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Effect of deep levels on semiconductor carrier concentrations in the case of "strong" compensation

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We analyze the carrier concentrations ($\equiv p$) resulting from both shallow and deep majority levels. We show that for comparable concentrations of shallow and of compensating levels, a small fraction of deep levels can decrease p by orders of magnitude. Also, a quantitative criterion for obtaining semi-insulating material is derived, and implications for obtaining conducting wide-band-gap materials are discussed. Another result: a steep ("deep") slope of $\ln p$ vs $1/T$ can result even from small percentages of deep levels.

The theory of the carrier concentrations in semiconductors is by now very well established.[1] However, some of the implications of the solutions in the case of "strong" compensation and deep impurity levels have apparently not been fully realized. This will be the case treated here, where by strong compensation (as applied to a p-type semiconductor) we mean

$$N_{A1} < N_D < (N_{A1} + N_{A2}) \quad , \tag{1}$$

with N_{A1} the concentration of a shallow acceptor (of energy E_1), N_{A2} that of a deep acceptor (of energy E_2), and N_D that of the donors of energy above E_2. It can be noted that the second part of Eq. (1), i.e., $N_D < (N_{A1} + N_{A2})$ determines that the material is p type.

Before giving the results of the present calculatons, I first wish to point out two systems of present interest where these results are of relevance. One is semi-insulating GaAs and related materials.[2] The second is large-band-gap semiconductors, where it has generally proven difficult to obtain well-conducting material.[3] It will be shown by the present work that the criterion for obtaining semi-insulating material is the first part of Eq. (1), i.e., $N_{A1} < N_D$ (or correspondingly $N_{D1} < N_A$ for n type), and that the second difficulty can be understood by a combination of a tendency toward compensation[4] plus some deep levels (even at low concentrations). A further point of interest is that, again for strong compensation, the temperature dependence of the carrier concentration can appear to give evidence of deep levels only (i.e., give E_{A2} as the activation energy) even with shallow levels present in larger concentration, i.e., $N_{A1} >> N_{A2}$.

With several majority levels, the implicit equation for the carrier concentration for monovalent levels has been given by Blakemore[1] (p. 156, Eq. 331.3). For two such levels, the resultant equation is cubic. Neglecting excited states and any change of E_2 with temperature (where inclusion of these factors would be tedious but straightforward), and for the Fermi level at least several kT above the valence band (for p material) this equation can be put in the form

$$\begin{aligned} x^3 &+ (x^2/g)[\exp(-\epsilon_1) + \exp(-\epsilon_2) + (gN_D/N_v)] \\ &+ (x/g^2)\{\exp[-(\epsilon_1+\epsilon_2)] - (gN_{A1}/N_v)[\exp(-\epsilon_1) + R\exp(-\epsilon_2)] + (gN_D/N_v)[\exp(-\epsilon_1)+\exp(-\epsilon_2)]\} \\ &+ (1/g^3)\{(g/N_v)[N_D - N_{A1}(1+R)]\exp[-(\epsilon_1+\epsilon_2)]\} = 0 \quad . \end{aligned} \tag{2}$$

Here R is the ratio of deep to shallow acceptor levels ($\equiv N_{A2}/N_{A1}$), N_v is the valence-band density of states, g is the acceptor degeneracy factor (assumed the same for both levels), $\epsilon_i = E_i/kT$, and $x = p/N_v$ where p is the hole concentration.

Equation (2) is quite general, but here I wish to emphasize the case $R << 1$, since this is the case which has been previously neglected and which is quite interesting. A plot of Eq. (2) for several such R 's is shown in Fig. 1, where (p/N_v) is given as a function of "closeness of compensation" $1-K$, where $K \equiv N_D/(N_{A1}+N_{A2})$ is the overall degree of compensation. The parameter values selected are expected to be typical for p-ZnSe, namely, $E_1 = 0.1$ eV, $E_2 = 0.7$ eV, $N_{A1} = 10^{17}$ cm^{-3}, $m^* = 0.75$, $g = 4$, and where the plot is shown for 300 K. It can be seen that for $(1-K) \approx R$, i.e., $N_D/N_{A1} \approx 1 - R^2 \approx 1$, there is a very drastic decrease in p for a very slight change in $(1-K)$, i.e., in N_D. For example, for $R = 0.01$, p at this point decreases by about five orders of magnitude for a 0.1% increase in N_D. Physically, this sharp decrease is easily understood: The Fermi level in the high-p range is close to the shallow level, but for $N_{A1} < N_D$ it is essentially pinned at the deep level. It is also interesting to note that although in the absence of deep levels ($R = 0$) p does decrease

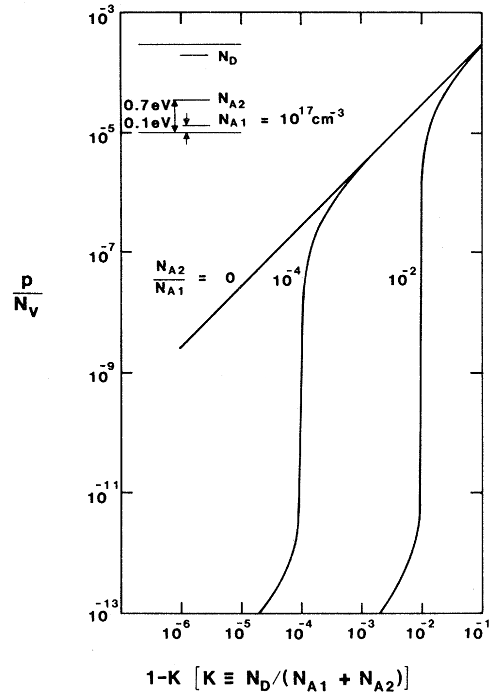

FIG. 1. Normalized 300-K hole concentration (p/N_v) plotted vs closeness of compensation $(1-K)$, where $K \equiv N_D/(N_{A1}+N_{A2})$, for different ratios of deep to shallow levels (N_{A2}/N_{A1}), and with the other parameters appropriate to *p*-ZnSe (see text).

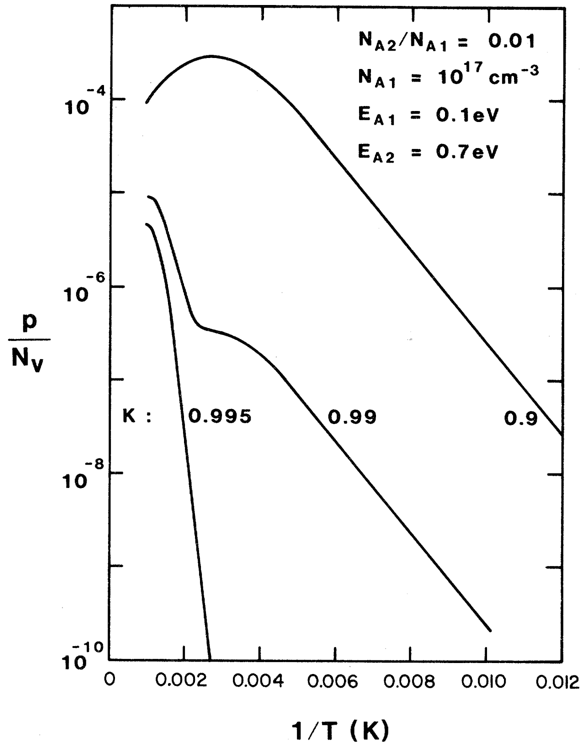

FIG. 2. Normalized hole concentration (p/N_v) vs reciprocal temperature for $N_{A2}/N_{A1}=0.01$ and various degrees of compensation (K). Other parameters as in Fig. 1.

with increasing compensation, i.e., decreasing $(1-K)$, this decrease is relatively slow; extremely close compensation would be required for very low carrier concentrations—for example, since $N_v = 1.63 \times 10^{19}$ cm^{-3}, one still obtains $p \approx 4\times 10^{12}$ for $(1-K)=10^{-4}$ (where reported carrier concentrations in *p*-ZnSe are less than this value[5]).

It is also of interest to check the temperature dependence of the carrier concentration. This is shown in Fig. 2 as (p/N_v) vs $(1/T)$ for three representative points in terms of the characteristics of Fig. 1: (1) $N_{A1} > N_D$, (2) $N_{A1} \approx N_D$, (3) $N_{A1} < N_D$. The results of the first case are standard and give a low-temperature slope of 0.1 eV (the decrease of p/N_v at high temperature is due to a continuing increase of N_v, whereas p tends toward saturation); the deep levels are present at too low a concentration to show up on the scale of the graph. For the second case, $N_{A1} \approx N_D$, both the shallow and the deep levels affect the result, and both the 0.1- and 0.7-eV slopes are seen. Lastly, for the case $N_{A1} < N_D$, *only* the deep (0.7-eV) slope is seen despite the fact that the shallow levels are present in far-larger concentration than the deep levels.

We now apply the present results to the class of "semi-insulating" materials.[2] It has long been known, and most frequently applied to GaAs, that the introduction of deep levels gives such material.[2] However, I am not aware of any prior quantitative prescription. Since from Fig. 1 one can see that there is an inflection point around $(1-K) \approx R$, this provides such a prescription via evaluation of $\partial^2(1-K)/\partial x^2 = \partial^2 N_D/\partial x^2 = 0$. I have solved Eq. (2) for N_D and obtained the second derivative. The result shows that for $(N_v/N_{A1})x \ll 1$, $\exp(-\epsilon_2) \ll \exp(-\epsilon_1)$, and $gx\exp(\epsilon_1) \ll 1$, where these conditions are expected to apply for most parameter ranges of intererst,

$$(N_{A1}/N_D) = 1 + O((N_v/N_{A1})x,\, gx\exp\epsilon_1,\, \exp(\epsilon_1-\epsilon_2)) \,. \tag{3}$$

This confirms the statement in the second paragraph that $N_{A1} < N_D$ is the criterion for obtaining semi-insulating material.

The present work also has implications in the area of conducting wide-band-gap semiconductors. It is known on thermodynamic grounds that such materials tend to be compensated.[4] From Fig. 1 it can be seen that for strong compensation the deep levels degrade the conductivity far beyond the value obtained at the same degree of compensation with only shal-

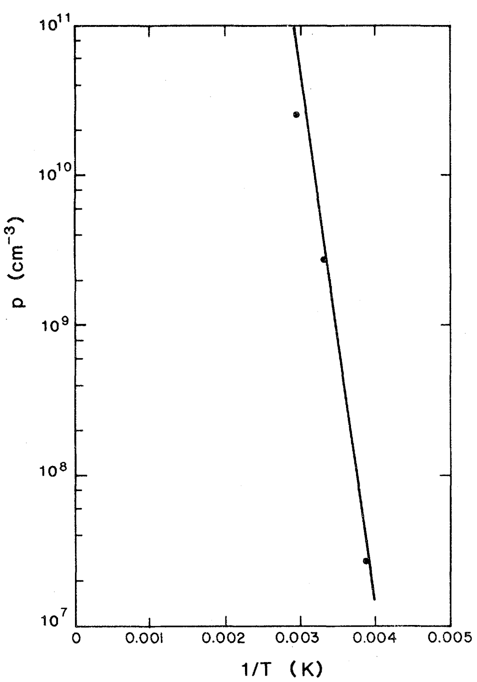

FIG. 3. Plot of hole concentration (p) vs reciprocal temperature. The dots represent the data for ZnSe (Li) given by Park *et al.* (Ref. 5), and the solid line is the fit given by Eq. (2), using $N_{A1} = 10^{17}$ cm^{-3}, $N_{A2}/N_{A1} = 0.1$, $K = 0.91$, $E_1 = 0.1$ eV, and $E_2 = 0.66$ eV.

low levels. Thus if a material has a tendency to incorporate accidental impurities with deep levels, it will be very difficult to obtain even partial conductivity (say $\rho \lesssim 100$ Ω cm). A second interesting aspect is that in such materials data of carrier concentation versus temperature frequently give a slope of a high activation energy, even when the intentional dopant is known to introduce a shallow level. An example here is ZnSe (Li). It is known from luminescence[6] that Li is a relatively shallow (0.114-eV) acceptor in ZnSe. However, a Hall study by Park *et al.*[5] showed an activation energy of 0.66 eV for material with 10^{-3} mol% Li (corresponding to 2×10^{17} atoms Li/cm^3). We show a fit to their data in Fig. 3, using $N_{A1} = 10^{17}$ cm^{-3}, $N_{A2}/N_{A1} = 0.1$, $K = 0.91$, $E_1 = 0.1$ eV, and $E_2 = 0.66$ eV. The fit is good at room temperature and below, less so at the higher temperature; the latter is probably at least partly due to a decrease in the Hall factor,[7] possibly also to a decrease of E_{A2} with increasing temperature (if the deep level is not pinned to the valence band). It does not seem to have been previously realized that data such as these, with steep (deep) slopes, can be explained also by a concentration of shallow levels which is higher than that of the deep levels.

In conclusion, the present work has produced three main accomplishments. First, it has given a quantitative criterion ($N_{A1} < N_D$ for p material, $N_{D1} < N_A$ for n type) for obtaining semi-insulating material. Second, it has given new insight into difficulties of preparing well-conducting wide-band-gap semiconductors. And lastly, it has shown that a slope, from carrier concentration versus $1/T$, which shows an E_A of deep levels, does not require that such deep levels be present at a dominant concentration.

ACKNOWLEDGMENTS

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[1] J. S. Blakemore, *Semiconductor Statistics* (Pergamon, New York, 1962).

[2] See, for example, *Semi-Insulating III-V Materials, Nottingham, 1980,* edited by G. J. Rees (Shiva, Kent, United Kingdom, 1980).

[3] See, for example, P. J. Dean, in *Defects and Radiation Effects in Semiconductors,* Institute of Physics Conference Series No. 46, edited by J. H. Albany (Institute of Physics, Bristol, 1979), p. 100; Y. S. Park and B. K. Shin, in *Topics in Applied Physics,* edited by J. I. Pankove (Springer, Berlin, 1977), Vol. 17, p. 133.

[4] See, for example, G. F. Neumark, J. Appl. Phys. 51, 3383 (1980); F. A. Kröger, *The Chemistry of Imperfect Crystals* (North-Holland, Amsterdam, 1964); G. Mandel, Phys. Rev. 134, A1073 (1964).

[5] A Hall measurement by Y. S. Park, P. M. Hemenger, and C. H. Chung, Appl. Phys. Lett. 18, 45 (1971) gave $p \approx 3 \times 10^9$ cm^{-3}, and other literature values are comparable.

[6] J. L. Merz, K. Nassau, and J. W. Shiever, Phys. Rev. B 8, 1444 (1973); and R. N. Bhargava, R. J. Seymour, B. J. Fitzpatrick, and S. P. Herko, *ibid.* 20, 2407 (1979).

[7] Park *et al.* (Ref. 5) assumed a Hall factor (r) of unity, where r is the ratio of Hall to drift mobility. Since $p \sim r$, a decrease in r with increasing temperature would manifest itself as a decrease in "effective" p. Such a decrease in r is likely; at low temperatures the dominant scattering is expected to be by ionized impurities, with $r \approx 1.98$, whereas at higher temperatures polar-optical scattering is predicted to be dominant, with $r \approx 1 - 1.13$ [D. Kranzer, J. Phys. C 6, 2977 (1973); J. Phys. Chem. Solids 34, 9 (1973)].