PHYSICAL REVIEW B VOLUME 49, NUMBER 11 15 MARCH 1994-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Resonant donors in semiconductors: Sc impurity in CdSe and $Cd_{1-x}Mn_xSe$

P. Głód and T. Dietl
Institute of Physics, Polish Academy of Sciences, PL-02 668 Warszawa, Poland
and Institut für Halbleiterphysik, Johannes Kepler Universität Linz, A-4040 Linz, Austria

T. Fromherz and G. Bauer
Institut für Halbleiterphysik, Johannes Kepler Universität Linz, A-4040 Linz, Austria

I. Miotkowski
Department of Physics, Purdue University, West Lafayette, Indiana 47907

(Received 4 October 1993; revised manuscript received 24 January 1994)

The electronic structure of the ground state associated with a resonant Sc donor in CdSe and $Cd_{1-x}Mn_xSe$ was investigated by far-infrared reflectivity and millikelvin magnetoresistance measurements. Similarities in the results for samples doped either with Sc or with In, particularly in the spectral region of the $1s$-$2p$ excitations and near the metal-insulator transition, demonstrate that the ground state of the Sc impurity is hydrogenic. Thus, our findings prove that the Coulombic part of the potential of a resonant donor impurity can create hydrogenic states in the forbidden energy gap. Furthermore, the data provide support for the two-fluid model of electronic states in the vicinity of the metal-insulator transition.

Doping of II-VI compounds has attracted a renewed interest in connection with light-emitting diodes,[1] effects of persistent photoconductivity,[2,3] and physics of charge transport in the vicinity of the metal-to-insulator transition (Refs. 2 and 4–8). In this context, doping of II-VI semiconductors with transition metals is of particular interest, as it can result in electronic properties which differ from those of materials doped with the standard group-III or group-VII substitutional impurities. Indeed, recent studies of zero-gap HgSe containing resonant donors Fe demonstrated clearly how Coulomb interactions among ionized donors stabilized an inhomogeneous mixed-valence phase, and thus resulted in an enhanced low-temperature mobility of conduction-band electrons.[9] Another interesting dopant appears to be Sc, as according to the Langer-Heinrich diagram,[10] the level derived from Sc $3d$ shell is expected to be degenerate with the conduction-band continuum of states in CdSe. It has been suggested[5] that such resonant donors could result in the formation of a "dilute metal," in which the absence of hydrogenic binding centers could lead to an alteration of the dominant mechanisms which induce electron localization.

Previous studies of Sc doped CdSe (Refs. 11 and 12) and $Cd_{0.95}Mn_{0.05}Se$ (Ref. 12) showed that such doping produces electrons, and therefore Sc acts as a shallow or resonant donor. In view of the electron configuration of Sc atoms ($3d^14s^2$) this means that states derived from the Sc $3d$ shell are located somewhere in the vicinity of the conduction-band edge.

In order to probe the nature of states introduced by Sc we have carried out a series of far-infrared reflectivity and magnetotransport measurements of CdSe and $Cd_{0.95}Mn_{0.05}Se$, doped either with Sc or In.[13] Our results demonstrate that in the studied materials the ground state of the Sc impurity forms a shallow effective-mass state, which is created by the long range Coulombic part of the impurity potential. Furthermore, the data allow us to estimate the lower limit of the energy separation between the resonant $3d$-like Sc level and the bottom of the conduction band.

Single crystals of CdSe and $Cd_{0.95}Mn_{0.05}Se$ were grown by the Bridgman technique with controlled selenium pressure. An appropriate amount of Sc or In had been added directly to the melt. The doping efficiency was quantitatively examined by room-temperature Hall measurements. We found a high doping efficiency for both Sc and In, typically better than 50% up to the electron concentrations of 5×10^{18} cm^{-3} which were the highest studied in this work. We also checked the impurity content by secondary ion mass spectroscopy and atomic emission spectroscopy. The former method exhibited an adequate sensitivity for both Sc and In impurities in CdSe and $Cd_{1-x}Mn_xSe$, and gave the respective Sc or In concentrations which agreed with the corresponding electron concentrations n_H resulting from the room temperature Hall data. Furthermore, we found that CdSe:Sc and CdSe:In with $n_H = 2\times10^{17}$ cm^{-3} showed only a weak, i.e., less than 1%, metastable change of the resistance after illumination at 4 K.

Far-infrared reflectivity measurements were performed in a Fourier spectrometer on samples which had been polished and then etched in a 5% solution of Br_2 in CH_3OH. The spectra for a nominally undoped CdSe sample with

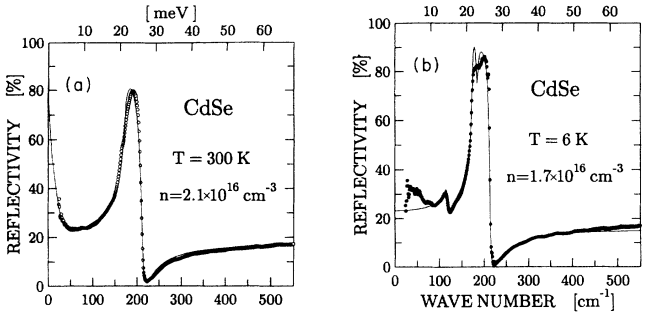

FIG. 1. Reflectivity spectra for a nominally undoped CdSe sample with a Hall concentration of $n_H = 4 \times 10^{16}$ cm^{-3} at 300 K, measured at 300 K (a) and 6 K (b). Solid lines represent the best fit describing the electron contribution to the dielectric function by a Drude term at 300 K and by a $1s$-$2p$ hydrogenic excitation at 6 K. The electron concentrations resulting from the fits are denoted by n.

a room-temperature Hall concentration $n_H = 4 \times 10^{16}$ cm^{-3} are shown for $T = 300$ K (open circle) and $T = 6$ K (full circles) in Fig. 1. In Fig. 2 the spectra for two In doped samples ($n_H = 2 \times 10^{17}$, $n_H = 4 \times 10^{17}$ cm^{-3}, respectively) are shown, as well as for two Sc doped samples which have the same Hall concentrations as the In doped ones. Since the metal-to-insulator transition occurs at 3×10^{17} cm^{-3} in n-type CdSe (Refs. 14 and 15), the doped samples cover the two sides of the transition. In addition to the reststrahlen structure due to the optical phonons with $\omega_{TO} = 175$ cm^{-1}, the low frequency region of the reflectivity spectrum contains a contribution from the carriers. As shown by solid lines, their contribution to the dielectric function can be described by the Drude term with the carrier concentration n that is in a reasonable agreement with n_H at 300 K. At low temperatures, however, because of electron freeze-out on impurities, the reflectivity spectrum changes considerably in the frequency range below 150 cm^{-1}. In the case of the undoped sample (Fig. 1) a sharp $1s$-$2p$ line is observed at 120 cm^{-1}. Its good agreement with a hydrogenic impurity model demonstrates that most of the electrons freeze out on noninteracting shallow centers. Though somewhat broadened, the same hydrogenlike impurity transition appears also for both In and Sc doped samples at low temperatures (Fig. 2). We conclude therefore that Sc and In create similar shallow effective-mass states in CdSe. However, in addition to the structure originating from localized electrons, a Drude-like contribution appears to persist in the reflectivity spectra of the doped samples down to 6 K. Our findings provide, therefore, evidence for a phenomenological two-fluid model of the electronic states at the localization boundary. Indeed, in this model[7,8,16] the electrons occupy two distinct sorts of states: strongly localized states and Fermi-liquid states, the latter contributing to the low frequency conductivity. In order to estimate their relative concentrations we fitted our 6 K spectra with both intraimpurity and the Drude term included. According to the results of the fitting procedure, presented by solid lines in Fig. 2, about 30% and 15% of the electrons reside in the strongly localized states for $n_H = 2 \times 10^{17}$ and 4×10^{17} cm^{-3}, respectively. The remaining electrons were recovered to contribute to the Drude-like conductivity.

The similarity of Sc and In impurity states has further been confirmed by results of millikelvin magnetotransport measurements on n-type $Cd_{1-x}Mn_xSe$. Previous magnetotransport studies of that material[4,6] and

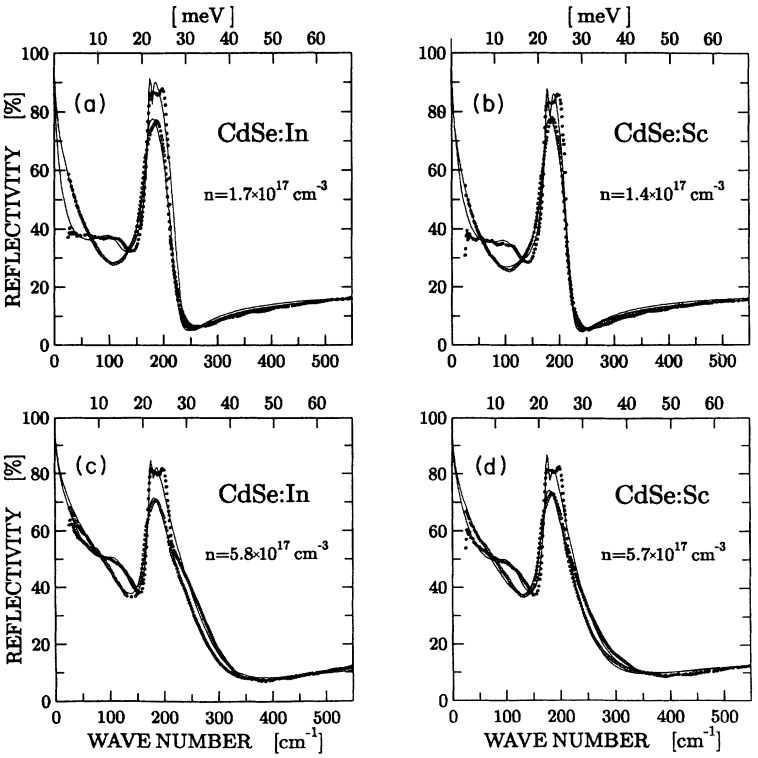

FIG. 2. Reflectivity spectra for In and Sc doped CdSe at 300 K and 6 K (open and full circles, respectively). Solid lines represent the best fit to data taken at 300 K and 6 K. The electron concentrations resulting from the fits at 300 K are denoted by n. The room temperature Hall concentrations are (a) 2×10^{17}, (b) 2×10^{17}, (c) 4×10^{17}, (d) 4×10^{17} cm^{-3}.

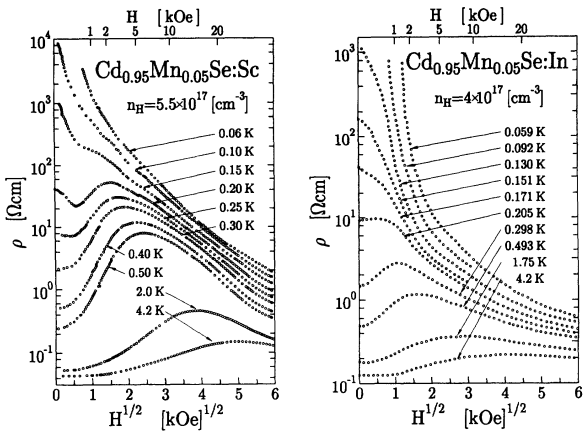

FIG. 3. Magnetoresistance of n-type $Cd_{0.95}Mn_{0.05}Se$ doped with Sc and In for samples with electron concentrations close to the metal-to-insulator transition. Data for the In doped sample are taken from Ref. 7.

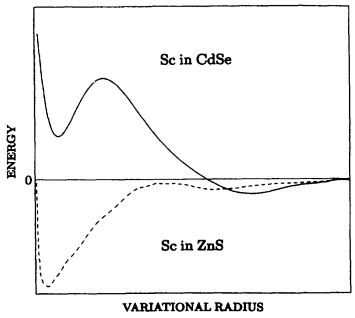

FIG. 4. Schematic representation of the electron ground state energy with respect to the conduction-band edge vs radius of a trial wave function in CdSe:Sc and ZnS:Sc. Minima correspond to the local and hydrogenic states.

$Cd_{1-x}Mn_xTe$ (Ref. 2) in the vicinity of the metal-to-insulator transition revealed a strong increase of the resistivity with decreasing temperature, accompanied by the appearance of a giant negative magnetoresistance. This behavior is completely different from that of nonmagnetic n-type CdSe.[4,7,14,15] These results were interpreted (Refs. 6–8) in terms of the two-fluid model discussed above. According to this model the conversion of extended into localized states starts already on the metal side of the transition. In magnetic semiconductors, localized electrons polarize within their Bohr orbits the Mn spins via s-d exchange coupling, thereby creating ferromagnetic bubbles. Such complexes are known as bound magnetic polarons, which act as centers of additional spin-disorder scattering for itinerant electrons. Their scattering efficiency is proportional to magnetic susceptibility, and therefore varies strongly with temperature and magnetic field. Furthermore, it can be expected that this efficiency depends rather substantially on the wave function of the impurity ground state. Accordingly, we compare in Fig. 3 the magnetoresistance at various temperatures of $Cd_{0.95}Mn_{0.05}Se$ samples doped with either Sc ($n_H = 5.5 \times 10^{17}$ cm^{-3}) or with In ($n_H = 4 \times 10^{17}$ cm^{-3}). It is seen that the data for either In or Sc doped $Cd_{0.95}Mn_{0.05}Se$ samples are quite similar. Thus, the results presented in Figs. 1–3 demonstrate that Sc creates a shallow-donor effective-mass state in the energy gap, just as In, which is a standard group-III substitutional donor. This surprising fact can be reconciled with the electronic structure of Sc assuming that according to the Langer-Henrich diagram[10] a state derived from the Sc $3d$ level is resonant in CdSe, i.e., is located above the bottom of the conduction band.

Applying hydrostatic pressure up to 23 kbar does not change the electron concentration in CdSe:Sc ($n_H = 5 \times 10^{18}$ cm^{-3}, $E_F = 81$ meV).[17] Consequently we estimate that the resonant level associated with Sc is at least 0.2 eV above the bottom of the conduction band. Thus, as shown schematically in Fig. 4, the experimentally observed $1s$ hydrogenic ground state associated with the Sc^{3+} ion results from the *long range Coulombic portion* of the total scandium impurity potential, possibly disturbed slightly by a short range core contribution. Such an interpretation is consistent with the absence of a Sc electron paramagnetic resonance signal in CdSe:Sc,[17] and its presence in ZnS:Sc.[18] In the latter material, the conduction-band edge lies above the $3d$-like state which is thus located in the energy gap.[10]

In conclusion, our results provide the experimental proof that the long range Coulombic part of the potential of resonant impurity states introduces hydrogenic states within the energy gap. This conclusion contradicts previous suggestions[5] about the possibility of the formation of a "dilute metal" in open-gap semiconductors doped with resonant impurities.

We thank M. Baj, C. Benoit à la Guillaume, J. M. Langer, and M. Sawicki for valuable comments. This work was supported in part by Polish KBN Grant No. 204669101, FWF Vienna Project No. 8446 TEC, and U.S.-Poland Maria Curie-Skłodowska Joint Found II through Grant No. PAN/NSF-92-113.

[1] M. Haase, J. Qui, J. DePuydt, and H. Cheng, Appl. Phys. Lett. **59**, 1272 (1991); H. Jeon *et al.*, *ibid.* **59**, 1945 (1991).
[2] I. Terry, T. Penney, S. von Molnar, and P. Becla, Phys. Rev. Lett. **69**, 1800 (1992).
[3] T. Wojtowicz, S. Koleśnik, I. Miotkowski, and J. K. Furdyna, Phys. Rev. Lett. **70**, 2317 (1993).
[4] T. Dietl, J. Antoszewski, and L. Świerkowski, Physica B+C (Amsterdam) **117-118**, 473 (1983).
[5] J. Gebhardt, G. Nimtz, B. Schlicht, and J. P. Stadler, Phys. Rev. B **32**, 5449 (1985); T. F. Rosenbaum, S. B. Field, D. A. Nelson, and P. B. Littlewood, Phys. Rev. Lett. **54**, 241 (1985).
[6] M. Sawicki *et al.*, Phys. Rev. Lett. **56**, 508 (1986).
[7] T. Dietl *et al.*, Phys. Scr. **T14**, 29 (1986).
[8] T. Dietl *et al.*, Phys. Rev. B **43**, 3154 (1991).
[9] A. Mycielski, J. Appl. Phys. **63**, 3279 (1988); Z. Wilamowski, K. Świątek, T. Dietl, and J. Kossut, Solid State Commun. **74**, 833 (1990).

[10] J. M. Langer, C. Delerue, M. Lannoo, and H. Heinrich, Phys. Rev. B **38**, 7723 (1988), and references cited therein.
[11] J. M. Baranowski and J. M. Langer, Phys. Status Solidi B **48**, 863 (1971).
[12] P. Głód *et al.*, Acta Phys. Pol. A **79**, 389 (1991).
[13] Preliminary report of this work was given in P. Głód *et al.*, Proceedings of the 17th International Conference on Defects in Semiconductors, Gmunden, 1993 [Mater. Sci. Forum **143-147**, 693 (1994)].
[14] D. M. Finlayson, J. Irvine, and L. S. Peterkin, Philos. Mag. B **39**, 253 (1979).
[15] Y. Zhang, P. Dai, M. Levy, and M. P. Sarachik, Phys. Rev. Lett. **64**, 2687 (1990).
[16] R. N. Bhatt and D. S. Fisher, Phys. Rev. Lett. **68**, 3072 (1992), and references cited therein.
[17] A. Sienkiewicz, H. Przybylińska, E. Litwin-Staszewska, P. Głód, and T. Dietl (unpublished).
[18] A. O. Barksdale and T. L. Estle, Phys. Lett. **42A**, 426 (1973); I. Broser and M. Schulz, J. Phys. C **7**, L147 (1974); M. Godlewski *et al.*, *ibid.* **14**, 2835 (1981).