

**Dalpian and Chelikowsky Reply:** In their Comment [1] on our Letter [2], Du, Efros, Erwin, and Norris (DEEN) argue that the formation energy of impurities does not play a role in the “self-purification” in semiconductor nanocrystals; i.e., the energy of these defects is not responsible for the difficulty of doping nanocrystals. DEEN propose that kinetic effects should be more important. In our Letter, we argued that both kinetic and energetic effects should be considered when studying dopants in nanocrystals. Our previous arguments are bolstered by a variety of recent calculations and experiments that show trends similar to ours [3–7].

DEEN performed calculations for Mn in CdSe nanocrystals using a plane wave basis set, and found no increase in the formation energy whatsoever, a result that is at variance with our Letter. Considering their calculations, we repeated our real space calculations with a higher convergence criterion, namely, a smaller grid spacing ( $h = 0.3$  a.u.). We found that the calculated relative heats of formation in our Letter were overestimated. Our newly calculated formation energies are reduced; however we find the energies for doping remain less favorable for the smaller nanocrystals. While our Letter focused on Mn in CdSe, this is a general result, applicable to many dopants and hosts. In Fig. 1, we show a variety of calculations for different systems. In all these cases an increase in the heats of formation are observed, even for defects with very low formation energies in bulk such as P in Si. In none of these cases is the heat of formation completely independent of size as found by DEEN for CdSe:Mn.

DEEN explain the lack of any size dependence in their calculated energetics by considering the placement of the impurity  $d$  levels as the size of the nanocrystal decreases: the gap level shifts up in energy, while the “bonding” level, located within the occupied states, shifts down. They argue these shifts essentially cancel and leave a net binding energy of zero. This explanation is *not* correct. Neither experiment nor theoretical calculations support DEEN’s explanation. Our calculations with both plane wave and real space codes show that the defect levels are

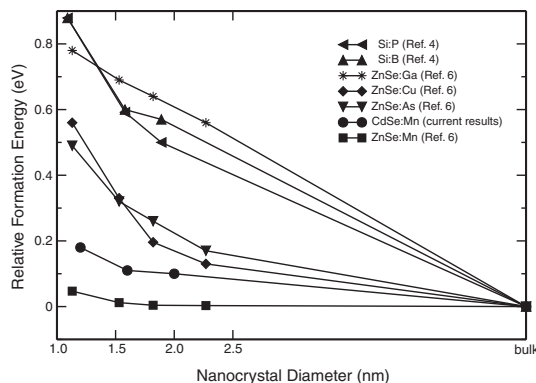


FIG. 1. Variation of the formation energy for several systems as a function of nanocrystal size.

energetically pinned relative to the vacuum level for CdSe:Mn, and do not move as the size of nanocrystal changes. We demonstrated this pinning in a similar system (Co in ZnSe) by calculations and experiment [8].

Another important observation is that, by changing the chemical potentials and moving towards an anion-rich environment, the incorporation of impurities increases [9]. This is clearly an energetic effect, that can be easily understood by analyzing Eq. (1) from our Letter [2]. In the anion-rich regime, the cation chemical potential gets smaller and, consequently, the impurity formation energy also gets smaller, explaining the larger incorporation of impurities [9].

An even stronger argument for the role of defect energies in the self-purification process can be made by an examination of the impurity energy as a function of the defect site. In particular, we have recently demonstrated that impurities within a nanocrystal can be *energetically driven* to the surface of nanocrystal, and consequently expelled from it, as expected by a self-purification mechanism [7]. This is a more robust argument than those based on the heat of formation as no intrinsic reference energy need be considered. It is also consistent with the generic result that impurities often segregate to the surface or to extended defects in solids to relieve strain energies.

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