CLASSIFICATION OF CHEMICAL ORDERING IN AMORPHOUS AND LIQUID SEMICONDUCTORS

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Binary non-crystalline semiconductors are classified in terms of their bonding at and away from stoichiometry. Density of states models are developed for example systems: \( \alpha \)-CsAu, \( \alpha \)-MgSb, \( \alpha \)-GaAs, \( \alpha \)-GeTe and \( \lambda \)-PbTe.

The composition dependence of the transport and optical properties of binary liquid or amorphous alloys can be used to understand the variation of their bonding, especially when there is little structural data available. There are five basic composition dependences of the resistivity \( R \) and thermopower \( S \) in which the two constituents C and A behave symmetrically. Other, asymmetric, behaviours can be developed. Figs. 1(a) and (b) show schematically \( R \) and \( S \) for good metallic alloys (e.g. \( \alpha \)-SnZn), and semiconductors with random covalent bonding (e.g. \( \alpha \)-SeTe), respectively. These two behaviours occur if the electronegativity differences between C and A are small (C is taken as more electropositive hereafter). For larger differences, heteroatom bonding is maximised giving ordering at some stoichiometry \( x_0 \). If the covalent coordination obeys the 8-N rule, as is common in non-crystalline phases, compensated semiconduction occurs for all \( x \) (fig. 1c), e.g. \( \alpha \)-GeTe \( 1-x \). Large electronegativity differences between metals can also produce a semiconductor, and it is now generally acknowledged that ionic ordering has occurred (e.g. \( \lambda \)-Li \( \lambda \)-Pb \( 1-x \)). For the compound \( C^+A^- \) the valence band is predominantly A-like and the conduction band C-like so that for \( x \neq 0.5 \)

\[
C \rightarrow C^+ + e^- \quad \text{or} \quad A \rightarrow A^- + e^+,
\]
causing \( \varepsilon_F \) movements equivalent to the
Fig. 1: The five archetypal composition dependences of resistivity and thermopower.

Fig. 2: Quantal orbital coordinates for various systems.