# SESSION PAa: SYMPOSIUM OF THE DIVISION OF CONDENSED MATTER PHYSICS: METASTABLE STRUCTURES AND ORDERING IN SEMICONDUCTORS

**Friday morning 20 March 1987; Grand Ballroom East at 8:00; C. B. Stringfellow, presiding**

8:OO

**PAa 1** ,Stability, Ordering, and **Metastability of Semiconductor Alloys.**' ALEX ZUNGER, *Solar Energy Research Institute.*

Bulk phase diagrams of all isovaLent semiconductor alloys appear to differ profoundly from those of metallic alloys: the former did not exhibit any compound formation and were invariably associated with positive mixing enthalpies An(n)(x)>n, suggesting disproportionation of the disordered (n) alloy $A_xB_{1-x}C$ into its constituents AC and RC at a sufficiently low temperature. These classic observations motivated previous models of semiconductor alloys to postulate a revulsive interaction $\Delta E^{(n)}>0$ (analogous to ferromagnetism) of each of the "building blocks" $A_nB_{4-n}C_4$ (0<n<4) with respect to its end-point constituents nAC + (4-n)RC. Applying first-principles self-consistent total energy calculations to the ordered $A_nB_{4-n}C_4$ phases, we find that $\Delta E^{(n)}$(V) represents a competition between destabilizing strain effects and potentialLy stabilizing "chemical" (or "spin-, flip") effects, such as charge transfer and polarization. Furthermore, the abiltty of the common atom C to utilize its cell-internal structural degrees of freedom (resulting in generally dissimilar A-C and R-C bond lengths) can substantially stabilize such ordered structures. .As a result, some systems can have $\Delta E^{(n)}<0$ (e.g., SI-C, CdTe-MnTe) and others (e.g., GaAs-AlAs, Si-Ce) have $\Delta E^{(n)}>0$. Using these volume (V)- dependent~interactton energies $\{\Delta E^{(n)}(V)\}$ in an approximate solution (through the Cluster Variation Method) of the appropriate spin l/2 f.c.c. Ising model (including up to four-body interactions), we calculate the alloy phase diagrams as well as AH(D)(x). We predict that: (i) Ordered stoichiometric phases and disproportionation can coexist in the same phase diagram, (ii) strain stabilize ordered phases when chemical interactions are attractive, but otherwise (iii) strain Leads to metastable ordered phases, and (iv) the interactions $\Delta E^{(n)}(V)$ can lead either to clustering or anti-clustering. Our predictions will be compared to unprecedented subsequent experimental observations of long-range order in semiconductor alloys reported recently.

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