**LED’s – Color vs. Temperature**

**by**

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The origin of the red shift of LEDs with increasing temperature can be traced to the change in the fundamental band gap of the semiconductor. For tetrahedrally-bonded semiconductors (C, Si, Ge - group IV, GaAs, InAs, GaP, GaSb, InSb - group III-group V, and II-VI materials with the zincblende crystal structure) the bonding is sp^3, just as you would have in a methane molecule. In GaAs, each cation (Ga) has 4 tetrahedrally-bonded anions (As) and each anion has 4 tetrahedrally bonded cations. The bands are formed from bonding and antibonding combinations of the Ga and As 3s and 3p states. The anion has slightly lower energies for the 3s and 3p than the cation. Both have slightly lower energies for the 3s than the 3p states. Thus when one forms molecular states between Ga and As one gets, in order:

highest energy - antibonding p states (predominately on Ga)
next energy - antibonding s states (predominately on Ga) - so-called “conduction band” or LUMO
next energy - bonding p states (predominately on As - so-called “valence band” or HOMO
lowest energy - bonding s states (predominately on As)

The energy splittings between the bonding and antibonding states is proportional to the square of the overlap of the wave functions on Ga with As. The closer the atoms are the larger the splitting, the farther they are the smaller the splitting. When one heats up the semiconductor the atoms get farther apart due to anharmonic phonon interactions, and thus the splittings between bonding and antibonding states get smaller. Thus the bonding p states move up in energy and the antibonding s states move down. The result is a smaller band gap and a red shift for band-to-band emission of light.

The strange effect of the blue-shifting LEDs comes from a transition between defect-bound excitons to band to band emission. The energy of a defect-bound exciton will be lower than that of band to band emission, at any temperature. However one can only get defect-bound exciton recombination that is efficient at low temperatures - at higher temperatures the exciton is free to move and is not bound to the defect. As a result one only sees band to band emission. So, even though the band gap of the material is decreasing as the temperature increases, because the nature of the emission is changing from defect-bound exciton emission at low temperature to band-to-band emission at high temperature, the overall effect is a blue shift.

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