Impurity Conduction and the Metal-Nonmetal Transition in Manganese-Doped Gallium Arsenide*

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Electrical-transport measurements between 20 and 550 K demonstrate impurity conduction below 100 K in Mn-doped GaAs samples with $N_a > 10^{19}$ cm^{-3}. Of a group of samples with $10^{19} < N_a < 3 \times 10^{19}$ cm^{-3} and moderate compensation ($K < 0.1$), some display metallic (activationless) impurity conduction, whereas others have a finite activation energy of about 0.015 eV in the impurity-conduction range. It is concluded that this energy should be identified as E_2 for impurity conduction in a semiconductor with "intermediate-range" doping, and that the transition range of N_a in which E_2 decreases before vanishing must be a narrow one. The values for E_2 are compatible with the models of Mycielski and of Mikoshiba for this conduction. Since the bound-state wave function for a manganese acceptor has a characteristic radius $a_L = 10.1$ Å, then the critical acceptor density N_c for a metal-nonmetal transition corresponds with the condition $a_L N_c^{1/3} = 0.28$. This denotes closer spacing than the Mott-Hubbard criterion because of the compact nature of the manganese wave function. Hopping conduction was not detected with samples containing less than 10^{19} cm^{-3} of Mn acceptors, and this also is to be expected from the charge distribution of the manganese bound state.

I. INTRODUCTION

The simplest model for an impurity state in a semiconductor is obtained by solving the Schrödinger equation for a scalar effective mass, m^*, and a scaled Coulomb ($e/\kappa r$) potential. Consideration of anisotropy of the effective-mass tensor can lead to considerable complication of the model, but leaves intact the idea of a Coulomb potential and of the resulting shallow effective-mass bound states. Our knowledge of shallow impurity states is much better than for deep impurities, and it is no surprise that both experiment and theory for impurity conduction have concentrated on shallow impurities.

In this paper, we are concerned with impurity conduction (IC) for relatively deep manganese acceptors in gallium arsenide. Shallow acceptors do exist in GaAs; thus elements such as Ge, Cd, or Zn provide acceptors with a hydrogenic ionization energy $E_H = 0.03$ eV, compatible with a Coulomb potential and a Bohr radius, $a_H = e^2/2\kappa E_H = 19$ Å. However, more compact acceptor states of larger ionization energy result when transition elements[1] are placed in GaAs, and the binding of a hole then results principally from a short-range core potential rather than a gradual Coulomb potential. (We look to the heavy-hole band as the dominant factor for the wave function and eigenenergy of the ground state.)

The thermal-ionization energy for manganese-doped gallium arsenide has variously been reported[1-4] in the range $0.06 < E_a < 0.10$ eV dependent on the acceptor and compensator concentrations, and it extrapolates back[4] to 0.110 eV for infinite impurity dilution. It has been observed that $E_a = 0.110$ eV is also the threshold energy for extrinsic photoconductivity[3] and for photoionization[5-7] of manganese centers. The magnitude and spectral dependences of the photoionization cross section for these centers[7] are in good accordance with the predictions of Lucovsky's δ-function-potential model,[8] a choice of potential which dictates a ground-state wave function with a radial dependence,

$$\psi(r) = (2\pi r^2 a_L)^{-1/2} e^{-r/a_L} . \quad (1)$$

This function is characterized by an effective radius,

$$a_L = (\hbar^2/2m_v E_a)^{1/2} = 10.1 \text{ Å}. \quad (2)$$

Just the same wave-function radius as in Eq. (2) is required by the quantum-defect models[9,10] of Bebb and Chapman, which start from a different formulation of the deep impurity problem. Thus Eq. (2) should serve as a reasonable guide for the radius of a manganese acceptor, and Eq. (1) for the radial dependence, even though the Lucovsky model obviously over simplifies the potential seen by a hole bound to a manganese center. Equations (1) and (2) are relevant to consideration of IC resulting from the overlap between neighboring impurities.

Free-hole transport for GaAs doped with transition-element acceptors was studied by Brown and Blakemore,[3] who pointed out that strongly doped samples were affected by IC below 100 K for Mn doping and below 200 K for Ni doping. The present paper constitutes the detailed study of IC in the GaAs:Mn system promised in Ref. 3. It is of interest for us to note that Vieland's original data[2] for R_H in GaAs:Mn was affected by IC at his lowest

temperatures, though this apparently went unrecognized at the time.

As with most other semiconductors, the literature on IC for GaAs has concentrated on shallow impurities. Meyerhofer[11] reported thermally activated IC for GaAs doped with shallow Zn or Cd acceptors. The Hall and resistivity data of Rosztoczy *et al.*[12] for GaAs containing shallow Ge acceptors suggests the persistence of hopping-type IC with N_a as small as 3×10^{16} cm^{-3}. Both metallic and activation types of IC were seen by Asai *et al.*[13] in epitaxial GaAs containing shallow donors, while Nasledov and Emel'yanenko, [14] and Nasledov[15] have reported metallic IC for n-type GaAs containing unidentified types of shallow donors. A hopping type of IC has been reported by Coates and Mitchell[16] for unidentified 0.1-eV defect centers resulting from neutron irradiation of GaAs.

For an extrinsic semiconductor sample in which IC occurs, the electrical conductivity can be approximated well below the exhaustion range in a crude but useful fashion by[17]

$$\sigma=\sigma_1 e^{-E_1/kT}+\sigma_2 e^{-E_2/kT}+\sigma_3 e^{-E_3/kT}, \qquad (3)$$

where $\sigma_1 \gg \sigma_2$ or σ_3, and $E_1 > E_2 > E_3$. The first term on the right-hand side is (for p-type material) the conduction of free holes in the valence bands. This dominates the behavior at higher temperatures. The second and third terms on the right-hand side of Eq. (3) concern two distinctly different mechanisms for IC, for which the respective opportunities depend greatly on the concentrations of majority and minority impurities. These have been discussed (within the context of what is expected for *shallow* impurities) by Davis and Compton[18] in the light of detailed measurements with Sb-doped Ge, and are reviewed by Mott and Davis[19] with reference to the general characteristics of IC by hydrogenic impurities in any semiconductor host.

The term $\sigma_3 e^{-E_3/kT}$ is the hopping conduction of holes tunneling from neutral to ionized acceptors in a partially compensated semiconductor. Hopping conduction does not by itself produce a very large conductivity, but with some shallow impurity systems it can be strikingly evident at low temperatures when the average spacing r_a between participating acceptors is as large as 10–20 times the bound-state radius a_H. Tunneling takes place with the acceptor ground states spread over an energy range, $E_3 \sim e^2/\kappa r_a$, as a result of the random Coulomb fields arising from compensating donors and ionized acceptors; thus the transitions have to be phonon aided and thermally activated. If tunneling to more remote but energetically favorable acceptors becomes a popular process at very low temperatures, then Austin and Mott[20] argue that the hopping conductivity term should convert to the form $\sigma_3' e^{-A/T^{1/4}}$.

Section IV of this paper will include arguments that the IC seen in the GaAs:Mn system is not of the hopping type, and that it corresponds with the $\sigma_2 e^{-E_2/kT}$ term in Eq. (3). Fritzsche[21] originally hypothesized, concerning this conduction, that (in p-type language) E_2 is associated with the energy necessary to place a second hole onto a neutral acceptor. Thus the "band" in which such conduction occurs was visualized by Fritzsche as being of positively charged acceptors (abbreviated as A^+ states). Some alternative mechanisms proposed since Fritzsche's suggestion have been reviewed by Pollak, [22] but the concept of conduction in A^+ states still seems to be the most viable. [18–19,23]

For a semiconductor doped with shallow impurities, it is the E_3 conduction which dominates the low-temperature behavior for a modest amount of doping (and some mandatory compensation). The E_2 form of IC only manifests itself with heavier doping and, in principle, may exert an influence only for an intermediate temperature range—though with sufficiently strong doping the E_3 conduction can be banished to indefinitely low temperatures. [18] E_2 and E_3 become indistinguishable as they collapse to zero for the critical impurity concentration N_c of a metal-nonmetal (MNM) transition, and the relationship between wave-function size and interimpurity spacing at the MNM transition condition is a matter of considerable discussion and literature.[19]

In one important sense, a semiconductor is not truly "metallic" until impurity overlap is so total that all acceptor states merge with the valence band, and E_1 also vanishes. However, in presenting the data which follows we shall speak of "metallic IC" when the *impurity* conduction itself is activationless, even though cooling from room temperature produces a massive depopulation of the valence bands.

II. EXPERIMENTAL

The manganese-doped GaAs used in this work came primarily from boat-grown crystals, grown in the [111] direction. Slices cut perpendicular to the growth axis were lapped to a 0.05-cm thickness, and bridge-shaped samples cut ultrasonically. These samples were then chemically polished in a nitric-hydrofluoric-acetic acid mixture, and Ohmic contacts of 95-at.% In and 5-at.% Zn were alloyed at 650 K. Each completed sample was glued at one end with model No. GE7031 varnish into a recessed insulating holder, which supported 0.005-cm gold wires from the sample contacts. This holder permitted safe transport of the sample from one cryostat to another. Evidence we shall present in the Sec. III vividly illustrates the need for the use of a minimum amount of GE7031 varnish, well away from the measurement area, in making mechanical and thermal contact between

the sample and its holder.

Measurements of the electrical conductivity and the Hall coefficient were made from room temperature downwards in a vacuum environment with cooling by a Cryo-Tip hydrogen-nitrogen Joule-Thomson refrigerator. (Data from 300 to 550 K was obtained in dry-nitrogen gas with an electrically heated enclosure which fitted between the magnet-pole pieces.) Conventional dc conductivity and Hall voltages (for a 4000-G magnetic field) were measured sequentially using a ten-channel scanning system and were recorded in digital form. The customary averages were made with respect to reversals of current and magnetic field, and data points were rejected for which the temperature drifted from its stabilized value during data acquisition.

Our Hall measurements were normally made as a matter of convenience with a 4-kG magnetic field, though we did verify with most samples that R_H was independent of field strength over the range 1–8 kG, both at room temperature and at low temperatures. For the samples which displayed "metallic" impurity conduction, it was possible to make Hall measurements down to 20 K, the low-temperature limit of our hydrogen Cryo-Tip. For these samples we verified that R_H at 20 K did not vary by more than 3% over this 1–8-kG range of mangetic field.

In view of this invariance of Hall coefficient, it may be presumed that all data lay within the "weak-field" Hall regime. The value of the Hall factor thus depends to some extent on the nature of the scattering mechanism. However, as a matter of convenience and simplicity, we arbitrarily decided to set the Hall factor as unity for the free-hole-conduction region and assumed that

$$p_0 = (1/eR_H) \tag{4}$$

in material characterization. In three of the figures which follow, an ordinate scale labeled as p_0 means that the quantity $1/eR_H$ is plotted. Now obviously $1/eR_H$ is very different from p_0 in the low-temperature IC region, but for the determination of bulk parameters from

$$\frac{p_0(p_0+N_d)}{N_a-N_d-p_0} = \frac{N_v}{\beta}\, e^{-E_a/kT}$$

$$= 4.27\times10^{14} T^{3/2} e^{-E_a/kT}\ \text{cm}^{-3}, \tag{5}$$

the resulting systematic error in quotations of N_a, N_d, and E_a should be trivial.

For each of our samples, Hall data from the highest temperature employed to the lowest temperature unaffected by IC was fitted to Eq. (5) in a nonlinear least-squares plot, using an IBM 360-44 or Univac 1108 computer. The Fermi level moved in a range compatible with the correctness of Eq. (5) in all cases. Table I shows the values of N_a, N_d, and E_a deduced in this way for ten GaAs:Mn samples in which we have studied IC. The quantities E_1 of Eq. (3) and E_a of Eq. (5) both describe the same process (conduction by free holes), but E_a is the more exact characterization of the thermal-ionization energy. It will be noted from Table I that E_a is much smaller for these samples than the 0.110-eV value of a very weakly doped sample.

III. IMPURITY CONDUCTION RESULTS

Figure 1 typifies the conduction behavior of GaAs:Mn samples doped with a little more than 10^{19} cm^{-3} of manganese. Cooling from room temperature shows the steady loss of conductivity due to reduction of p_0, and IC takes over a little below 100 K. Sample Nos. M9 and M16 have activationless or metallic IC, yet the comparably doped and compensated sample Nos. M12 and M15 have a distinct activation energy for IC. The measured values for E_2 for these and other samples appear in the last column of Table I. The companion data for Hall effect is shown in Fig. 2, with the ordinate of $1/eR_H$ described as a matter of convenience as the "free-hole density" p_0. It will be seen that the low-temperature values of $1/eR_H$ for the metallic sample Nos. M9 and M16 are more than three orders of magnitude smaller than the respective values of $N_a - N_d$. For sample Nos. M12 and M15, dashed curves at low temperatures indicate the disappearance of the Hall voltage below noise level.

For these same four samples, Fig. 3 displays the temperature dependence of the quantity σR_H which can correctly be described as the Hall mobility μ_H for the free-hole-conduction range. Interpretation of σ, R_H, and the combination σR_H must (at best) be treated in terms of a two-band model for the transition range, and we shall comment in the Sec. IV on the significance of σR_H in the IC regime. In the interim, μ_H or "Hall mobility" is a convenient name for the quantity displayed. The customary temperature dependence of phonon scattering is visible at high temperatures, and IC takes

TABLE I. Characterization of Mn-doped samples showing impurity conduction.

Sample no.	N_a (cm^{-3})	Compensation $K = N_d/N_a$	E_a (eV)	E_2 (eV)
M9	2.37×10^{19}	0.069	0.0657	0 (metallic)
M14	2.48×10^{19}	0.096	0.0614	0 (metallic)
M18	1.61×10^{19}	0.074	0.0641	0 (metallic)
M19	1.66×10^{19}	0.031	0.0748	0 (metallic)
M16	1.66×10^{19}	0.076	0.0616	0 (metallic)
M16A	1.66×10^{19}	0.076	0.0616	0.0089
M10	1.92×10^{19}	0.047	0.0700	0.0156
M12	2.46×10^{19}	0.039	0.0711	0.0165
M13	2.05×10^{19}	0.038	0.0718	0.0141
M15	2.25×10^{19}	0.054	0.0686	0.0161

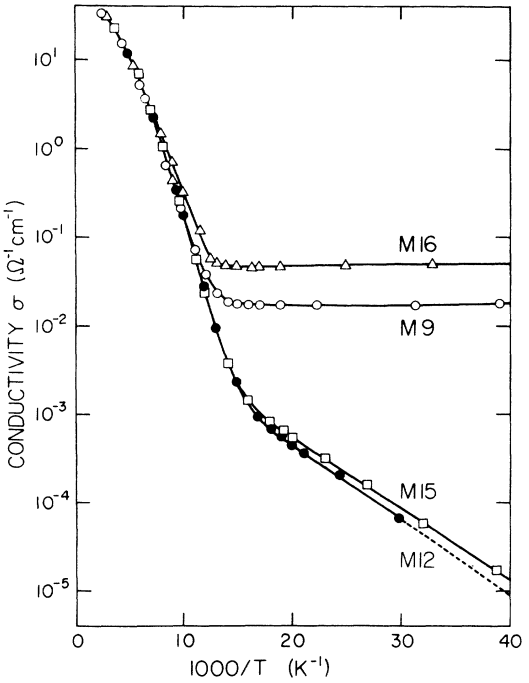

FIG. 1. Electrical conductivity vs reciprocal temperature for samples Nos. M16, M9, M15, and M12.

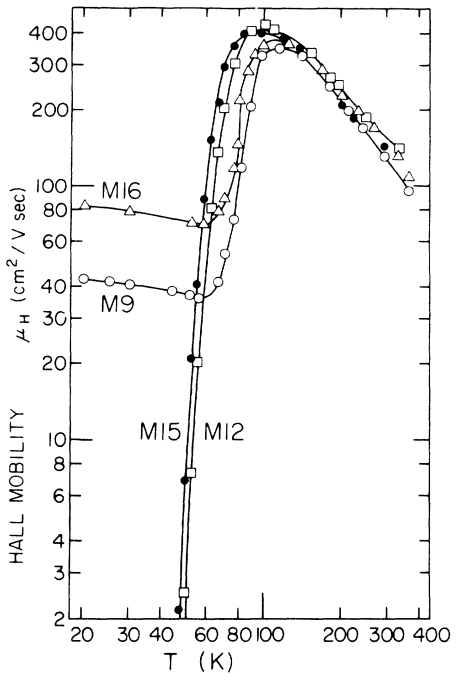

FIG. 3. Hall mobility $\mu_H = \sigma R_H$ vs temperature for the samples of Figs. 1 and 2.

over at low temperatures before one has much of a chance to see ionized impurity scattering of free holes.

Figure 4 demonstrates that the metallic IC seen for sample No. M16 of Figs. 1–3 is preserved essentially without change to much lower temperatures. Several other metallic-type samples were checked at 4.2 K with similar findings.

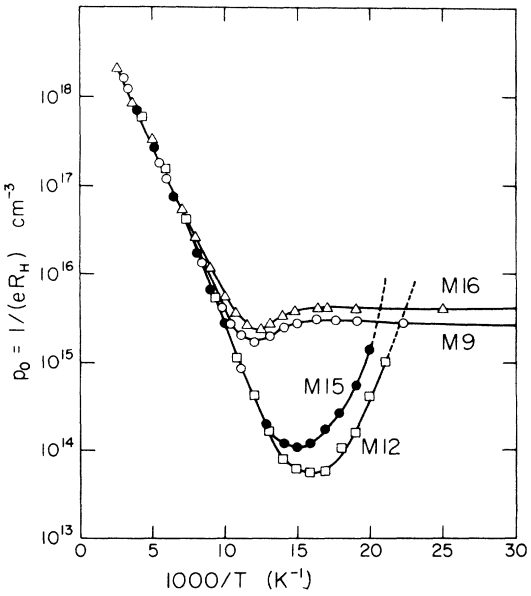

FIG. 2. Hall-effect data for samples Nos. M16, M9, M15, and M12 vs reciprocal temperature.

It was a matter of natural interest for us to explore whether the IC activation energy E_2 for manganese declines continuously to zero upon increased doping (as found for germanium with either antimony[18] or gallium[22] doping), or whether the collapse to a MNM transition is precipitous, as postulated by Mott.[24,25] Our examination of additional samples and crystals has not brought out any strong evidence of a continuous downwards progression of E_2. We make this comment despite the apparently intermediate activation energy of sample No. M16A in Fig. 5, a sample whose story we shall pick up again shortly.

In Fig. 5 (and in the companion, Figs. 6 and 7), sample No. M19 may in some respects be regarded as transitional. The conductivity of this sample is as conventionally metallic looking as for four other samples we studied, but $1/eR_H$ does reach a much more prominent low-temperature minimum than in any other metallic sample. This divergence is reflected in the curve for Hall mobility from 50 K downwards, and the low-temperature asymptote of Hall mobility is smaller than for any of the other metallic samples.

As will be discussed further in the Sec. IV, we believe that material inhomogeneity led to filamentary metallic conduction in all of the five samples listed in the upper part of Table I, and that this in-

homogeneity resulted in the different-seeming Hall behavior of sample No. M19. A clear indication of the effects of inhomogeneity lies in the behavior of sample No. M16A, which was cut as a miniature-sized sample from the central part of *metallic* sample No. M16. It is proper for us to note that the impurity distribution in the material of sample No. M16A could have been affected when contacts were affixed to this tiny sample, for it was too small for our usual alloyed contacts and had to be heated strongly while gold thermocompression bonds were made to it. Thus we must treat the IC results for sample No. M16A with more caution than for other samples. Even so, it seems very likely that sample No. M16 was a metallic-conduction sample via channels which were not included in the cross-sectional area of sample No. M16A.

There was a brief flurry of excitement when the conductivity data for sample No. M13 labeled σ(original) in Fig. 8 was plotted. This looked, surprisingly enough, as though it might be a candidate for the Mott $T^{1/4}$ relation in hopping conduction.[20] However, inspection of the sample mounting revealed an excessive amount of GE7031 varnish, indicating probable thermal strain and piezoresistance of the sample. As the second conductivity curve dramatically shows, re-etching and remounting in a strain-free manner returns this sample to activated IC behavior similar to that seen in four other samples.

The experience of IC in other semiconductor systems, notably those involving shallow impurities, leads one to anticipate weaker hopping-type IC in GaAs:Mn samples with $N_a < 10^{19}$ cm^{-3}. This we have looked for without success in numerous samples and conclude that any IC in such material has a conductivity of less than 10^{-7} ohm^{-1} cm^{-1}.

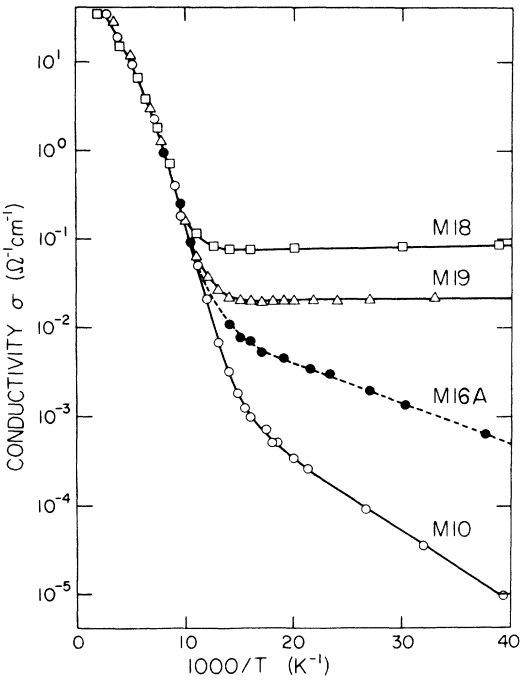

FIG. 5. Conductivity vs reciprocal temperature for samples Nos. M18, M19, M16A, and M10.

IV. DISCUSSION

It will be apparent from the tabulated values in Table I that our data does not show any neat divi-

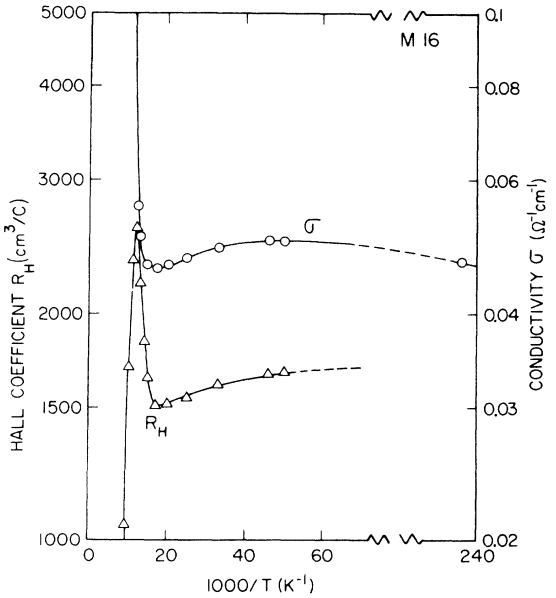

FIG. 4. Conductivity and Hall coefficient for M16, with the former extended downwards to 4.2 K.

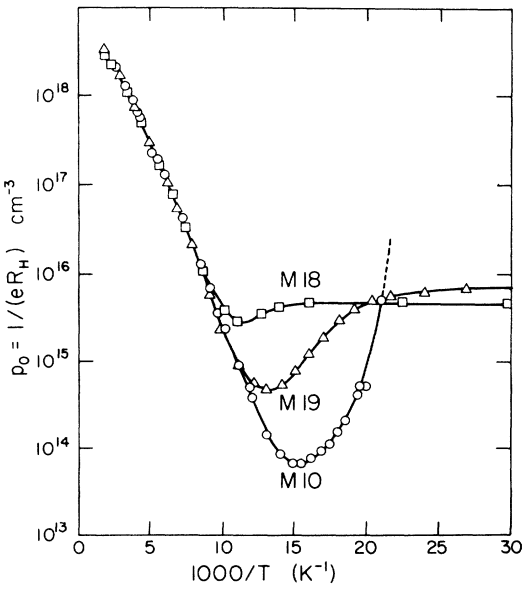

FIG. 6. Hall-effect data for samples Nos. M18, M19, and M10 vs reciprocal temperature.

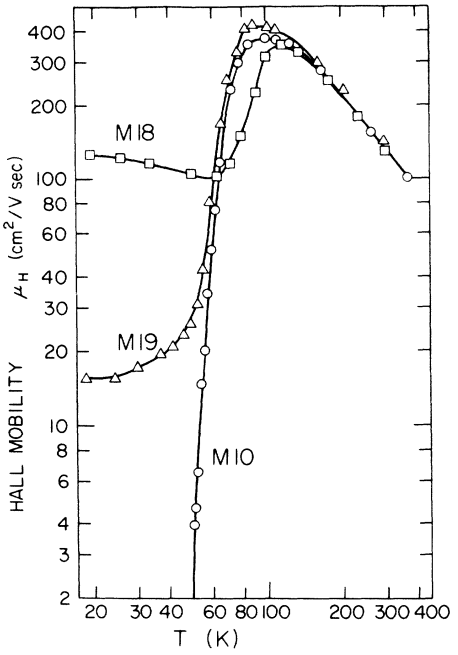

FIG. 7. Hall mobility $\mu_H = \sigma R_H$ vs temperature for the samples of Fig. 6.

sion of activated IC below some critical acceptor density N_c and of metallic IC for higher densities. We have done no more than indicate the range of values within which N_c must lie for completely homogeneous material, and the evidence strongly suggests that none of our crystals were truly homogeneous.

The distinction between the material properties of the two groups of samples in Table I does not lie alone in their election to display metallic conduction or not. Note that, with one exception (sample No. M19), the metallic group are perceptibly more compensated than the nonmetallic group. With the same notable exception, E_a has an appreciably smaller mean value for the upper group than in the lower group.

The small conductivity $\sigma_2 \cong 0.04\ \Omega^{-1}\,\mathrm{cm}^{-1}$ shown at low temperatures by the metallic IC samples is indicative of such conduction only within filamentary channels occupying a small portion of the entire cross section. For a comparison with the degenerate electron-gas conduction model of Mott and Twose[25] yields a meaningless value for the mean free path of 10^{-10} cm if the holes contributed by all acceptors are assumed to be active in conduction. Suppose alternatively that we take the value of $1/eR_H$ in the metallic conduction range at its face value as a density of participating "impurity-band" carriers and regard σR_H as the mobility of these carriers. This supposition does not work either, for the resulting "mean free path" still comes out as only a fraction of the interacceptor spacing.

Thus we conclude that metallic IC does not permeate the full volume of any of our samples. For the samples in the upper half of Table I, it occurs in enough connected microscopic regions to provide continuous metallic paths through the sample. For the samples in the lower half of Table I, any metallic regions are too sparse to achieve connectivity.

An extensive literature has accumulated on the topic of a MNM transition for a randomly distributed set of impurities in a semiconductor. For shallow (hydrogenic or effective-mass) impurities, Mott[24] and Mott and Davis[19] apply Thomas-Fermi screening arguments to suggest a critical concentration N_c such that

$$a_H N_c^{1/3} \simeq 0.20 \text{ to } 0.25. \tag{6}$$

The MNM transition was independently predicted by Hubbard.[26] He was able to show that electron-electron correlations will split a one-electron band into two pseudobands. For the impurity conduction problem, the separation of these pseudobands can be associated with the quantity we have referred to as E_2. Hubbard finds that each sub-band is broadened as the lattice parameter decreases, narrowing the gap between them. He is able to predict a critical concentration at which the gap disappears, and this critical concentration is essentially identical to that for Mott's screening argument in the derivation of Eq. (6).

In the construction of an empirical relation of the form of Eq. (6) for GaAs : Mn, we shall use the value $N_c = 2.1 \times 10^{19}\ \mathrm{cm}^{-3}$ which is the arithmetic mean

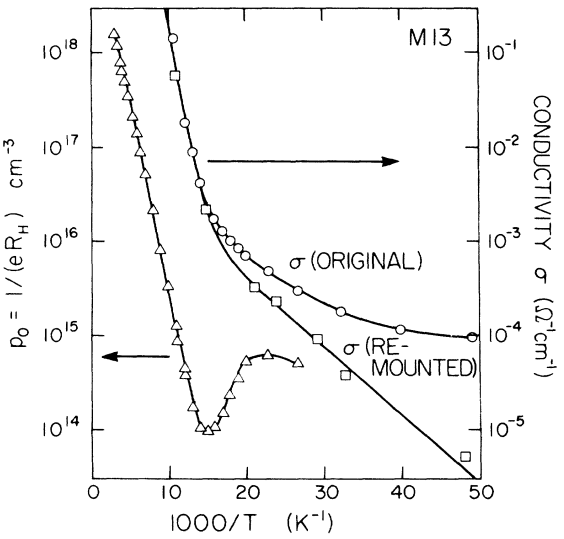

FIG. 8. Conductivity (before and after strain-free mounting) and Hall effect (after remounting) for sample No. M13 vs reciprocal temperature.

of N_a for all nine nonequivalent samples in Table I. Both the δ-function-potential[8] or quantum-defect[9,10] models suggest that $a_L = 10.1$ Å should be used as the characteristic wave-function radius, and then

$$a_L N_c^{1/3} = 0.28. \tag{7}$$

Thus manganese acceptors must be rather more closely spaced for a MNM transition than would be inferred from the Mott-Hubbard criterion. This apparent discrepancy is in fact entirely reasonable, for the radius a_L in the deep-acceptor wave functions is a much more real boundary for bound charge than is the Bohr radius of a scaled hydrogenic wave function. As an illustration of this contrast, 68% of the charge density for a hydrogenic 1s state lies *outside* a sphere of radius a_H, whereas only 14% of the charge density associated with the wave function of Eq. (1) lies outside a sphere of radius a_L.

Hubbard's electron-correlation approach[26] was extended when Kikuchi[27] explicitly considered a random array of centers. The potential fluctuations inherent in a doped semiconductor were included as the chief band broadening mechanism leading to disappearance of the gap. Kikuchi obtained good agreement with experimental values for E_2 in Sb-doped Ge, but only after considerable adjustment of the effective bound-state radius. Unfortunately, Kikuchi's model was solved numerically and graphically and did not lead to an analytic expression for E_2 which could readily be compared with other data. We have not felt justified in embarking on the extensive numerical work required for a comparison of his model with our data, partly because his graphical solution was specific for a situation of zero compensation. We shall discuss our data in terms of two specific analytic expressions arising from other models for E_2.

The character of a deep impurity bound state, in providing a large charge density within a sphere of radius a_L and not much outside, has much to do with our observations of E_2-type impurity conduction in samples doped just below the MNM transition, yet the absence of hopping conduction for less strongly doped samples. Conditions are most unfavorable for hopping conduction between manganese centers, for there is very little overlap until they get quite close to each other. Thus ψ^2 for the Lucovsky wave function [Eq. (1)] at a distance ma_L from a manganese center is smaller by a factor of $2m^2$ than ψ^2 for a hydrogenic state at distance ma_H.

Having concluded that hopping IC of the Mott and Twose[25] or Miller and Abrahams[28] type (tunneling between well-separated acceptors in a partly compensated system, with activation energy E_3) is not seen and should not be seen with our heavily doped GaAs:Mn, we must now rationalize the observed activated IC in terms of models for E_2-type conduction. As remarked in the Introduction, E_2-type conduction is often viewed as conduction in a "band' of A^+ states, though there have been alternative hypotheses.

One of these alternatives is the suggestion by Mycielski[29] that E_2 might be associated with the energy required for hopping *over* (as opposed to tunneling through) the Coulomb barrier between a full and an empty acceptor. He shows that for this process

$$E_2 = E_a^0 - (3Se^2/\kappa) N_a^{1/3}, \tag{8}$$

where E_a^0 is the thermal-ionization energy for an isolated acceptor (i.e., 0.110 eV for Mn in GaAs) and the dimensionless parameter S accounts for the distinction between $N_a^{-1/3}$ and the interacceptor spacing r_a. Mycielski considered the consequences for a set of impurities distributed over a hypothetical close-packed superlattice (equivalent to fcc symmetry, with 12 equidistant acceptor nearest neighbors); for this case $S = 0.89$, since $1/r_a = (N_a/\sqrt{2})^{1/3} = 0.89 N_a^{1/3}$. Equation (8) with S set at 0.89 for the GaAs : Mn system would not permit E_2 to collapse to zero until N_a exceeded 4×10^{19} cm^{-3}, and would require that $E_2 \simeq 0.03$ eV for $N_a = 2\times10^{19}$ cm^{-3}. This is, of course, much larger than the values of E_2 that we observe.

However, the acceptor distribution even in an ideally homogeneous real semiconductor does not lie upon a regular superlattice; there is a distribution of interacceptor spacings. Conduction as envisaged by Mycielski would be heavily weighted by those interacceptor spacings which are smaller than the average value. Thus it seems legitimate to find a value for S which yields an approximately correct value for E_2; we expect the parameter S to exceed 0.89 to a degree which reflects the increased importance of transitions to acceptors at less than the average spacing.

The entirely plausible choice $S = 1.15$ permits E_2 for Mn acceptors to collapse to zero for an acceptor concentration $N_a = 2.1\times10^{19}$ cm^{-3}. This choice for S results in $E_2 = 0.015$ eV for $N_a = 1.4\times10^{19}$ cm^{-3}. Thus the Mycielski model is not incompatible on energy grounds with the values for E_2 we have observed. This contrasts with the experience of Pollak[22] with Ga-doped Ge, who could not compare his values of N_a and E_2 with Mycielski's model except by adoption of a (physically unreasonable) value for S considerably *smaller* than 0.89.

Since the Mycielski model envisages transitions of holes from full to empty acceptors, this conduction cannot take place unless there is some compensation. We were not successful in getting GaAs with a large manganese density and very small compensation, thus are not able to report on this factor relative to the viability of the Mycielski model.

Frood[30] has suggested that E_2 might be the energy necessary to excite a hole from an acceptor ground state to a band formed from excited states. This model has not found wide acceptance when compared with data for shallow impurities in semiconductors and seems much less plausible for a deep impurity system such as GaAs:Mn, in which the excited states are very shallow[31] compared with the ground-state binding energy.

Both Mikoshiba[32] and Nishimura[23] have considered hole conduction in a band (the A^+ band) formed from states of positively charged acceptors. Mikoshiba's model uses a hydrogenic model for the neutral impurity ground state, and a screened hydrogenic wave function for a hole in the weakly bound positive acceptor ion state. This model yields an expression for the effective activation energy

$$E_2 = E_a - (ne^2s^2/\kappa a_0^2)(a_0 + sr_a)\, e^{-sr_a/a_0}, \qquad (9)$$

Here the adjustable parameter n is the mean number of nearest neighbors, $s = 0.7$ is the screening parameter for an isolated A^+ ion, E_a is the acceptor ionization energy for the heavily doped material, and a_0 is the wave-function radius for the neutral state. Mikoshiba takes the interacceptor spacing r_a to be $r_a = (3/4\pi N_a)^{1/3}$, and statistical arguments for a random-acceptor distribution show that there is a high probability that any acceptor will have at least two other acceptors within such a distance. Substituting $E_a = 0.07$ eV for our heavily doped material in Eq. (9), using $a_0 = a_L = 10.1$ Å for a manganese neutral center, and requiring that E_2 decrease to zero for $N_a = 2.1\times10^{19}$ cm^{-3} yield the result that $n = 2.3$. This is in fact an entirely reasonable value for the effective number of cooperating neighbor acceptors, since we expect that each acceptor will usually be involved in hole-transfer traffic with either two or three other acceptors.

E_2 rises from zero with decreasing acceptor concentration at a rather slower rate for Mikoshiba's model than in Mycielski's model. The use of $E_a = 0.07$ eV, $a_0 = 10.1$ Å, and $n = 2.3$ in Eq. (9) yields an energy $E_2 = 0.015$ eV for an acceptor density $N_a = 1.1\times10^{19}$ cm^{-3}. This is a rather smaller acceptor density than those shown in Table I for samples with a finite E_2, but not to a degree which would indicate an incompatability between our results and the concept of IC in an A^+ band.

Thus our results for activated IC in GaAs:Mn could legitimately be interpreted on the basis of Mycielski's model,[29] but are also compatible with the predictions of E_2 arising from an A^+ band.[23,32] The later interpretation of E_2 is the one which has been found most readily applicable for discussions of IC with shallow impurity systems.[18,22]

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