Magnetoresistance in Degenerate CdS: Localized Magnetic Moments*

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The magnetoresistance of CdS samples doped with In has been measured. The samples had electron concentrations between 8.3×10^{17} and $1.2\times10^{19}\,\mathrm{cm}^{-3}$. The data up to 8 kG were taken over a wide range of temperatures; however, the temperature was limited to the liquid-helium range for fields between 8 and 150 kG. It was found that the observed magnetoresistance is negative to much higher temperatures and fields than has been reported for any other semiconductor. The data are analyzed as the sum of a negative and a positive component. Although qualitative features of the negative component at low fields are consistent with the localized-magnetic-moment model of Toyozawa, we found that there exist quantitative disagreements with the calculations using the second-order perturbation expansion of the s-d exchange Hamiltonian. Some evidence for inclusion of higher-order terms is provided by the logarithmic temperature dependence of the resistivity at zero field. The positive component, because of the magnetic field dependence of the Hall coefficient, is interpreted in terms of the magnetic freeze-out. A semiempirical expression, $\Delta\rho/\rho_0 = -B_1\ln(1+B_2^2H^2) + B_3^2H^2/(1+B_4^2H^2)$, is suggested to describe the behavior of the observed magnetoresistance. Least-squares fits to this expression are provided along with the consistent and reasonable values of the calculated negative and the positive components.

I. INTRODUCTION

In semiconductors, as the density of impurity atoms becomes high, a transition from a nonmetallic to a metallic state occurs, and the resistivity (ρ_0) and the Hall coefficient (R_H) become relatively temperature independent. This transition occurs as a result of delocalization due to the overlapping of impurity electron wave functions ("impurity banding") and is observed to occur at a concentration where the mean interatomic distance is about four times the effective Bohr radius. This is in good agreement with a theoretical estimate by Mott[1] and has been referred to as the "Mott transition." Alexander and Holcomb[2] have given a synthesis of the most significant features of the semiconductor-to-metal transition in n-type group-IV materials. They also discuss evidence of a second transition associated with the entry of the Fermi level into the conduction band. The critical concentration for this transition has been estimated to be $5.1(n_c)_{\mathrm{Mott}}$.[2]

It is found that semiconductors in this region of metallic impurity conduction exhibit an anomalous negative magnetoresistance at low fields. Negative magnetoresistance was first observed by Sasaki and Ouboter[3] in heavily doped n-Ge. Many n-type semiconductors have since been investigated.[4-15] Besides being observed in the degenerate semiconductors, negative magnetoresistance has also been reported in the transition (or the intermediate) region of impurity conduction.[8,11]

In these semiconductors the experimentally observed magnetoresistance is generally negative at low fields, then passes through a minimum, and becomes positive at higher fields owing to the admixture of stronger positive components. In general, the lower the carrier concentration or temperature, the lower the field required for this change in sign of magnetoresistance. At the very highest concentrations there is little or no positive contribution and the magnetoresistance remains negative to the highest fields.

In the present work we report the results of magnetoresistance measurements on n-type CdS samples doped with In, with electron concentrations between 8.3×10^{17} and $1.2\times10^{19}\ \mathrm{cm}^{-3}$ (at room temperature). At low fields (up to 8 kG), the measurements have been made over a wide range of temperatures, whereas at high fields (8 to 150 kG), the measurements were made between 1.3 and 4.3 °K. After presenting our results, we shall discuss the various methods by which the negative magnetoresistance has been analyzed. The ambiguities in extracting the true negative component imposed by the mixing of insufficiently characterized positive components at high fields will be discussed.

Our results for CdS, like those obtained for other degenerate semiconductors, have the same qualitative features as suggested by Toyozawa[16] in his localized-magnetic-moment model. However, quantitative agreement is lacking both in terms of his theory and with respect to calculations made by Yosida[17] on the basis of a similar model for Cu-Mn alloys. Evidence will be presented suggesting the necessity of extension of the calculations based on the model of localized magnetic moments. A new semiempirical expression, and its possible relationship to the available calculations to third order in the s-d exchange interaction, will be given.

TABLE I. Resistivity (ρ) and mobility (μ_H) of the CdS samples at 300 and 4.3 °K. Carrier concentration (n) at 300 °K is also given.

	$n=1/R_He$	ρ		μ_H	
	(10^{18} cm^{-3})	(Ω cm)		(cm^2 V^{-1} sec^{-1})	
Sample [a]	300 °K	300 °K	4.3 °K	300 °K	4.3 °K
8.3 – 17	0.83	0.0281	0.5050	268	22
9.9 – 17	0.99	0.0242	0.1100	258	72
1.6 – 18	1.6	0.0155	0.0270	252	145
1.9 – 18	1.9	0.0143	0.0220	230	149
2.7 – 18	2.7	0.0106	0.0150	219	155
3.0 – 18	3.0	0.0095	0.0116	218	179
3.5 – 18	3.5	0.0083	0.0096	215	186
4.6 – 18	4.6	0.0062	0.0066	220	206
5.0 – 18	5.0	0.0060	0.0065	208	197
1.2 – 19	12.0	0.0030	0.0030	172	174

[a]Sample numbers give the values of carrier concentration at room temperature, e.g., $8.3-17 \equiv 8.3\times10^{17}$ cm^{-3}, etc.

II. EXPERIMENTAL DETAILS

Single crystals of ultrahigh-purity-grade CdS doped with In were obtained from Eagle-Picher Co. The samples were cut ultrasonically into spider shapes with dimensions approximately 10 $\times 2\times 2$ mm^3 with two symmetrically placed sets of side contacts. Electrical leads were attached either by direct ultrasonic soldering with Cerroseal -35 solder or by mounting on a specially prepared glass slide, the details of which have been discussed by Khosla.[18] Standard four-probe dc potentiometric measurements were made using a Keithley 148 nanovoltmeter. A Keithley 260-nV source was used to apply a bucking potential. A programmed constant current was employed using a Kepco power supply. Low-field measurements were obtained with a 6-in. Varian electromagnet. For data up to 150 kG, measurements were made at the Francis Bitter National Magnet Laboratory. Using an x-y recorder and the field sweep, direct plots of $\Delta\rho$ versus H were obtained.

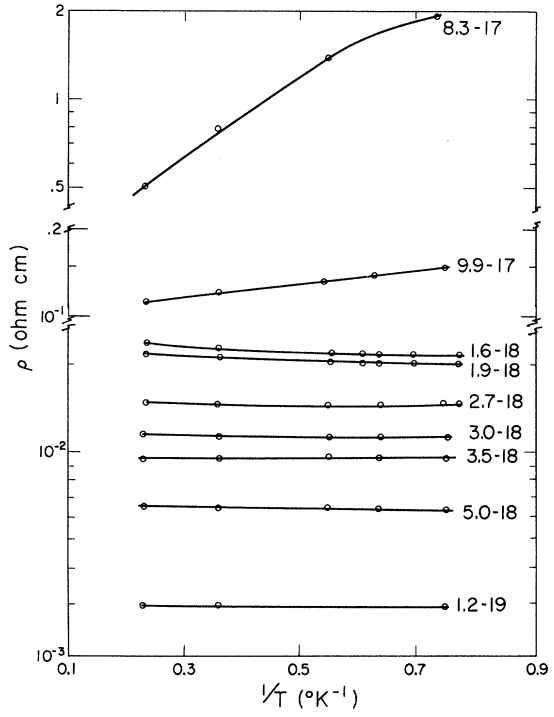

FIG. 1. Resistivity versus $1/T$. (Sample numbers represent the room-temperature carrier concentration, e.g., $8.3-17 \equiv 8.3\times10^{17}$ cm^{-3}, etc.)

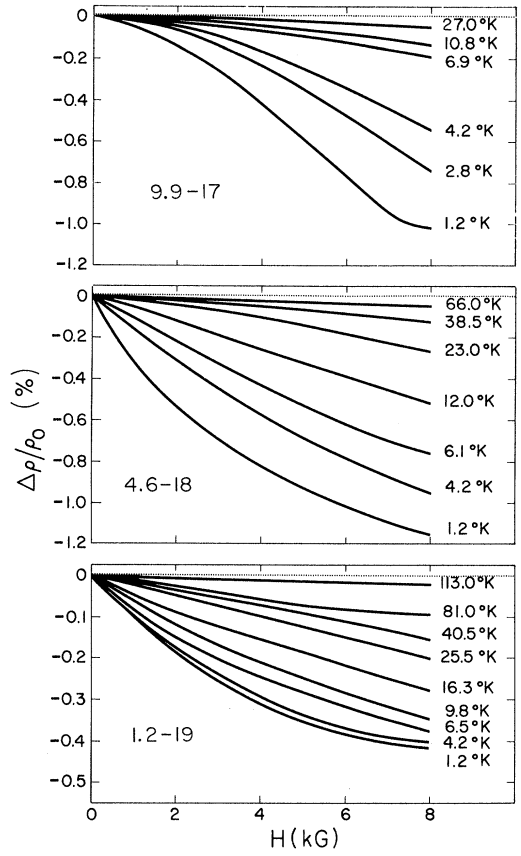

FIG. 2. Low-field magnetoresistance versus magnetic field at various temperatures ($H\perp I$).

III. RESULTS

Table I gives the values of resistivity and Hall mobility at 300 and 4.3 °K for the various samples used in our study. The carrier concentrations obtained from Hall-coefficient measurements at room temperature are also given. Figure 1 shows the resistivity versus $1/T$ at low temperatures. For samples 8.3-17 and 9.9-18, the resistivity in-

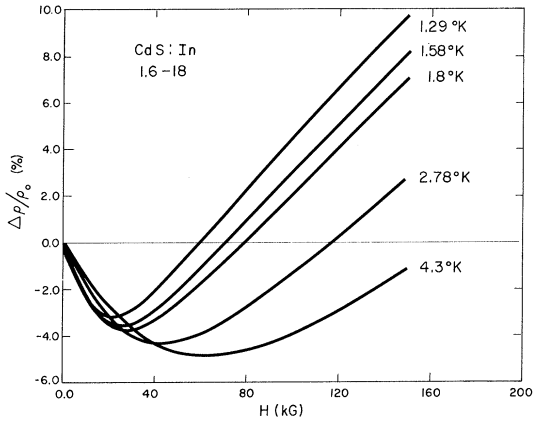

FIG. 3. Magnetoresistance versus magnetic field for sample 1.6 – 18 at the temperatures indicated ($H \perp I$).

creases with decreasing temperature, whereas ρ is nearly independent of temperature for the remaining samples. (The slight decrease in the resistivity with decreasing T in samples 1.6-18 to 4.6-18 will be discussed in Sec. IV D.) In CdS, the Mott criterion[1] and our measurements indicate the critical carrier concentration for delocalization at approximately 1.0×10^{18} cm^{-3}. This suggests that samples 8.3-17 and 9.9-17 are below the "Mott transition." Samples 5.0-18 and 1.2-19, for which the resistivity is independent of temperature, may be classified as above the second transition where the impurity band merges with the conduction band ($\geq 5\times10^{18}$ cm^{-3} in CdS).

In Fig. 2, representative results of the transverse magnetoresistance measurements to 8 kG for three of the samples are shown as a function of temperature. In another paper,[19] we have shown that the maximum temperature to which the negative magnetoresistance is observable is approximately equal to the impurity band transition temperature, and have discussed the relevance of this observation to the local moment model. The field dependence

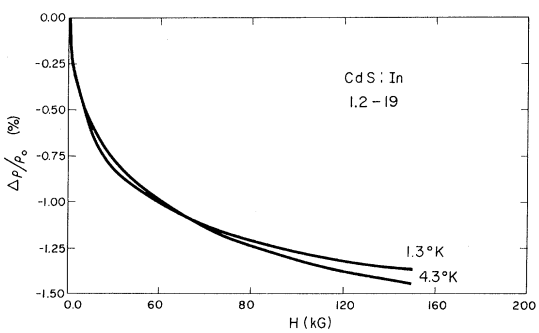

FIG. 4. Magnetoresistance versus magnetic field for sample 1.2 – 19 at 1.31 and 4.3 °K ($H \perp I$).

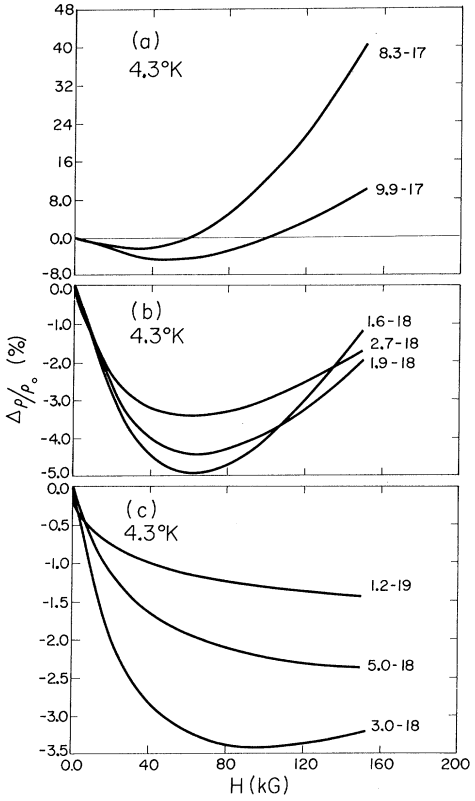

FIG. 5. Magnetoresistance versus magnetic field for various samples at $\approx$4.3 °K. Note the change of scales for $\Delta\rho/\rho_0$ in (a), (b), and (c). A systematic concentration dependence is evident ($H \perp I$).

of the $\Delta\rho/\rho_0$ versus H curves in Fig. 2 will be taken up later. The transverse magnetoresistance for sample 1.6-18 up to 150 kG at various temperatures is shown in Fig. 3, and is characteristic of those samples having strong positive components. The field at which the magnetoresistance changes sign can be related to the temperature by an expression of the form $H/T \approx$ const. At higher concentrations the magnitude of the positive magnetoresistance decreases and $\Delta\rho/\rho_0$ remains negative to much higher fields. At very high concentration the magnetoresistance is negative to 150 kG at all temperatures. This is demonstrated in Fig. 4 for sample 1.2-19. In Figs. 5 and 6 the transverse magnetoresistance data for various samples are plotted versus magnetic field at 4.3 and 1.3 °K. The data have been divided into three concentration ranges, (a), (b), and (c), merely for the sake of clarity. These figures clearly show the systematic concentration dependence at a particular temperature.

The most noteworthy feature of the present data is that the magnetoresistance is negative to much higher fields than observed in any other semicon-

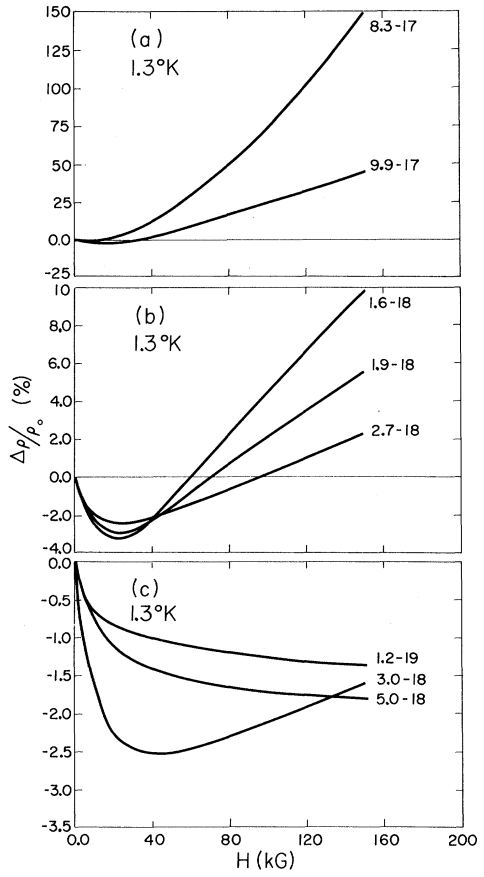

FIG. 6. Magnetoresistance versus magnetic field for various samples at ≈ 1.3 °K. Note the change of scales for $\Delta\rho/\rho_0$ in (a), (b), and (c). A systematic concentration dependence is evident ($H \perp I$).

ductor, and for very high-concentration samples it is negative to 150 kG at all temperatures. Also, the low-field data of Fig. 2 show a finite negative magnetoresistance to much higher temperatures than previously reported.

IV. ANALYSIS AND DISCUSSION

A. Background

The phenomenon of negative magnetoresistance was first believed to be due to inhomogeneities and dislocations[20] in the material. This possibility has been ruled out because (i) the phenomenon is observed in homogeneous samples, (ii) it is independent of the surface treatment or the dimensions of the sample, (iii) the magnitude of the effect is quite reproducible in samples from different sources, and (iv) there is a systematic dependence on the carrier concentration and temperature.

In 1960, Toyozawa[21] proposed a theory of negative magnetoresistance. He suggested that the impurity band may consist of several subbands originating from excited and ground states of the delocalized electrons, and that the mobility of the excited-state subbands would be larger than that for the ground state because of the larger extent of the excited-state wave function. Thus, it was postulated that the observed negative magnetoresistance might result from a transfer of electrons to the higher-mobility bands owing to the relative shift of excited-state energy levels due to the linear Zeeman effect. However, it is not clear how the Zeeman energy at low fields, which is very small compared to the energy difference between primary quantum levels, could significantly enhance the transfer of carriers. No qualitative predictions as to the concentration and temperature dependencies were put forth. Furthermore, detailed knowledge of each sub-impurity-band and the effect of the random distribution of impurities is necessary, thus making this an intractable if not improbable model.

Toyozawa[16] subsequently proposed the model accepted at present based on the existence of localized magnetic moments by noting the similarities between the observed negative magnetoresistance in semiconductors and dilute alloys such as Cu-Mn.[17] He suggested that because of statistical fluctuations in donor density and correlation effects, some electrons could be localized at the donor sites giving rise to a localized magnetic moment similar to that of the Mn ions in the Cu-Mn alloy system.

This concept provides good qualitative agreement with the observed concentration and temperature dependence of the negative magnetoresistance[19]: (i) It decreases as the carrier concentration increases and (ii) it increases as the temperature decreases. However, many quantitative expectations, particularly regarding field dependence, are not borne out in experiments. It is to these problems that we will address ourselves here.

B. Negative Component

For magnetic scattering of conduction electrons from localized magnetic moments, Yosida[17] showed theoretically that second-order perturbation calculations yield a decrease in resistivity proportional to the square of the magnetization M of the magnetic ions in a weak field, i.e.,

$$\Delta\rho/\rho_0 \propto -M^2 . \tag{1}$$

Applying this result to the analogous situation in semiconductors, Toyozawa[16] defined the magnetoresistance coefficient S by the relation

$$S \equiv \lim\ (\Delta\rho/\rho_0 H^2) \text{ as } H \to 0. \tag{2}$$

This quantity is thus proportional to the square of the magnetic susceptibility of the local moments. By plotting $(-S)^{-1/2}$ versus temperature, Toyozawa,[16] using the data of Sasaki *et al.*[4] on n-Ge, showed that this "susceptibility" obeyed a Curie-

Weiss law with a negative Curie temperature, i.e.,

$$(-S)^{1/2} = C/(T-\theta) \ . \qquad (3)$$

Such behavior is considered consistent with the local-moment picture with the moments (localized electron spins) having a weak antiferromagnetic exchange interaction. This analysis, employed in detail by Sasaki[9] for n-Ge and perpetuated by later investigators,[10–13] provided the first, and to our knowledge, the only substantial quantitative agreement with the predictions of Eq. (1).

If $\Delta\rho/\rho_0$ is proportional to M^2, then at very low fields the negative magnetoresistance should be $\propto H^2$, and it is only in this region that the foregoing analysis is valid. Our present data show that *only* in this extremely weak-field region can the second-order theory be quantitatively validated. Moreover, there is inherent in Eq. (1) a saturation property which is inconsistent with experimental observations and analyses.

The magnetoresistance of CdS samples up to 8 kG (see Fig. 2) show that $\Delta\rho/\rho_0 \propto H^n$, where n is always less than 2 and is concentration and temperature dependent. Similar results were obtained by Roth *et al.*[6] and Khosla[12] in fitting their magnetoresistance data on n-Ge and n-Si up to 20 kG and

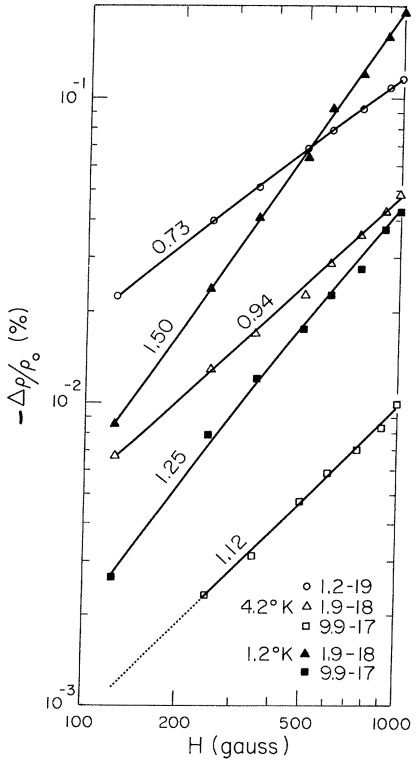

FIG. 7. Negative magnetoresistance versus magnetic field between 125–1000 G to show that $\Delta\rho/\rho_0 \propto H^n$, where $n < 2$ $(H \perp I)$.

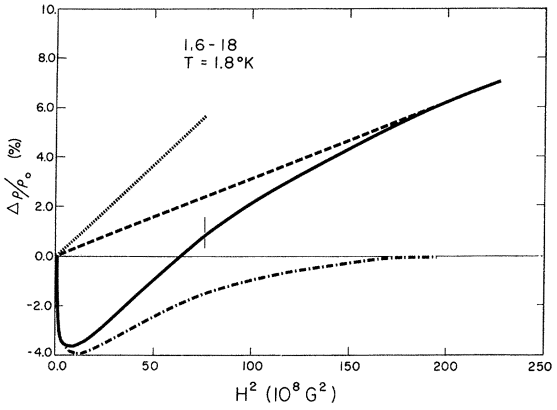

FIG. 8. Magnetoresistance versus H^2 for sample 1.6–18 at 1.8 °K. Solid line represents experimental data; dotted line represents conventional positive component if the data were taken only up to ≈75 kG (indicated by the vertical line); dashed line represents the positive component as a result of the extrapolation of the high-field data to pass through the origin; dot-dashed line represents the negative component obtained by subtracting the observed magnetoresistance from the dashed line.

n-InSb up to 8 kG, respectively, to an empirical expression

$$\Delta\rho/\rho_0 = -aH^c + bH^2 \ . \qquad (4)$$

They found a systematic dependence of the coefficients a and c on concentration and temperature with the value of c generally less than 1 and approaching 0.5 for high-concentration samples. In the lowest-concentration Ge or Si samples, the value of c approached 1.5. Thus, if there is an H^2 region of field dependence in these materials, it is at very low fields and moves lower with increasing concentration. Even in dilute alloys such as Cu-Mn and Cu-Fe, Monod[22] has shown that $\Delta\rho/\rho_0 \propto H^n$, where $n = 1.7$–1.8. Katayama and Tanaka[14] have reported that $-\Delta\rho/\rho_0 \propto H^2$ only up to about 50 G in InSb. Detailed analysis of the data below 1 kG on our CdS samples show no H^2 region down to at least 150 G (see Fig. 7).

This is disturbing since it implies the subsequent saturation at low fields also. Direct experimental evidence for such a saturation is lacking. For example, in our most degenerate sample, 1.2-19, no saturation is observable even up to 150 kG (see Fig. 4). Furthermore, if the exact expression for $\Delta\rho/\rho_0$ (assuming the proportionality to M^2) is taken of the form

$$\Delta\rho/\rho_0 = -c[B_J(x)]^2 \ , \qquad (5)$$

where $B_J(x)$ is the Brillouin function[23] with $x = Sgu_BH/kT$, then anomalously large S or g values

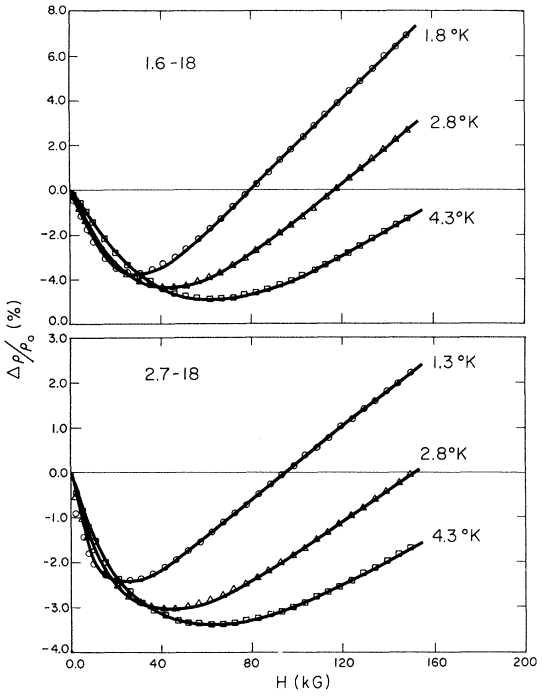

FIG. 9. Representative fits to Eq. (6) of the text for samples 1.6 – 18 and 2.7 – 18 at the temperatures indicated.

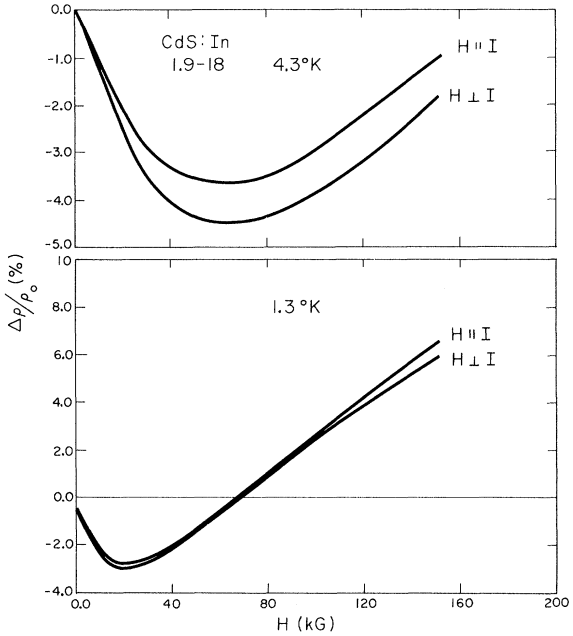

FIG. 10. Comparison of the longitudinal and transverse magnetoresistance for sample 1.9 – 18 at 4.3 and 1.3 °K.

are required to explain the derived saturation fields, as Sasaki[9] has pointed out for n-Ge. Such large values of the effective local moment would also be expected to produce anomalies in magnetic resonance and susceptibility measurements. However, no conclusive experimental evidence of these effects has been found (see, e.g., Ref. 2). Indeed, a straightforward attempt to establish a least-squares fit to our cadmium sulfide data using an expression of the form of Eq. (5), fails for the reasons noted above. The only way saturation has been shown to occur is by the graphical method.

For graphical analysis, the assumption that the positive component is proportional to H^2 owing to the Lorentz force is made. Based on this assumption the magnetoresistance data are plotted versus H^2.[9-14] A line is drawn to pass through the origin, which is parallel to the actual data at the highest field. This new line is thus assumed to represent the normal positive component. The difference between this designated positive component and the observed magnetoresistance is claimed as the negative component. With such an analysis the saturation of the negative component is inevitable. However, if one extends the data to higher fields, as we have done for CdS, this method is no longer applicable. For example, if we plot our data for sample 1.6-18 versus H^2 at 1.8 °K as in Fig. 8 the high-field region can be directly extrapolated to pass through the origin (see dotted line of Fig. 8). Subtracting the observed magnetoresistance from this line yields a negative component which goes to zero after passing through a minimum (see dot-dashed line of Fig. 8). Excellent empirical fits[24] over the whole concentration and temperature range can be obtained using an expression of the form

$$\Delta\rho/\rho_0 = -aH^c e^{-dH/T} + bH^2 , \qquad (6)$$

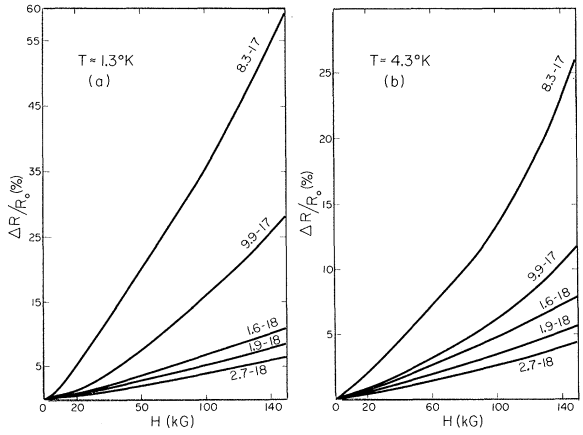

FIG. 11. Relative change in the Hall coefficient $\Delta R/R_0$ versus H for low-concentration samples 8.3 – 17 to 2.7 – 18.

which is consistent with the above analysis. This is demonstrated in Fig. 9 for two of the samples. However, the vanishing of the negative component at high fields is not consistent with the localized-magnetic-moment model. If we had taken data only to 70 or 75 kG, as shown by a vertical line in Fig. 8, we could also have been tempted to obtain a forced saturation, but the data to the highest magnetic field do not indicate that this graphical method is valid. Hence, we conclude that saturation, which is a basic feature of the second-order theory, cannot be directly inferred from the data.

C. Positive Component

In order to separate the true negative component it is apparent that we must know the exact nature of the positive component. It is therefore relevant to reexamine the possible origins of the positive magnetoresistance contributions in degenerate semiconductors.

In a degenerate electron system, the classical Lorentz-force terms in the magnetoresistance should be zero to first order in kT/ϵ_F.[25] Thus, attributing the positive magnetoresistance to this effect for samples above the Mott transition is questionable. It is apparent that the data shown in Figs. 3, 5, and 6 show no clear indication of an H^2 dependence at high fields. Furthermore, as shown in Fig. 10, the longitudinal magnetoresistance for CdS is equal to or slightly larger than the transverse, a fact not consistent with the Lorentz-force concept.

Straub *et al.*[26] have measured the magnetoresistance and Hall coefficient of As-doped Si samples in the impurity conduction range. They attribute the significant field dependence of the Hall coefficient and the magnetoresistance to a decrease in the density of states at the Fermi level and the magnetic-field-induced Mott transition. [Note that this is in contradiction to their earlier claim,[6] with regard to Eq. (4), that the positive term is the conventional magnetoresistance which satisfies the ellipsoidal symmetry relations in oriented samples.] Sugiyama[27] has also endorsed the magnetic freeze-out model for his Ge samples. Freeze-out effects have also been inferred from the field dependence of the Hall coefficient in n-InSb by Sladek.[28] In Fig. 11 we see that our lower-concentration CdS samples, where the positive component is strong, also show a significant field dependence for the Hall coefficient, thus indicating that a similar mechanism is operating here. We thus endorse the basic interpretation of Straub *et al.*[26] in regard to the positive magnetoresistance. Unfortunately, knowledge of the field dependence of the magnetoresistance due to such shrinking of the electronic wave functions in a magnetic field in the impurity conduction regime is is not yet available. It is at least not evident that it just obeys an H^2 dependence. Our data for some of the samples of CdS and those of Straub *et al.*,[26] in fact, indicate a power less than 2 at higher fields and lower temperatures and concentrations. One approach to the problem of freeze-out has been to assume conduction in two bands of differing conductivities in which the magnetic field induces a change in the relative populations (e.g., conduction band and impurity band). Calculations based on such a model show[29] that the magnetoresistance may be given by

$$\Delta\rho/\rho_0 = AH^2/(1+BH^2) \quad , \tag{7}$$

where A and B are related to the conductivities and relaxation times of each group of carriers. The magnetoresistance will therefore saturate at some high field depending upon the size of B. Figure 12 is representative of the fact that, for lower concentration samples, there is a tendency toward a decreasing power of H at very high fields. Since Eq. (7) does seem to represent the qualitative features of the data, we shall employ it for empirical fitting. The validity of using this expression is further supported when the magnitude of the positive component obtained from empirical fits is compared with the relative change in the Hall coefficient as discussed in Sec. IV E.

D. Third-Order Terms

Since the empirical approach yields little helpful information and the second-order theory appears to be inadequate except in very weak fields, it is conceivable that calculations to higher orders in the s-d exchange Hamiltonian may be required. Some evidence is available which tends to justify such an approach. The reasons for using higher-order terms can be inferred from the low-temper-

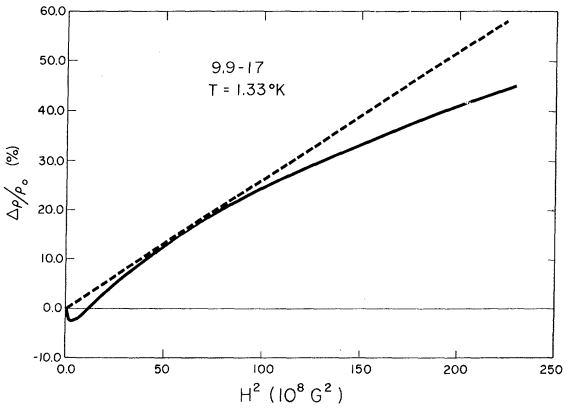

FIG. 12. Magnetoresistance versus H^2 for sample 9.9 – 17 at 1.33 °K, representative of the fact that, for lower concentration samples, as the magnetic field increases the positive component deviates from the H^2 dependence ($H \perp I$).

ature resistance anomalies, where the resistivity is not independent of temperature, as would be expected in degenerate semiconductors and as has been observed by Sasaki[9] in n-Ge and by Katayama and Tanaka[30] in n-InSb. Kondo[31] has shown, for dilute alloys, that calculations using a third-order perturbation expansion of the s-d exchange scattering of conduction electrons from localized spins yields a logarithmic dependence of the resistivity on temperature which can be expressed in its simplest form by

$$\rho_0 = a + b \ln T. \tag{8}$$

Here, a represents the residual resistivity and b is proportional to J, the s-d exchange integral. Kondo[31] concluded that J is negative, thereby causing the resistivity to increase with decreasing temperature. However, there seem to be conflicting interpretations regarding the sign of J. In Rh-Fe alloys, [32] the resistivity was interpreted with J positive, whereas the susceptibility for the same alloys could be attributed to a negative exchange interaction. Katayama and Tanaka[30] found a negative J for n-InSb, but Sasaki[9] reported J as positive in n-Ge. In a later paper, however, Sasaki[33] claims that J can be shown to be negative if one plots $-(\Delta\rho/\rho_0)_{\text{sat}}\cdot\rho_0 (= -(\Delta\rho)_{\text{sat}})$ versus T. As shown in Fig. 13 our CdS samples, above the Mott transition, show a logarithmic decrease in resistivity with temperature implying a positive, or ferromagnetic exchange interaction. Reasonable values of J can be obtained from the least-squares fit with Eq. (8) shown as the solid line of Fig. 13. Fischer[34] and Kondo[35] seem to have resolved the anomaly in the sign of J by showing that the effect of ordinary potential scattering on exchange scattering from magnetic impurities in metals can result in a change in the sign of J under certain conditions.

The sign of the exchange interaction is not crucial to the problem under consideration, however. What is pertinent is that terms to third order are necessary to account for the logarithmic temperature dependence of the resistivity and may therefore be important to the discussion of the magnetoresistivity.

Beal-Monod and Wiener[36] have calculated the magnetoresistance for dilute alloys from the third-order perturbation expansion of the s-d exchange Hamiltonian, but assume from the outset that third-order terms are much smaller than second-order terms to facilitate calculations of the relaxation time. Thus, the expressions they derive seem to fit their data on Cu-Mn alloys, where they can otherwise be fitted reasonably well only by assuming that $\Delta\rho/\rho_0$ is approximately proportional to the square of the magnetization. However, in the case of Cu-Fe alloys the above is not true and Beal-Monod and Weiner[36] need to modify their terms. Even in Cu-Mn alloys, as the field increases, the second- and third-order contributions become equally significant. This situation is reminiscent of our CdS data, as discussed in Sec. IV B, where $\Delta\rho/\rho_0$ is not $\propto H^2$ beyond the extreme weak-field region. Thus, higher-order calculations without the dominance of second-order terms may be necessary to account for the semiconductor data. Appelbaum[37] has derived such an expression using third-order expansion of the s-d exchange Hamiltonian to explain zero-bias tunneling anomalies. Appelbaum's expressions can be applied to magnetoresistivity results if one changes the tunneling rates to the appropriate scattering rates. Whereas the s-d interaction enhances tunneling through a barrier giving rise to larger conductance, it increases the resistivity in bulk semiconductors because of enhanced scattering. With the application of magnetic field, the conductance in the junctions and the resistivity in the semiconductors decreases.

The expressions of Appelbaum, after simple modifications, can be written as

$$\Delta\rho/\rho_0 = AN_A \frac{\sigma_J^2}{\sigma_0^2} \langle M\rangle \tanh\frac{\Delta}{2kT} + C\left(\frac{\langle M\rangle}{S(S+1)}\tanh\frac{\Delta}{2kT} + \frac{M^2}{S(S+1)} - 1\right) F(0)$$

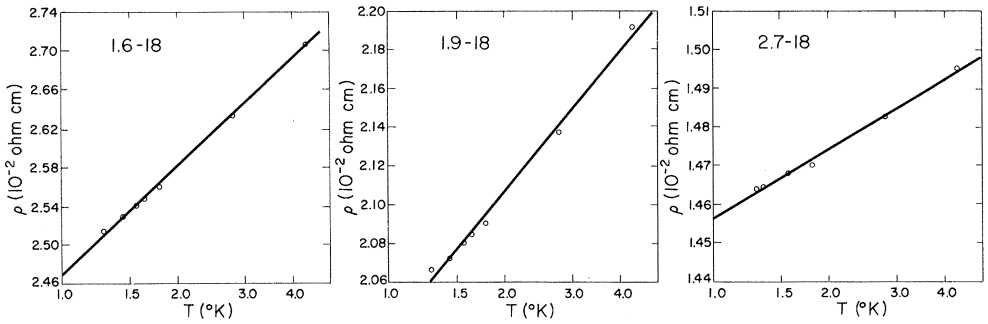

FIG. 13. Resistivity versus log temperature. (Solid lines are the fits to the equation $\rho = a + b \ln T$.)

$$+C\left(1+\frac{M^2}{S(S+1)}+\frac{\langle M\rangle}{S(S+1)}\tanh\frac{\Delta}{2kT}\right)F(\Delta)\,, \quad (9)$$

where

$$C=-2S(S+1)N_A\sigma_J^2 J/\sigma_0^2\,.$$

σ_J is the exchange scattering cross section, σ_0 is the scattering cross section due to other scattering mechanisms, M is magnetization, $\Delta=g_0\mu H$, and the other symbols have their usual meaning. The function $F(\Delta)$ has been evaluated numerically[37] and can be represented in the form

$$F(\Delta)\approx\rho_F\ln\left(\frac{\Delta^2+(\alpha kT)^2}{E_0^2}\right)^{1/2}\,, \quad (10)$$

where E_0 is a variable energy cutoff parameter and ρ_F is the density of states at the Fermi level. Losee and Wolf[38] have suggested a further modification of the Appelbaum theory[37] to include the intrinsic lifetime broadening of the spin-flipped intermediate states in the third-order transition probability[31] given by

$$W_{ij}\propto\delta(E_i-E_j)\sum_{k\neq i}\frac{H'_{ik}H'_{jk}H'_{ji}}{E_i-E_k}\to J\rho_F \times\int_{-E_0}^{E_0}\frac{\tanh(\beta\epsilon/2)d\epsilon}{E_i-\epsilon}\,\delta(E_i-E_j)$$

and the related g shift of the Zeeman transition. Suhl[39] has shown that if the intermediate energy states have an inherent width Γ described by a normalized shape function $R(\epsilon)$, the integral in the third-order transition probability above must be modified by replacing $\tanh(\frac{1}{2}\beta\epsilon)$ by the convolution

$$S(\epsilon)=\int_{-\infty}^{\infty}R(\epsilon')\tanh(\tfrac{1}{2}\beta)(\epsilon-\epsilon')d\epsilon'\,. \quad (11)$$

The distribution appropriate to lifetime broadening is the Lorentzian

$$R(\epsilon)=\frac{\Gamma}{\pi}\frac{1}{(\Gamma^2+\epsilon'^2)}\,.$$

$S(\epsilon)$, like $\tanh(\frac{1}{2}\beta\epsilon)$, is essentially a step function at the Fermi energy $\epsilon=0$, but the broadened step in $S(\epsilon)$ becomes no narrower than the larger of (Γ, kT). Including these broadening effects, $F(\Delta)$ becomes

$$F(\Delta)\approx\rho_F\ln\left(\frac{\Delta^2+(\alpha kT)^2+\Gamma^2}{E_0^2}\right)^{1/2}\,, \quad (12)$$

where $\Gamma=2S\pi(2J\rho_F/g_0)^2\Delta$,[40] and g_0 is the unshifted g factor. Using (11) and (12), we can rewrite Eq. (9) as

$$\Delta\rho/\rho_0=\left(\frac{\Delta\rho}{\rho_0}\right)_2+\left(\frac{\Delta\rho}{\rho_0}\right)_{3a}+\left(\frac{\Delta\rho}{\rho_0}\right)_{3b}\,, \quad (13)$$

where

$$\left(\frac{\Delta\rho}{\rho_0}\right)_2=-A_1\langle M\rangle S(\epsilon)\,, \quad (14)$$

$$\left(\frac{\Delta\rho}{\rho_0}\right)_{3a}=-A_1J\rho_F[S(S+1)+\langle M^2\rangle]\times\ln\left\{1+\left[1+4S^2\pi^2\left(\frac{2J\rho_F}{g_0}\right)^4\right]\frac{\Delta^2}{(\alpha kT)^2}\right\}\,, \quad (15)$$

$$\left(\frac{\Delta\rho}{\rho_0}\right)_{3b}=A_1\langle M\rangle S(\epsilon)\times\ln\left(\frac{(\alpha kT)^2[(\alpha kT)^2+\Delta^2+\Gamma^2]}{E_0^4}\right)\,, \quad (16)$$

where $A_1=AN_A\sigma_J^2/\sigma_0^2$.

The second-order term $(\Delta\rho/\rho_0)_2$ is then essentially similar in form to the average magnetization ($\langle M\rangle$) squared except for broadening corrections. Equations (15) and (16) together represent the third-order terms.

E. Empirical Expression

Fits to Eq. (13) for high-concentration samples showed that $(\Delta\rho/\rho_0)_{3a}$ given by Eq. (15) was always dominant. This is perhaps not very surprising since the other two terms $(\Delta\rho/\rho_0)_2$ and $(\Delta\rho/\rho_0)_{3b}$ given by expressions (14) and (16) have an H^2 dependence at low fields, which the data do not show, as has been discussed earlier in Sec. IV B. Based on these observations we suggest a semiempirical expression of the form

$$\Delta\rho/\rho_0=-B_1\ln(1+B_2^2H^2)\,, \quad (17)$$

which, as we shall show, may be justified by detailed consideration of expressions (14)–(16).

The fit to Eq. (17) for sample 10, where no positive component is evident, is shown in Fig. 14. For samples where a small positive component is mixed with the observed negative magnetoresistance, such as samples 3.0-18 and 5.0-18, and for lower concentration samples where the magnetoresistance becomes positive at higher fields, the positive component was represented by Eq. (7). For these samples, the observed magnetoresistance is represented by the compound expression

$$\Delta\rho/\rho_0=-B_1^2\ln(1+B_2^2H^2)+B_3^2H^2/(1+B_4^2H^2)\,. \quad (18)$$

The fits to this expression for various samples are shown in Figs. 14 and 15 at various temperatures. In order to avoid any misinformation resulting from a false representation of the positive component, fits with Eq. (17) alone were made on various samples with data below 10 kG, where the positive component is negligible. It was found that the values of B_1 and B_2 from the two approaches were comparable. Table II lists values of the parameters from the fits to Eq. (18). [It is important to emphasize that reasonable least-squares fits at both

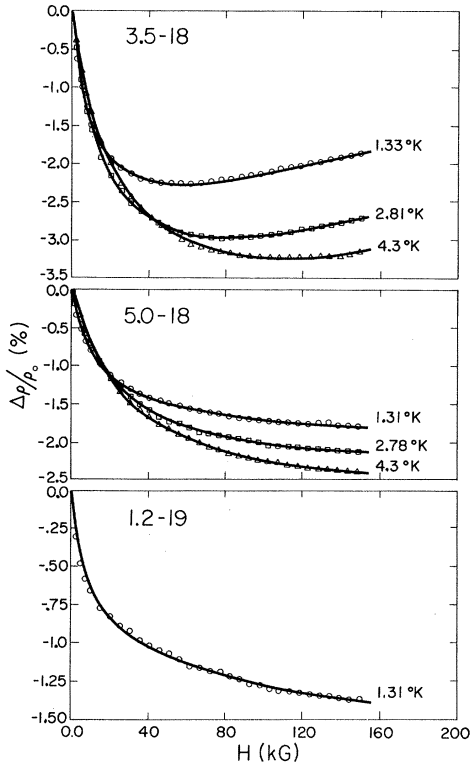

FIG. 14. Least-squares fits to the empirical logarithmic expression (represented by the solid lines). For samples 3.5 – 18 and 5.0 – 18 there is an admixture of small positive component [expression (18)]. Sample 1.2 – 19 is fitted to expression (17) of the text only.

high and low fields are obtained using Eq. (17) for the negative component with several choices for the positive term, while poor and inconsistent fits are obtained in all field regions using only second-order expressions with the same positive terms.] In Table II, we find that the values of the parameters have a very systematic temperature and concentration dependence. And when the negative component is evaluated in the compound expression (18), using the values of the parameters B_1 and B_2 from the fits, it is found that the negative component has a concentration dependence consistent with the localized-magnetic-moment model[16]; the negative component of the magnetoresistance decreases as the carrier concentration increases. This is demonstrated in Fig. 16. The decrease in magnitude of the negative component of the magnetoresistance for sample 9.9-18 is also consistent with observations on other materials.[33]

We also find that the ratio of the evaluated positive component to the relative change in Hall coefficient in the CdS samples is similar to that found by Straub *et al.*[26] for As-doped Si. Following the arguments of Edwards[41] and Kubo,[42] Straub *et al.*[26] showed that the ratio $(\Delta\rho/\rho_0)/(\Delta R/R_0)$ is less than or approximately equal to 2. They obtained a value of 1.67 for this ratio for their Si samples. When we plot the evaluated positive component of the magnetoresistance of expression (18) against $\Delta R/R_0$ (Fig. 17), the ratio is found to be 1.85.

This consistent independent behavior of the negative and the positive component from the compound empirical expression gives us added confidence with regard to our fits, and the respective models they imply.

Returning to Eqs. (14)–(16), we note that Eq. (17) is similar to the expression $(\Delta\rho/\rho_0)_{3a}$ where

$$B_1 = A_1 J \rho_F \left[S(S+1) + \langle M^2 \rangle\right]$$

and

$$B_2^2 = \left[1 + 4S^2\pi^2\left(\frac{2J\rho_F}{g_0}\right)^4\right] \frac{g_0^2\mu^2}{(\alpha kT)^2} \quad .$$

For most of the samples, it is found that B_2 is in-

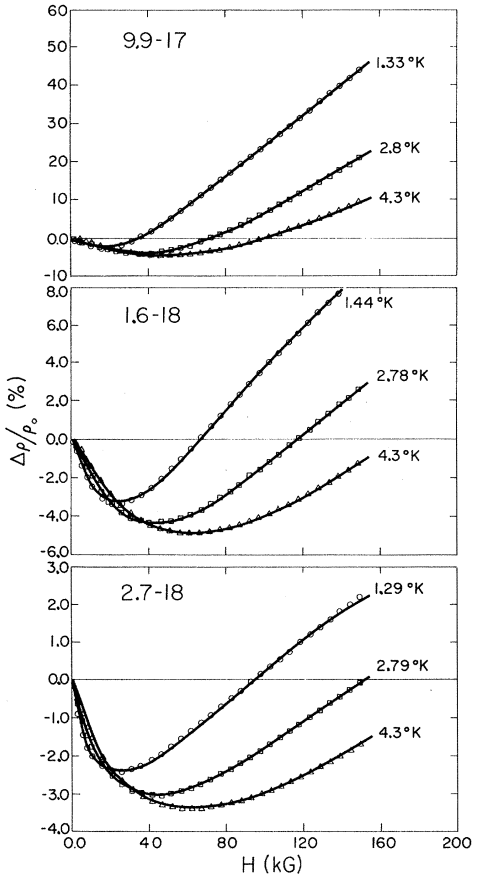

FIG. 15. Least-squares fits to the compound expression (18) (represented by the solid lines) for various samples at the temperatures indicated.

TABLE II. Values of the parameters to fit the empirical expression: $\Delta\rho/\rho_0 = -B_1^2 \ln(1 + B_3^2H^2) + B_3^2H^2/(1 + B_4^2H^2)$. Values of α are derived from those of B_2.

Sample	Temp. (°K)	B_1	B_2 (10^{-3})	B_3 (10^{-5})	B_4 (10^{-5})	α for $J\rho = 0.4$, $S = \frac{3}{2}$
8.3 – 17	4.3	0.175	0.058	0.487	0.055	1.02
	2.8	0.153	0.090	0.817	0.203	1.02
	1.36	0.115	0.147	1.010	0.482	0.66
9.9 – 17	4.3	0.177	0.062	0.354	0.282	0.96
	2.8	0.168	0.085	0.475	0.428	1.07
	1.33	0.096	0.329	0.662	0.645	0.58
1.6 – 18	4.3	0.130	0.112	0.214	0.324	0.53
	3.78	0.124	0.159	0.302	0.536	0.58
	1.29	0.106	0.267	0.464	0.882	0.74
1.9 – 18	4.3	0.114	0.138	0.180	0.329	0.43
	2.8	0.106	0.210	0.252	0.541	0.43
	1.32	0.084	0.514	0.369	0.869	0.37
2.7 – 18	4.3	0.084	0.285	0.139	0.278	0.20
	2.8	0.079	0.428	0.190	0.502	0.21
	1.29	0.064	1.200	0.263	0.796	0.16
3.0 – 18	4.3	0.079	0.270	0.082	0.211	0.22
	2.81	0.074	0.408	0.116	0.487	0.22
	1.33	0.064	0.840	0.157	0.779	0.22
3.5 – 18	4.3	0.071	0.363	0.064	0.048	0.16
	2.81	0.070	0.442	0.102	0.521	0.20
	1.33	0.059	0.787	0.122	0.746	0.24
5.0 – 18	4.3	0.060	0.246	0.033	...	0.24
	2.78	0.056	0.303	0.036	...	0.30
	1.31	0.046	0.652	0.029	...	0.30
1.2 – 19	4.3	0.039	0.688	...	...	0.08
	2.78	0.038	0.928	...	...	0.09
	1.31	0.037	1.015	...	...	0.19

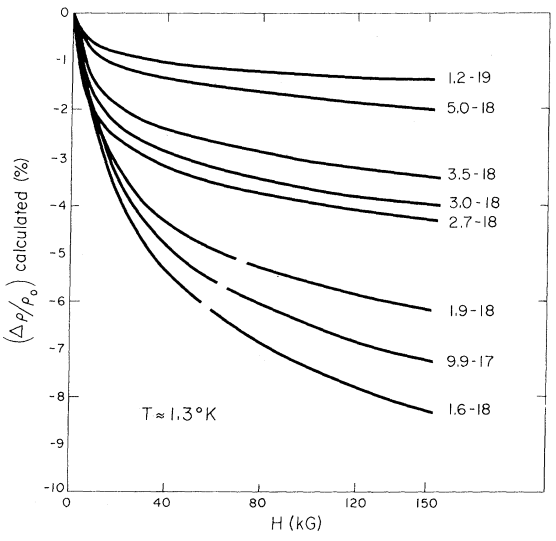

FIG. 16. Calculated negative component of magnetoresistance for various samples using the values of the fitted parameters B_1 and B_2.

deed proportional to $1/T$. No definite knowledge about the value of the parameters S, $J\rho_F$, and α is available. However, some speculative comments may be made if we use the value of $J\rho_F$ found by Losee and Wolf,[43] who have interpreted their tunneling results in CdS in terms of the s-d interaction and broadening effects. They obtain the value of $J\rho_F = 0.4$. We assume this value of $J\rho_F$ to be applicable to our magnetoresistance results. S can be as large as $\frac{3}{2}$ without introducing significant additional field dependence due to $\langle M^2 \rangle$. The value of S is, however, further limited by the necessity that Γ be less than Δ, implying that $2\pi S(2J\rho_F/g_0)^2 < 1$.

Appelbaum[37] suggested that the value of α in Eq. (10) be ≈ 1. However, our numerical fits to the integral $F(\Delta)$ indicate a value of ≈ 1.8 and experimental values reported in the literature vary considerably. Shen and Rowell[44] found $\alpha \approx 1.5$ from their tunneling measurements. Recently, Wolf and Losee[45] found that they can fit their tunneling data on n-Si using $\alpha = 2.12$, the value varying slightly with temperature. At the same time, to fit zero-bias tunneling anomalies in $A1$-I-$A1$ tunnel

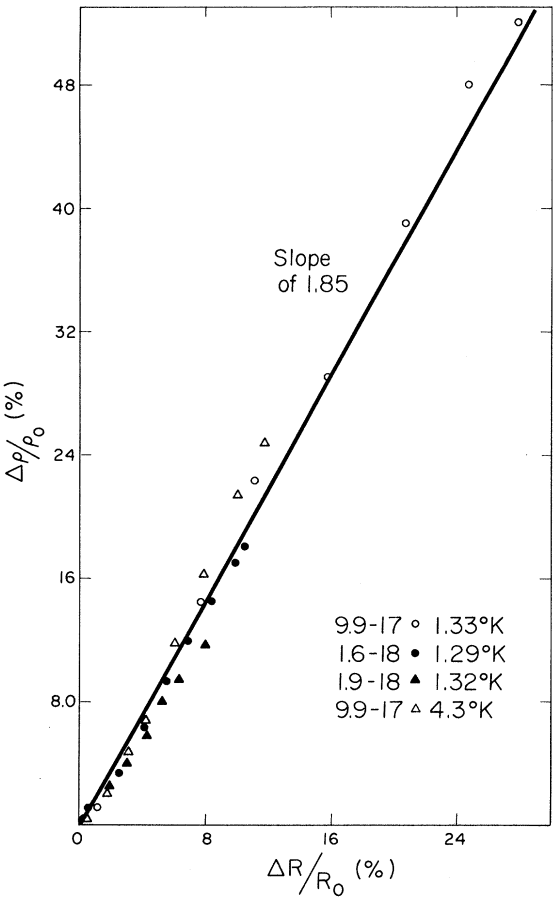

FIG. 17. Plots of derived positive magnetoresistance $\Delta\rho/\rho_0$ versus relative change in the Hall coefficient $\Delta R/R_0$ to show that magnetic freeze-out effects are responsible for the positive component. (See Ref. 25.)

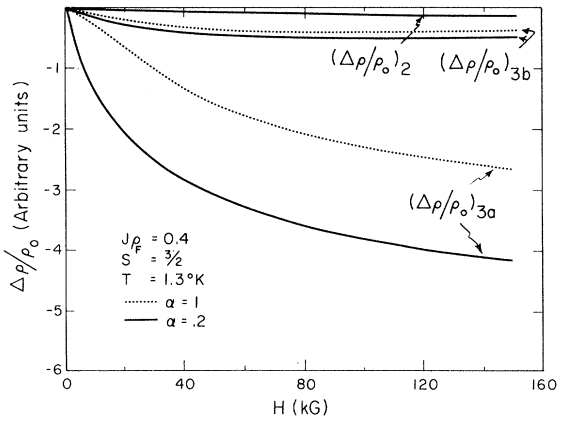

FIG. 18. Calculations of $(\Delta\rho/\rho_0)_2$, $(\Delta\rho/\rho_0)_{3a}$, and $(\Delta\rho/\rho_0)_{3b}$ in expression (13) of the text for the values of the parameters indicated to show that $(\Delta\rho/\rho_0)_{3a}$ is the dominant term.

junctions Nielsen[46] claims to have used values of α as large as 10 and suggests that a different value be chosen for each temperature. The reported values thus vary by an order of magnitude, lending some justification for adjusting the value of α for magnetoresistivity results also. Whether the value of $\alpha = 1$ or 0.2 (for $S = \frac{3}{2}$), as found from our fits (see Table II), the term $(\Delta\rho/\rho_0)_{3a}$ is the dominant term, as shown in Fig. 18, where all three terms have been calculated with the same values of $J\rho_F, S$, and T.

Our derived value of α (see Table II) is a constant of temperature and concentration for samples above 2.7×10^{18} cm^{-3}. At lower concentrations, α increases (B_2 decreases), probably because of the appearance of a very low-field H^2 dependence of the negative magnetoresistance in these samples. Whether this is a true characteristic of the parameter α or an indication of the need to include other terms [Eqs. (14) and (16)] with inherent low-field H^2 dependences cannot be readily determined.

It seems that the magnetic scattering from local moments in the depletion region of Schottky-barrier metal-semiconductor junctions is essential in the understanding of the zero-bias tunneling anomalies.[43–45] It is interesting, therefore, that a similar least-squares fit to the tunneling data of Losee and Wolf on Cu-CdS[43] and Au-Si[45] junctions to our semiempirical expression (17) is possible (see

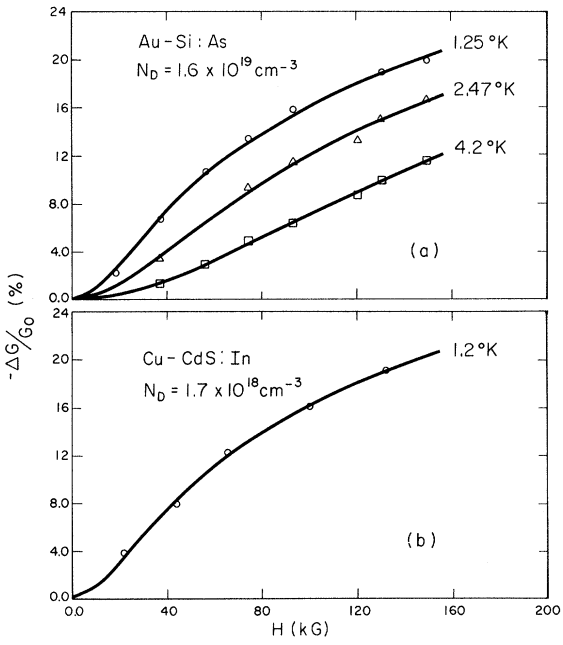

FIG. 19. Tunneling conductance data on Au-Si (Ref. 45) and Cu-CdS (Ref. 43) junctions (analyzed on the basis of the localized-magnetic-moment model by Wolf and Losee) are fitted to our logarithmic empirical expression represented by the solid lines.

TABLE III. Value of the parameters to fit the empirical expression $\Delta G/G_0 = -B_1^2 \ln(1+B_2^2H^2)$ for Cu-CdS and Au-Si tunneling junctions. Values of α are derived from those of B_2 using $S=1/2$ and $J\rho=0.40$ and 0.41 for CdS and Si, respectively.

Junction	Temp. (°K)	B_1	B_2 (10^{-4})	α (derived from B_2)	α (tunneling)
Cu-CdS[a]	1.2	0.233	0.434	2.71 ±0.03	1.7[b] ±0.25
Au-Si[c]	4.2	0.279	0.125	2.89 ±0.03	2.26[c] ±0.02
Au-Si[c]	2.47	0.253	0.240	2.56 ±0.03	2.12[c] ±0.02
Au-Si[c]	1.25	0.233	0.429	2.83 ±0.03	2.00[c] ±0.02

[a]See Ref. 43.
[b]D. L. Losee (private communication).
[c]See Ref. 45.

Fig. 19). Furthermore, when the values of $J\rho_F$ equal to 0.40[43] and 0.41[45] for Cu-CdS and Au-Si junctions, respectively, are used, it is found that for $S=\frac{1}{2}$, the values of α are very close to those obtained by them in the analysis of their data from other considerations (see Table III).

Thus, although some adjustment of parameters is required to relate the empirical fits to the data to the existing scattering theory, the evidence seems to be strong for including third-order terms, even to the point of dominance, to explain the negative magnetoresistance in CdS and perhaps, by analogy, in other degenerate semiconductors as well. Of course, this then raises the question of whether fourth- and even higher-order terms should be included. In addition one would like to ascertain if corrections to the form of the magnetization function, or a detailed account of effects peculiar to the bulk material, such as multiple scattering, may resolve the remaining discrepancies. More quantitative knowledge about the positive contributions is also essential to an accurate determination and analysis of negative magnetoresistance.

V. SUMMARY

Magnetoresistance measurements on CdS samples in the metallic impurity conduction region show negative magnetoresistance to much higher temperatures and magnetic fields than in any other semiconductor.

Although qualitative features of the data at low field are consistent with the localized-magnetic-moment model of Toyozawa, there is little quantitative agreement with the second-order perturbation calculations of the *s-d* exchange Hamiltonian. For samples showing positive magnetoresistance at high fields, the Hall coefficient is found to be field dependent. This is interpreted in terms of freeze-out instead of the conventional notion that it is due to the Lorentz force. From the logarithmic temperature dependence of resistivity at zero field in CdS and that of Ge, Si, and InSb available in the literature, it is inferred that calculations to higher-order terms in the *s-d* exchange Hamiltonian should be included.

A semiempirical expression is suggested to interpret the data. The negative component of the expression is inferred from the available calculations to third order of *s-d* exchange Hamiltonian, and the positive component is a result of assuming two-band conduction. The least-squares fits to this equation give reasonable and consistent values of parameters.

It is our contention that the localized-moment model seems both plausible and correct; however, further theoretical work is necessary to determine the exact nature of the higher-order *s-d* interaction in the bulk material and the positive magnetoresistance due to magnetic freeze-out.

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*High magnetic field measurements made at the Francis Bitter National Magnet Laboratory, Cambridge, Mass.

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