

The increase in $1/R_H$ above about 150 V/cm at 33.5°K shows that the conduction-band density increases during acoustoelectric saturation. One does not usually think of carrier heating during acoustoelectric saturation because the electric field energy goes into sound wave amplification. Moore and Smith[3,20] have interpreted the carrier increase during acoustoelectric saturation at low temperatures to be caused by impact ionization of filled donors. This ionization is due to the few electrons that do not take part in sound wave amplification.[22] We should also remark that the electric field is highest at the anode during acoustoelectric saturation.[23] The electric field mentioned in this paper is the average field over a 2-mm region in the middle of the crystal. Electric-field-distribution measurements, however, during acoustoelectric saturation[20,23] show that the electric field is uniform in the center of the crystal.

At 25.5°K [Fig. 3(b)] there is an impurity-conduction contribution to the Hall effect because the mobility is lower than the calculated value of 7400 cm²/V sec. The qualitative discussion of the field dependence of the Hall effect at 25.5°K is the same as that given above for 33.5°K. The conductivity does not decrease with increasing field during acoustoelectric saturation because of the conduction-band density increase.

At 20.5°K and below impurity conduction dominates the conductivity, thus complicating the interpretation of the Hall effect. Figures 3(c) and (d) show positive evidence for impurity conduction; namely the Hall mobility begins to increase at a lower field than where the conductivity begins to increase. This result is expected because the current is carried by impurity conduction, whereas the conduction-band electrons determine the Hall effect. We expect Ohmic behavior in impurity conduction at these moderate fields; thus, the conductivity will not change until the conduction-band conductivity has increased to the same order of magnitude as the impurity conductivity. Since $\mu_H=\mu_c{}^H\sigma_c/\sigma$, the Hall mobility changes as soon as the conduction-band mobility becomes field-dependent. This effect is made graphic by the initial decrease in $1/R_H=\sigma/\mu_H$.

Below 21°K the mobility and conductivity both increase before the drift velocity saturates. We do not expect drift-velocity saturation at the conduction-band density of 4×10^{11} cm^{-3} at 20.5°K, because this density is below the minimum for the observation of the acoustoelectric effect.[20] Nevertheless, when the electron density has increased sufficiently, the acoustoelectric effect can be observed.

We expect the field dependence of the Hall mobility at 14.2°K to be qualitatively the same as at 20.5°K. Therefore, we give the same interpretation of the transport at 14.2°K as at 20.5°K. Above 650 V/cm the rapid increase of the free-electron density could be due to the same process that causes the carrier increase at low fields. An alternative explanation for the rapid carrier increase would be field-assisted tunneling from a donor to the conduction band.[24] The average electric field is too low for this process.[24] However, the high field at the anode or the piezoelectric field accompanying the sound wave could produce tunneling.

At low temperatures the rate of increase of conduction-band electrons during the acoustoelectric effect is greater than at 33.5°K. The low-electron concentration at these temperatures decreases the strength of the acoustoelectric interaction resulting in less reduction of electric heating. Therefore, the rate of impact-ionization and/or change in electron-donor recombination probability[21] is enhanced.

The conductivity versus field curve shown in Fig. 4 for sample 1 at 4.2°K is similar to the 14.2°K curve and is given the same interpretation.

V. COMPARISON OF THEORY TO EXPERIMENT

For a better understanding of the experimental results, we shall apply a quantitative theory of hot-electron effects.[25] In the Appendix we show the results of a calculation of the conduction-band mobility. Electron scattering by acoustic phonons and ionized impurities is included in the calculation. We can use the theoretical mobility values in conjunction with our Hall-effect data to determine the field dependence of

[22] A. R. Moore, J. Appl. Phys. **38**, 2327 (1967).
[23] A. Many and I. Balberg, J. Phys. Soc. Japan Suppl. **21**, 474 (1966).
[24] A. G. Chynoweth, in *Progress in Semiconductors*, edited by A. F. Gibson and R. E. Burgess (John Wiley & Sons, Inc., New York), Vol. 4, p. 100.
[25] R. S. Crandall, following paper, Phys. Rev. **169**, 585 (1968).

the conduction-band density in the region of impurity conduction.

In Fig. 5 we plot the product of the Hall mobility and the conductivity versus electric field. This figure represents a replotting of the data in Figs. 3(a)–3(d). Because of arguments given earlier, $\mu_H \approx e\mu_c^2 n_c/\sigma$. The curves in the figure are $\mu_c^2(E)$ determined from Eq. (A1). The solid line represents inclusion of an ionized-impurity density equal to the acceptor density; the dashed line represents no ionized impurities. The theoretical curves are normalized to the low-field data because impurity conduction precludes absolute mobility determinations. The calculated conduction-band mobility at zero field is shown by the dashed line in Fig. 1.

Because impurity conduction is not observed at 33.5°K, the measured Hall mobility is that of the conduction band. We can therefore fit the calculated mobility, Eq. (A1), to the Hall data to determine the ionized-impurity-scattering mobility and the lattice-scattering mobility. The lattice-scattering mobility parameters determined in this manner are given by Eqs. (4a) and (4b). The theoretical curve is not shown above 85 V/cm. At this field, electrons with an energy greater than that of a longitudinal optical phonon contribute 5% to the calculated current. At higher fields the contribution is much higher. This point is discussed in more detail in the following paper.[25] Because we have not included the optical phonon interaction in the theory, we can not trust the calculation in this high-field region. The theory is also inapplicable above 100 V/cm because of the acoustoelectric effect. Nevertheless, the region of applicability is sufficient to determine $\mu_c^P(0)$ within 50%. The value of the piezoelectric-scattering mobility $\mu_c^P(0)$ is the same as that measured by Onuki and Shiga.[8] The value of the deformation-potential-scattering mobility $\mu^D(0)$ is a factor of 2 higher than that found by the above authors. We should remark that we cannot determine the value of $\mu^D(0)$ within a factor of 2. This quantity is most accurately determined in the region where the mobility begins to decrease with increasing electric field. In our experiment, however, the effects not included in the calculation dominate in this region. At lower temperatures, where impurity conduction precludes determination of the absolute value of the conduction-band mobility, we see from Fig. 5 that the calculated mobility values are at least consistent with experiment.

For the temperatures below 33°K we show the calculated curves up to the electric field E_c where electrons with energies below an optical-phonon energy contribute over 90% to the calculated current. We expect optical-phonon emission to limit any further increase in the mobility due to the reduction of ionized-impurity scattering at high fields. Thus we expect that the actual mobility will not increase much at fields above E_c. If we believe this interpretation, then the increase

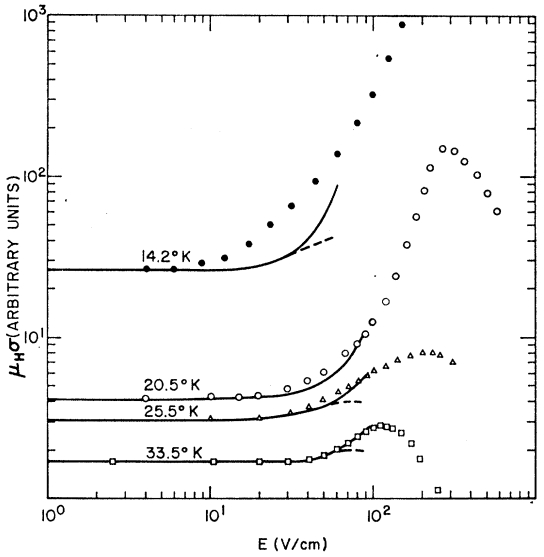

FIG. 5. The product $\mu_H\sigma \cong \mu_c^2 n_c e$ versus electric field. The data at different temperatures are not on the same scale. The solid lines are $\mu_c^2(E)$ calculated from Eq. (A1) including ionized-impurity scattering. The dotted lines are $\mu_c^2(E)$ excluding ionized-impurity scattering. (●) 14.2°K; (○) 20.5°K; (△) 25.5°K; (□) 33.5°K.

in $\mu_H\sigma$ above 90 V/cm at 20.5°K is caused mainly by a conduction-band electron-density increase. This increase can be caused by an increase in the electron-ionized donor-recombination probability,[21] or by impact ionization of the filled donors. We have no way of telling which process dominates. Since the theory[25] shows a few electrons above 0.021 eV, the donor-binding energy, impact ionization is likely. The bend-over in the 20.5°K $\mu_H\sigma$ curve above 250 V/cm is presumably caused by the acoustoelectric effect. At 14.2°K the $\mu_H\sigma$ curve lies above the calculated curve; thus there is an indication of a carrier-density increase above 10 V/cm. However, the experimental error in the determination of μ_H is large at this temperature. The theoretical and experimental curves are the same within experimental error.

There is little agreement between theory and experiment if ionized-impurity scattering is omitted, as can be observed by comparing the dashed lines (lattice scattering) and solid lines (impurity- and lattice-scattering) in Fig. 5. The dashed lines are shown only in the region where the optical-phonon interaction can be ignored. We have normalized both curves to the zero field mobility (the mobility including ionized-impurity scattering is lower than the lattice-scattering mobility). This decrease in the mobility due to impurity scattering is why the mobility (solid line) increases more in the high-field region than does the lattice-scattering mobility. The ionized-impurity-scattering mobility increases with increasing field until it equals the lattice-scattering mobility, then the two mobilities are the

same. In other words, impurity scattering is absent at high fields.

VI. SUMMARY

We have shown that electron conduction below 22°K in semiconducting CdS is due to impurity conduction. The electron donors are responsible for the impurity conduction. Conduction-band mobility and carrier-density variations were shown to cause non-Ohmic electron transport. In the impurity-conduction regime the absolute value of the conduction-band mobility can not be determined from low electric-field Hall-effect measurements. The use of hot-electron theory to interpret the electric field dependence of the Hall effect, however, permits a determination of the conduction-band mobility in the impurity-conduction regime. Acoustic-phonon and ionized-impurity scattering were shown to determine the electron mobility at low temperatures.

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APPENDIX

In another paper[25] we have obtained a solution of the Boltzmann transport. We consider that electrons interact with acoustic phonons via the deformation and piezoelectric potentials. The elastic-scattering mechanism is ionized impurities. When the piezoelectric-scattering anisotropy[13] is included, the electron mobility obtains the following form:

$$\mu_c(E)=\left(\int_0^\infty \frac{dZ\,Z^2(aZ+1)f(Z)}{(aZ+1)(a_cZ+1+b_c/Z)+P_c^2Z}\right)\times(kT)^{3/2}\frac{(1/2)!}{\hbar^3(2\pi)^5}(2m)^{3/2}\mu_c^P(0)\,, \quad \text{(A1)}$$

where

$$f(\epsilon)=N\exp\left(-\int_0^{\epsilon/kT}\frac{dZ(aZ+1)(a_cZ+1+b_c/Z)}{(aZ+1)(a_cZ+1+b_c/Z)+P_c^2Z}\right) \quad \text{(A2)}$$

is the symmetric part of the electron distribution function. The normalization constant N is defined by

$$\int_0^\infty f(\epsilon)\epsilon^{1/2}d\epsilon=2\pi^2\hbar^3/(2m)^{3/2}. \quad \text{(A3)}$$

The remaining parameters are

$$Z=\epsilon/kT\,,\quad a=0.79[\mu_c^P(0)/\mu_D(0)]\,,$$
$$a_c=0.63a\,,\quad b_c=(3\mu_c^P(0)/\mu_e(0))(L(\epsilon)/L(3kT))\,,$$

and

$$P_c^2=0.67(E_c\mu_c^P(0)/S_c)^2.$$

$\mu_e(0)$ is the zero-field ionized-impurity-scattering mobility, E_c is the electric field, S_c is the longitudinal sound velocity,[13] $L(\epsilon)$ is the Conwell-Weisskopf factor,[17] given by

$$L(\epsilon)=\ln[1+K^2\epsilon^2/(ZeN_I^{1/3})^2], \quad \text{(A4)}$$

where N_I is the impurity density, Ze the charge on the impurity, and K the dielectric constant. We use the Conwell-Weisskopf expression because the Brooks-Herring factor[26] is unrealistic for the low-carrier densities in these experiments.[27] The zero-field mobilities $\mu_c^P(0)$ and $\mu^D(0)$ refer to scattering by acoustic phonons interacting via the piezoelectric and the deformation potential, respectively.

[26] Reference 12, Eq. (115a).
[27] Reference 12, p. 83.