

Acceptor doping in ZnSe versus ZnTe

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It is a long-standing puzzle that ZnSe is difficult to dope *p* type, while ZnTe—which is very similar to ZnSe—is very easily doped *p* type. We report *ab initio* calculations which show that the solubilities of Li and Na acceptors are much greater in ZnTe than the solubilities of the same acceptors in ZnSe. We trace the origin of this difference to the bonding properties of the acceptors with the neighboring chalcogens. Our results also explain the experimentally observed dependence on dopant concentration of the dislocation density in *p*-type ZnSe epilayers grown on GaAs.

Efforts to make optical devices from wide band-gap II-VI semiconductors like ZnSe have been hampered by the fact that they can be easily doped either *n* type or *p* type but not both.¹⁻⁴ For example, ZnSe is easily doped *n* type, but only recently, after many years of extensive effort, it became possible to dope it sufficiently *p* type so the blue lasers could be fabricated.⁵ In contrast, ZnTe can only be doped *p* type.^{2,3} This difference between ZnSe and ZnTe is particularly striking because the two materials are very similar in most of their properties. Indeed, selenium derives its name (from the Greek for Moon) from its resemblance to tellurium (from the Latin for Earth).

Over the years, there have been many suggestions to account for these doping difficulties.⁶⁻¹⁴ Among the most popular were (1) compensation, either by native point defects (vacancies, interstitials, or antisites) or by dopant atoms at alternative sites (e.g., interstitials) where they would act as traps that capture free carriers; (2) strong lattice relaxations which convert the anticipated shallow dopants into nondoping deep levels; and (3) low solubility for dopants.

In a recent paper,¹⁵ we constructed a quantitative theory which includes all of the above phenomena on an equal footing. We carried out first-principles calculations for *p*-type ZnSe, and found that (a) native defects have concentrations that are too small to affect doping levels; (b) nondoping impurity configurations play only a minor role in limiting doping; and (c) the dominant effect is the solubility of the acceptors (Li, Na, and N), limited by the formation energy of other phases, such as Li₂Se, etc. These results provide a definitive account of the relative roles of the mechanisms that can potentially limit the doping of *p*-type ZnSe. But the question remains: Why does ZnTe behave differently?

In this letter we present a first-principles theoretical study of the solubilities of acceptors in ZnSe and ZnTe. We show that the solubilities of Li and Na acceptors in ZnTe are much higher than their solubilities in ZnSe. These

results—which contain no adjustable parameters or experimental inputs—provide a natural explanation for the observed difference between the two semiconductors. We trace the origin of the solubility difference between the two materials to the bonding properties between the dopants and the neighboring chalcogens. Our calculated solubilities also provide a simple explanation for a set of experimental observations regarding the dislocation structure of *p*-type ZnSe grown epitaxially on GaAs substrates.

We first give a brief review of the theoretical methods used in the calculations. Full details are provided elsewhere.^{15,16} The total energies of ZnSe, ZnTe, and the acceptor defects are calculated using norm-conserving pseudopotentials¹⁷ and density-functional theory in the local-density approximation.¹⁸ These calculations successfully describe the bulk properties of both ZnSe and ZnTe by using a mixed-basis set to capture the behavior of the Zn *d* electron states.¹⁶ Calculations for acceptor defects are performed in 32-atom supercells, and relaxations are included. The estimated error bar for the defect total energy calculations is 0.1 eV.

The formation energy of a Li_{Zn} acceptor in ZnSe is determined by the relative abundance of Zn, Se, and Li atoms in the environment in which the crystal is grown. As a consequence, the formation energy of the acceptor is a function of the chemical potentials for the Zn and Li atoms, μ_{Zn} and μ_{Li} . The Zn chemical potential is defined as the energy required to add a Zn atom to the system. Since forming a substitutional Li_{Zn} acceptor requires the addition of one Li atom to the crystal and the removal of one Zn atom, the formation energy of the neutral acceptor is

$$E_{\text{form}}(\text{ZnSe:Li}_{\text{Zn}}) = \mathcal{E}(\text{ZnSe:Li}_{\text{Zn}}) - \mu_{\text{Li}} + \mu_{\text{Zn}}, \quad (1)$$

where $\mathcal{E}(\text{ZnSe:Li}_{\text{Zn}})$ is a total energy derived from a supercell calculation for substitutional Li. Given the formation energy, the acceptor concentration is determined by the usual Boltzmann form. Thermodynamics places limits on the values of the Zn and Li chemical potentials. The

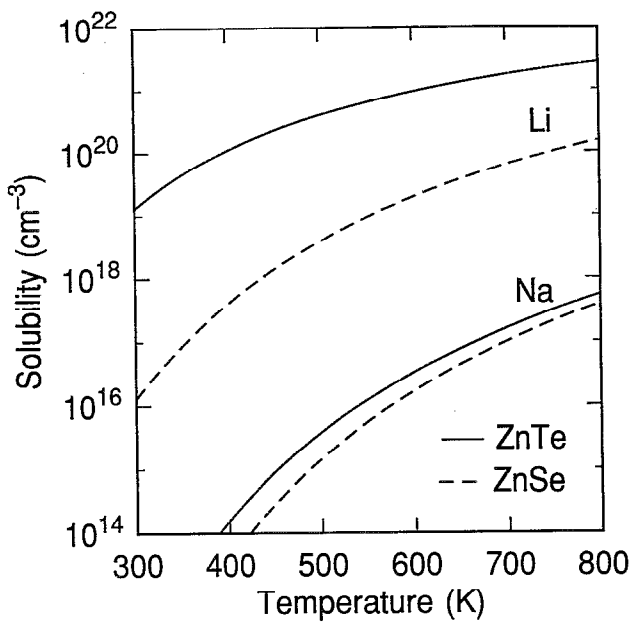


FIG. 1. Calculated solubility limits for Li and Na in ZnSe and in ZnTe as a function of temperature

upper limit of the Zn chemical potential is given by ZnSe in equilibrium with bulk Zn, while the lower limit is for ZnSe in equilibrium with bulk Se. The upper bound on the Li chemical potential is due to equilibrium with Li_2Se . In our work, we perform the appropriate total-energy calculations for these bulk materials using the same theoretical methods that we use for the acceptor defects.

Dopant solubilities are a direct consequence of the limits on the chemical potentials. This is because the chemical potential limits determine a minimum value for the dopant formation energy in Eq. (1). This, in turn, becomes a maximum value for the dopant concentration. The solubility limit¹⁹ is simply the sum over all charge states (in our case neutral and -1) of the maximum acceptor concentrations. The minimum formation energy for Li in ZnSe occurs when ZnSe is in equilibrium with bulk Se and with Li_2Se . The Zn and Li chemical potentials for this point are

$$\begin{aligned} \mu_{\text{Zn}} &= \mathcal{E}(\text{Zn}) + \Delta H_f(\text{ZnSe}) \quad \text{and} \\ \mu_{\text{Li}} &= \mathcal{E}(\text{Li}) + \frac{1}{2} \Delta H_f(\text{Li}_2\text{Se}), \end{aligned} \quad (2)$$

where $\mathcal{E}(\text{Zn})$ and $\mathcal{E}(\text{Li})$ are the total energies of bulk Zn and bulk Li metals, and $\Delta H_f(\text{ZnSe})$ and $\Delta H_f(\text{Li}_2\text{Se})$ are heats of formation. The calculations for the solubility limits of Na in ZnSe and of Li and Na in ZnTe are completely analogous, with the solubility limits determined by equilibrium with Na_2Se , Li_2Te , and Na_2Te , respectively.

Figure 1 shows the calculated solubilities for Li and Na in both ZnSe and ZnTe. The small uncertainties in the calculated formation energies translate into an error bar of one order of magnitude in the solubilities;²⁰ but when comparing solubilities in similar systems, the relative errors are much smaller. The figure shows two trends quite clearly. First, the solubility of Li is much higher than that of Na in both materials. Second, the solubility of Li in ZnTe is 10–1000 times larger than in ZnSe. These trends are in full agreement with the known facts: while acceptor concentrations of about 10^{17} cm^{-3} have been achieved in ZnSe

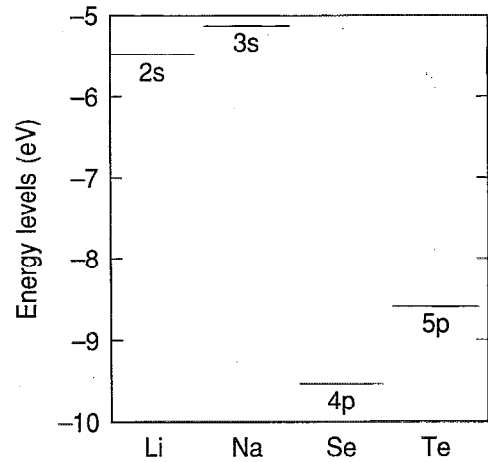


FIG. 2. Atomic level diagram for Li, Na, Se, and Te. Energy levels are taken from Ref. 23.

doped with Li,^{21,22} we know of no reports of successful doping of ZnSe or ZnTe with Na. Most important, these results explain—without the use of any adjustable parameters or experimental input—why it is so much harder to make p -type ZnSe than it is to make p -type ZnTe.

The difference in solubilities between ZnSe:Li and ZnTe:Li follows directly from the difference in the minimum formation energies. From Eq. (1) we have

$$\begin{aligned} E_{\text{form}}(\text{ZnSe:Li}_{\text{Zn}}) - E_{\text{form}}(\text{ZnTe:Li}_{\text{Zn}}) \\ = \mathcal{E}(\text{ZnSe:Li}_{\text{Zn}}) - \mathcal{E}(\text{ZnTe:Li}_{\text{Zn}}) + \Delta\mu. \end{aligned} \quad (3)$$

The $\mathcal{E}(\text{ZnSe:Li}_{\text{Zn}}) - \mathcal{E}(\text{ZnTe:Li}_{\text{Zn}})$ term is the difference in bonding energies between Li in ZnSe and in ZnTe. The $\Delta\mu$ term is determined by the possible phases that could form in the chemical environment; using Eq. (2) in Eq. (1), it is

$$\begin{aligned} \Delta\mu &= \Delta H_f(\text{ZnSe}) - \Delta H_f(\text{ZnTe}) - \frac{1}{2} [\Delta H_f(\text{Li}_2\text{Se}) \\ &\quad - \Delta H_f(\text{Li}_2\text{Te})]. \end{aligned} \quad (4)$$

Our calculations find that the $\Delta\mu$ term is small: it is 0.01 eV for Li doping and -0.14 eV for Na doping. Thus, the difference in acceptor solubilities in ZnSe vs ZnTe comes mainly from the bonding energy term, which is 0.26 eV for Li and 0.27 eV for Na. This bonding energy difference can be understood by examining the electronic energy levels of Li, Na, Se, and Te. Both Li and Na sit on substitutional Zn sites, surrounded by four Se or Te neighbors. The bonds form primarily from the top s state of the acceptor and the top p state of the chalcogen. When the s and p states are closer in energy the strength of these bonds increases, which lowers the formation energy. Figure 2 shows the positions of these states, using atomic energy levels from Ref. 23. The Te $5p$ state is 1 eV higher in energy than the corresponding Se $4p$ state; consequently Te bonds more strongly than Se to both Li and Na. Also, the Na $3s$ state is higher than the Li $2s$ state, so that Na bonds are weaker and its solubility lower than that of Li. The solubility of Na

also suffers from a size mismatch problem: while Li has roughly the same radius as Zn, Na has a larger radius, making it harder to fit into the lattice.

Our calculated acceptor solubilities can also be used to explain another experimental puzzle. In epitaxial growth of ZnSe on GaAs substrates there is a small lattice mismatch between the two materials, which can be relieved by the formation of misfit dislocations. In a series of experiments^{24,25} with *p*-type ZnSe doped with Li, Na, and N, it was found that a large density of threading dislocations does appear, but only when the acceptor concentration is above a critical value. These critical acceptor concentrations were measured to be $< 10^{16}$, 10^{18} , and 10^{19} cm⁻³, for Na, Li, and N doping, respectively. At the experimental growth temperature of 250 °C, our calculated solubilities for Na and Li in ZnSe are 4×10^{15} and 6×10^{18} cm⁻³. We have also calculated the solubility for N in ZnSe,¹⁵ and find that it is 2×10^{19} cm⁻³ at 250 °C. Thus the experimental critical doping densities agree with the calculated solubilities to within the uncertainties of the calculations. In particular, the critical acceptor densities and the solubilities display the identical trend as one goes from Na to Li to N. This strongly suggests that the sudden increase in dislocations occurs when the solubility limit is reached; at this point the excess acceptors may form microprecipitates which can act as nucleation sites for dislocation loops (which would otherwise be kinetically inhibited). We know of no other explanation for the experimental facts.

In summary, we have performed *ab initio* calculations of acceptor solubilities and find much higher solubilities for acceptors in ZnTe than in ZnSe, providing a straightforward explanation of why it is so much easier to make *p*-type ZnTe than ZnSe. Our calculated solubilities also correlate very well with sudden increases in the threading dislocation density, suggesting that the increase is caused by introducing excess dopant atoms above the solubility limit.

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- ¹H. Tews, H. Venghaus, and P. J. Dean, *Phys. Rev. B* **19**, 5178 (1979).
- ²H. Venghaus and P. J. Dean, *Phys. Rev. B* **21**, 1596 (1980).
- ³J. L. Pautrat, J. M. Francou, N. Magnea, E. Molva, and K. Samindayer, *J. Cryst. Growth* **72**, 194 (1985).
- ⁴R. Bhargava, *J. Cryst. Growth* **86**, 873 (1988).
- ⁵M. A. Haase, J. Qiu, J. M. DePuydt, and H. Cheng, *Appl. Phys. Lett.* **59**, 1272 (1991).
- ⁶G. Mandel, *Phys. Rev.* **134**, A1073 (1964).
- ⁷Y. S. Park and B. K. Shin, in *Topics in Applied Physics* (Springer, Berlin, 1977), Vol. 17, p. 133.
- ⁸A. K. Ray and F. A. Kröger, *J. Electrochem. Soc.* **125**, 1348 (1978).
- ⁹Y. Marfaing, *Prog. Cryst. Growth Charact.* **4**, 317 (1981).
- ¹⁰R. W. Jansen and O. F. Sankey, *Phys. Rev. B* **39**, 3192 (1989).
- ¹¹J. D. Dow, R.-D. Hong, S. Klemm, S. Y. Ren, M.-H. Tsai, O. F. Sankey, and R. V. Kasowski, *Phys. Rev. B* **43**, 4396 (1991).
- ¹²G. F. Neumark, *J. Appl. Phys.* **51**, 3383 (1980).
- ¹³D. J. Chadi and K. J. Chang, *Appl. Phys. Lett.* **55**, 575 (1989).
- ¹⁴G. F. Neumark, *Phys. Rev. Lett.* **62**, 1800 (1989).
- ¹⁵C. G. Van De Walle, D. B. Laks, G. F. Neumark, and S. T. Pantelides, *Phys. Rev. B* **47**, 9425 (1993).
- ¹⁶D. B. Laks, C. G. Van de Walle, G. F. Neumark, P. E. Blöchl, and S. T. Pantelides, *Phys. Rev. B* **45**, 10 965 (1992).
- ¹⁷D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).
- ¹⁸J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).
- ¹⁹In our previous work on ZnSe (Ref. 15), we included the effects of interstitial Li and native defects. This increases the calculated solubility by about 20% by counting interstitial Li and because the native defects shift the Fermi level slightly. These effects are not treated in this letter since they have only a minor impact on the doping.
- ²⁰For solubilities larger than about 10^{20} cm⁻³, there is an additional uncertainty because the formula for the concentrations assumes the dilute limit.
- ²¹J. M. DePuydt, M. A. Haase, H. Cheng, and J. E. Potts, *Appl. Phys. Lett.* **55**, 1103 (1989).
- ²²M. A. Haase, H. Cheng, J. M. DePuydt, and J. E. Potts, *J. Appl. Phys.* **67**, 448 (1990).
- ²³W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, CA 1980).
- ²⁴L. H. Kuo, L. Salamanca-Riba, J. M. DePuydt, H. Cheng, and J. Qiu (unpublished).
- ²⁵J. M. DePuydt (private communication).