[13]Note that while the correction due to CEC depends on the size of the system and vanishes at large N, the difference E^P-E^V remains constant instead.
[14]J. N. Mundy, Phys. Rev. B 3, 2431 (1971).
[15]C. H. Bennett, in *Comptes-Rendus du Dix-Neuvième Colloque de Métallurgie, Saclay, 1976* (Centre d'Etudes Nucléaires de Saclay and Institut National des Sciences et Techniques Nucléaires, France, 1977), Vol. 2.
[16]J. N. Mundy, T. E. Miller, and R. J. Porte, Phys. Rev. B 3, 2445 (1971).
[17]A. Da Fano, G. Jacucci, and A. Rahman, to be published.
[18]A. Seeger, private communication; B. Alefeld, private communication.

Negative Magnetoresistance in Very Strong Accumulation Layers on ZnO Surfaces

Y. Goldstein and Y. Grinshpan
The Racah Institute of Physics, The Hebrew University of Jerusalem, 91000 Israel
(Received 2 June 1977)

Negative transverse magnetoresistance was observed in quantized accumulation layers on the $(000\bar{1})$ face of ZnO single crystals. The results are interpreted in terms of surface scattering center with giant magnetic moments, possibly due to the formation of charged clusters. Good quantitative agreement is found between theory and experiment.

We report on magnetoresistance (MR) measurements in very strong accumulation layers on ZnO surfaces. The measurements were carried out at low temperatures T (2–80 K), with the magnetic field B perpendicular to the surface (transverse MR) and in the range of surface electron concentrations ΔN of 8×10^{12} to 7×10^{13} cm^{-2}. In this range the electrons in the accumulation layer become a quasi two-dimensional degenerate electron gas.[1,2] The MR was found to be negative over the entire experimental range. It depends quadratically on B/T for small B/T, and saturates at high B/T. The results are interpreted in terms of magnetic scattering centers with giant magnetic moments, of the order of $100\mu_B$ (where μ_B is the Bohr magneton). The agreement between theory and experiment is considered good.

Bulk negative MR has been observed by several workers[3-7] in doped semiconductors. Most of these workers concluded that the MR is caused by the presence of huge effective magnetic moments, up to $(50-100)\mu_B$. Measurements on surface channels,[8] on the other hand, almost always show the presence of only positive transverse MR and only in a very few instances was a negative effect found.[9-11] The most comprehensive work on negative transverse MR in surface channels is that of Eisele and Dorda[10] on silicon inversion layers, at relatively low electron concentrations ($\sim10^{12}$ cm^{-2}). These authors assume, somewhat arbitrarily, that the effective magnetic moment of the scattering centers is about $2\mu_B$. The negative effect they found, however, was partially masked by the sumultaneous presence of positive MR and thus it was difficult to compare their data to a theoretical model. Such a positive effect is absent in our samples up to the highest fields used (~60 kG).

The measurements were performed on the $(000\bar{1})$ polar face of ZnO grown by Airtron Co. The samples were cut, mechanically polished, and chemically etched. The bulk resistivity at the temperature range studied was effectively infinite. Small contacts were attached to the sides of the sample to serve as voltage probes for conductivity and Hall-effect measurements. The strong accumulation layers were obtained by exposing the surface to helium ions produced by an electrical discharge in helium atmosphere.[12]

Figure 1 shows semilog plots of the transverse MR, $\Delta\rho/\rho$, at 4.5 K vs B for different ΔN values. The straight lines in the figure were drawn with a slope of 2. We see that the negative MR is proportional to B^2 at low fields and tends to saturate at higher fields. The deviation from quadratic behavior occurs at lower fields the higher the value of ΔN, and $-\Delta\rho/\rho$ increases with increasing ΔN.

Figure 2 shows the dependence of $\Delta\rho/\rho$ on B/T for a fixed $\Delta N=6.5\times10^{13}$ cm^{-2}. The points corresponding to different temperatures follow the same curve, thus showing that $\Delta\rho/\rho$ is a function of B/T. At low B/T values, $\Delta\rho/\rho$ is proportional to $(B/T)^2$; it deviates from this square dependence for $B/T\gtrsim100$ G/K, and saturates (see below) at very high magnetic fields.

To explain our results one has to assume, similarly as in the semiconductor bulk, that part of the scattering is due to localized magnetic mo-

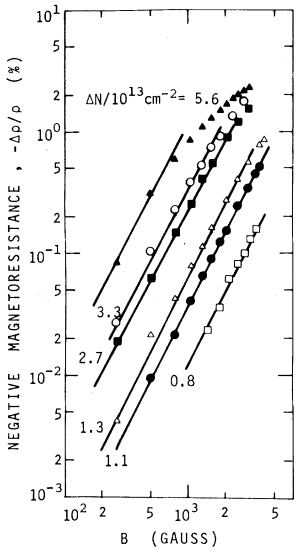

FIG. 1. Negative transverse magnetoresistance, $-\Delta\rho/\rho$, vs magnetic field B at 4.5 K for different ΔN values. Slope of straight lines is 2.

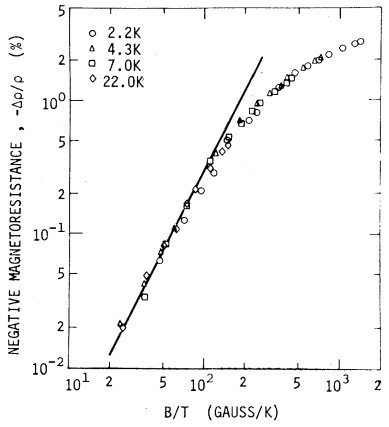

FIG. 2. $-\Delta\rho/\rho$ vs B/T for same sample as in Fig. 1 for $\Delta N = 6.5\times10^{13}$ cm^{-2} and different temperatures as marked. Slope of straight line is 2.

ments at the surface. As the moments align in the magnetic field, the scattering is reduced and a negative MR obtains. To compare our results quantitatively to a theoretical model we use a somewhat modified version of Boon's[13] theory for bulk semiconductors, as adapted by Eisele and Dorda[10] to surface channels. We express the magnetic-field-dependent surface conductance as

$$\Delta\sigma(B) = qN_+(B)\mu_+(B) + qN_-(B)\mu_-(B). \quad (1)$$

Here N_+ and N_- are the surface electron concentrations for spins parallel and antiparallel to the field, respectively; μ_+ and μ_- are the corresponding mobilities; and q is the magnitude of the electronic charge. We now rewrite Eq. (1) as

$$\delta\sigma_B = (q\Delta N/2)[\delta\mu_+(B) + \delta\mu_-(B)] + q\delta N[\mu_-(B) - \mu_+(B)], \quad (2)$$

where $\delta\sigma_B \equiv \Delta\sigma(B) - \Delta\sigma_0$, $\delta\mu_\pm(B) \equiv \mu_\pm(B) - \mu$, $\delta N \equiv [N_-(B) - N_+(B)]/2$, and $\Delta\sigma_0$ and μ are the conductance and mobility in the absence of the field. We assume that the magnetic scattering centers act in parallel with the magnetic-field-independent scattering centers and that the electronic mean free path $\lambda_\pm(B)$ is given by $1/\lambda_\pm(B) = 1/\lambda_0 + 1/\lambda_{s\pm}(B)$, where λ_0 is the mean free path due to the nonmagnetic centers and $\lambda_{s\pm}(B)$ is the mean free path due to the magnetic centers alone. Developing the theory along lines similar to Boon's[13] we obtain

$$\frac{-\Delta\rho}{\rho} \simeq \frac{\delta\sigma_B}{\Delta\sigma_0} = \eta^2\,\frac{1 + 1/\pi\lambda^2\Delta N}{1/\lambda^2 - \eta^2}, \quad (3)$$

where λ is the mean free path in the absence of a magnetic field and $\eta = \tanh(g\mu_B B/2kT)/\lambda_s$. Here $g\mu_B$ is the magnetic moment of the scattering centers, k is Boltzmann's constant, and λ_s is the mean free path due to the magnetic centers in the absence of a magnetic field.

Boon[13] and, following him, Eisele and Dorda[10] assumed that the second term in Eq. (2) is dominant and consequently neglected the first term. This approximation amounts to neglecting 1 in Eq. (3) compared to $1/\pi\lambda^2\Delta N$. While this may have been justified in the case of silicon surfaces, we find that on ZnO surfaces the opposite is true. For typical values of $\Delta N = 5\times10^{13}$ cm^{-2} and $\mu = 50$ cm^2/V sec, we obtain $\lambda = 60$ Å and $1/\pi\lambda^2\Delta N$ becomes about 0.02. Thus, in our case this term is the one that is usually negligible and we can write

$$\delta\sigma_B/\Delta\sigma_0 \simeq \eta^2/(1/\lambda^2 - \eta^2). \quad (4)$$

For a quasi two-dimensional electron gas we obtain approximately[2] $\lambda^2 \approx 2\pi(\hbar/q)^2\mu^2\Delta N$. In addition, usually $1/\lambda^2 \gg 1/\lambda_s^2$ and hence $\eta^2 \ll 1/\lambda^2$ so that

$$\delta\sigma_B/\Delta\sigma_0 \simeq 2\pi(\hbar/q)^2\mu^2\Delta N \tanh^2(g\mu_B B/2kT)/\lambda_s. \quad (5)$$

For low fields, this reduces to

$$\delta\sigma_B/\Delta\sigma_0 \simeq (\pi/2)(\hbar\mu_B/kq)^2(g/\lambda_s)^2\mu^2\Delta N(B/T)^2. \quad (6)$$

This $(B/T)^2$ dependence agrees well with the ex-

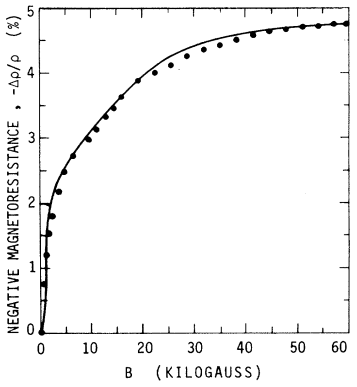

FIG. 3. $-\Delta\rho/\rho$ vs B at 4.2 K and $\Delta N = 7.5 \times 10^{13}$ cm^{-2}. Curve calculated by assuming two kinds of magnetic scattering centers as explained in text.

perimental results at low B/T values. Moreover, inspecting Fig. 1, we also find a qualitative agreement with respect to the dependence on ΔN. However, this may be fortuitous because both μ and g/λ_s are ΔN dependent. The values of g, as estimated from the deviations from quadratic behavior in Figs. 1 and 2, range from 35 at $\Delta N = 2.7\times10^{13}$ cm^{-2} up to 120 at $\Delta N = 6.5\times10^{13}$ cm^{-2}.

At higher fields, Eq. (5) [or Eq. (4)] cannot be fitted to the experimental data using a single value of g. The fast rise of the MR at low fields and a very gradual saturation at high fields (see Fig. 3) indicate that the MR must be due to at least two kinds of magnetic centers with different g factors. We can incorporate this in the theory by substituting $\eta_1+\eta_2$ for η in Eq. (4), where η_1 and η_2 pertain to the two kinds of centers, and are defined similarly to η using pertinent values of $g_{1,2}$ and $\lambda_{s1,2}$. In Fig. 3 we plot $-\Delta\rho/\rho$ (dots) vs B up to 60 kG. The curve was calculated for two kinds of magnetic centers, one with $g_1 = 100$ and $\lambda_{s1} = 970$ Å and the other with $g_2 = 6$ and $\lambda_{s2} = 1840$ Å. The agreement is seen to be good over the entire range.

The ZnO data presented are distinguished by the fact that the MR is negative over the entire experimental range. This is in contrast to other surface channels studied[9-11] where the positive MR largely masks the negative effect. The reason for this difference in behavior is that in ZnO channels the mobility is quite low (50–100 cm^2/V sec) so that the positive MR ($\simeq 0.4\mu^2B^2$) is expected to be only about 0.1% at 60 kG, which is negligible compared to the negative effect, about -5%. The reason for this rather surprisingly high negative MR may be due to the large g values of the scattering centers, which result in a strong influence on the conductivity, even at such low mobilities.

Several models have been suggested to account for localized magnetic moments in semiconductors but none of them explains satisfactorily the occurrence of the large moments encountered experimentally. Toyozawa[14] proposes a model in which part of the impurity sites in the doped semiconductor are relatively isolated and thus have localized moments. These sites interact with the conduction electrons as well as with some of the neighboring sites and in this way give rise to relatively large moments ($\sim 10\mu_B$). Boon[13] considers a disordered system where the low-energy electrons become localized and act as magnetic scattering centers. Andrianov *et al.*[5] suggest the formation of impurity clusters having relatively large magnetic moments. Any one of the above models, adapted to the surface, could explain the *functional* dependence of the observed negative MR. We have chosen to compare our results to the theory based on Boon's model[13] because its assumptions seem to be closest to the condition prevailing[11] in surface channels. However, for large magnetic moments, Toyozawa's theory[14] predicts also a square dependence of the MR on $\tanh(g\mu_B/kT)$. Thus, apart from a factor of 2 in g, both theories predict the same functional dependence.

The scattering mechanism in the ZnO surface channel is not quite understood yet. From mobility measurements[15,16] as a function of ΔN it appears that the dominant surface scattering is due to charged centers. It is very tempting to identify the charge in these centers with the positive charge on the surface necessary to balance the space charge in the accumulation layer. The occurrence of this charge in large clusters could explain the functional dependence of the mobility. Similar clusters were indeed found[17,18] at the Si-SiO_2 interface and were interpreted[19] as due to image forces. The giant magnetic moments found here may possibly be due to the electrons shielding these centers, in a similar way as proposed by Toyozawa[14] for the semiconductor bulk. The dependence of g on ΔN could then be due to increasing cluster size with increasing ΔN.

This work was initially supported by a grant from the United States–Israel Binational Science Foundation (BSF, Jerusalem, Israel) and subsequently by a grant from the Ministry of Technology and Research (GFK) of the Federal Republic of Germany.

[1]F. Stern and W. I. Howard, Phys. Rev. 163, 816 (1967).
[2]D. Eger, A. Many, and Y. Goldstein, Surf. Sci. 58, 18 (1976).
[3]W. Sasaki, J. Phys. Soc. Jpn., Suppl. 21, 543 (1966).
[4]R. P. Khosla and R. J. Sladek, J. Phys. Soc. Jpn., Suppl. 21, 557 (1966).
[5]D. G. Andrianov, G. V. Lazareva, A. Savel'ev, and V. I. Fistul', Fiz. Tekh. Poluprovodn. 9, 210 (1974) [Sov. Phys. Semicond. 9, 141 (1975)].
[6]E. I. Zavaritskaya, I. D. Voronova, and N. V. Rozhdestvenskaya, Fiz. Tekh. Poluprovodn. 6, 1945 (1972) [Sov. Phys. Semicond. 6, 1668 (1973)].
[7]O. V. Eml'yanenko, T. S. Lagunova, K. G. Masagutov, D. N. Nasledov, and D. D. Nedegolo, Fiz. Tekh. Poluprovodn. 9, 1517 (1975) [Sov. Phys. Semicond. 9, 1001 (1976)].
[8]T. Sugano, K. Hoh, H. Sakaki, T. Iizuka, K. Hirai, K. Kuroiwa, and K. Kakemoto, J. Fac. Eng., Univ. Tokyo, Ser. B 32, 245 (1973).
[9]K. Hess, Phys. Status Solidi (a) 31, 159 (1975).
[10]I. Eisele and G. Dorda, Phys. Rev. Lett. 32, 1360 (1974).
[11]S. Pollitt, M. Pepper, and C. J. Adkins, Surf. Sci. 58, 79 (1976).
[12]Y. Goldstein, A. Many, D. Eger, Y. Grinshpan, G. Yaron, and M. Nitzan, to be published.
[13]M. R. Boon, Phys. Rev. B 7, 761 (1973).
[14]Y. Toyozawa, J. Phys. Soc. Jpn. 17, 986 (1962).
[15]Y. Grinshpan and Y. Goldstein, to be published.
[16]M. Nitzan and Y. Goldstein, to be published.
[17]T. H. DiStefano, Appl. Phys. Lett. 19, 280 (1971).
[18]R. Williams and M. H. Woods, J. Appl. Phys. 43, 4142 (1972).
[19]R. Williams and M. H. Woods, Appl. Phys. Lett. 22, 458 (1973).

Electronic Structure of CeN Studied by X-Ray–Photoemission Spectroscopy

Y. Baer and Ch. Zürcher
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Hönggerberg, CH-8093 Zürich, Switzerland
(Received 25 July 1977)

The core levels and the valence-band region of CeN have been studied by x-ray photoemission. Clear evidence is found that Ce has a mixed valence between 3 and 4 in this compound. A comparison of the 4*d* spectra of the Ce pnictides and of pure Ce at different temperatures leads to the conclusion that the α phase of this metal corresponds very likely to an intermediate valence.

In many respects Ce shows quite exceptional properties, both in the pure metal and in compounds. These properties are related to the fact that Ce is the first element of the lanthanide series; its 4*f* shell is occupied by at most one single electron which has the largest orbital radius of the whole series and is expected to be very weakly bound. It is not well established today whether the peculiar behavior of Ce, which manifests itself in anomalous changes of the lattice constants, has to be attributed to a delocalization of the 4*f* states forming a band or to an intermediate valence arising from an interplay of 4*f* states with 5*d* states.

The $\gamma \rightarrow \alpha$ transition in pure metallic Ce provides apparently one of the clearest examples of a transition driven by a configuration modification in the outermost electronic levels. The magnetic and lattice constant data[1] can be explained in a promotion model by a valence change from 3.0 to 3.7, which should be clearly reflected by photoemission spectra. Unfortunately the hydrostatic pressure required to produce the α phase at low temperature cannot be realized at the present time in the existing photoelectron spectrometers. The available spectra[2,3] correspond to the trivalent γ phase (with only a low concentration of α phase for cooled samples). Until now it has not been possible to locate by photoemission the energy position of the occupied 4*f* level in γ-Ce. An attempt has been made to analyze the x-ray–photoemission spectroscopy (XPS) spectra of the valence bands of La, Ce, and their aluminum alloys. An ingenious but questionable manipulation of the data places the 4*f* states 0.5 eV below the Fermi energy.[4]

In the XPS spectra of Ce halides, the position of the 4*f* level could be determined by comparison with La halides.[5] In CeF_3, only an isolated peak above the valence states is observed. In the available spectra of Ce pnictides (CeAs, CeSb) the situation is again quite confusing.[6] No characteristic 4*f* structure is found, although it is established that these compounds are trivalent at room temperature. Magnetic data might provide indications of a valence modification at low temperatures.[7] In addition, CeP shows an anomalous volume contraction at a pressure of 100 kbar,[8]