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BOND EQUILIBRIUM THEORY IN COVALENTLY BONDED ALLOYS

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Abstract.- Bond equilibrium theory (BET) has been extended to include polymer chains whose units are molecular groups attached to other units by one, two, or three links. Because As-Se and similar alloys contain high densities of atoms with threefold (3F) bonding, it is likely that a large fraction of the As atoms of the liquid alloy are in molecular groups. Initial results of a study of As$_x$Se$_{1-x}$ are presented.

Bond Equilibrium Theory (BET) for Atomic Constituents.- In a study of Se-Te alloys (1), it has been shown that the concentration of a bond defect $\gamma$ containing $n$ bonds on an atom of chemical species $A$ is

$$c^n_A = x_A p_n \exp[-\beta(g_\gamma + q_\gamma E_F)]$$

where $q_\gamma$ is the charge number, $\beta = 1/kT$, and $E_F$ is the Fermi energy. (Concentrations are normalized to the density of atoms in the alloy.) $g_\gamma$ is the free energy of formation from the fully bonded atom. Aside from the polymer factor $p_n$, this expression is the same as for the equilibrium concentration of crystal impurities or lattice defects in the theory of Kröger and Vink (2). $x_A$ is the fugacity of an $A$ atom. Its value is determined by the requirement that the total concentration of the $A$ atoms adds up to the atomic fraction $x_A$ in the alloy. If bonding is nonrandom, the expressions are somewhat more complicated. The discussion in this paper will be restricted to random bonding, i.e., the energy of an AB bond is assumed equal to the average for AA and BB.

The polymer factors $p_n$ are the result of the topological constraints which relate the number of possible configurations of polymer molecules to the total concentrations $c_n$ of covalently bonded atoms which have $n$ bonds, for the different values of $n$. The theory has been worked out for polymers formed from atoms which have 1, 2, or 3 bonds, in an approximation which ignores structures containing loops. Since each 3F atom creates a chain branch which must be terminated by a 1F atom, the concentration of polymer molecules is $(c_1-c_3)/2$. The branch ratio $\lambda = 2c_3/(c_1-c_3)$, i.e., the average number of chain branches per molecule, is an important parameter in the theory. The polymer factors have values given by

$$p_1 = c_2^{2+\lambda} \left[\frac{2B/h}{(1+2\lambda)(c_1+2c_2+3c_3)}\right]^\frac{1}{2}$$

$$p_2 = c_2$$

$$p_3 = \left[\frac{2(1+\lambda)(c_1+2c_2+3c_3)}{Bh(1+2\lambda)}\right]^\frac{1}{2}$$

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B and h are parameters relating to the coordination and bond angle restrictions as described in Ref. 1. Appropriate values for chalcogenide alloys seem to be B = 6 and h = 2. b is a parameter whose value increases slowly with λ, from b = 1 for \(\lambda \leq 3\) to 2.618 when \(\lambda \to \infty\) (1). In the limit \(\lambda \gg 1\), \(p_1 \propto \lambda\) and \(p_3 \propto \lambda^{-1}\).

The values of the free energy parameters are often unknown, and one hopes to derive their values by comparison of the predictions of BET theory with experimental data. It is therefore desirable, if possible, to use the BET equations to provide relations between concentrations of important constituents, without knowing the values of the parameters \(g_Y\) or at most having a rough estimate. In this approach, a valuable consideration is the effect of \(\lambda\) on the relative concentrations of 1F and 3F constituents. If \(c_1 - c_3 \to 0\), \(\lambda\) becomes large, causing \(p_1\) to increase and \(p_3\) to decrease, which ensures that \(c_1/c_3 > 1\).

**BET for Molecular Constituents.**—The driving mechanism which tends to increase the ratio \(c_1/c_3\) is of course the increase in entropy due to the larger numbers of smaller molecules. In Se-Te alloys, ring molecules attached to chains by a single 3F atom have been found to play an important role as a result of this mechanism (3). Such rings act as 1F constituents which are molecular rather than atomic, and an extension of BET to include 1F molecular constituents has been derived in Ref. 3. Although the discussion was in terms of ring molecules, the basic theory is applicable to any molecular cluster which is attached to a chain by a single link. In the case of Se-Te, the 1F rings become important because the thermal excitation of ion pairs (1F D- ions and 3F D+ ions) requires less energy than excitation of a pair of neutral dangling bonds (1F D0 atoms). Singly attached \(R^+\) rings containing a \(D^+\) atom provide a means of forming ion pairs \((D^- - R^+)\) which are both 1F constituents.

As-Se and related alloys have high densities of 3F atoms so that \(c_3\) is large. The results in Se-Te suggest that molecular \(r\) groups provide a mechanism for incorporating the 3F atoms of As-Se in molecular structures in which \(c_3 < c_1\). In this description, \(c_1\), \(c_2\), or \(c_3\) refer to concentrations of molecular constituents with 1, 2, or 3 links to other members of a polymer chain. It has been possible to generalize the theory presented in Ref. 3 to include molecular groups which have 1F, 2F, 3F bonding. The original work also takes into account molecular groups which are not attached to chains, and therefore can be categorized as OF constituents. The results are described as follows: The concentration \(c_{m1}^n\) of an \(n\)-F molecular constituent based on a molecule which is composed of \(v_m\) atoms is

\[
c_{m1}^n = p_n O_m p_m x_a^{v_m-1} \exp[-\beta(g_{my} + q_y E_F)]
\]

where \(g_{my}\) is the free energy of formation of the molecule with a structure \(m\) from the atoms in their reference state, and \(q_y\) is the charge number. \(p_m(<1)\) is the ratio of the number of configurations of the molecule to the number of configurations of \(v_m\) atoms in an unrestricted linear chain. (It is the same as \(R_m\) in Ref. 3.) \(O_m\) is a multiplicity factor describing distinguishable configurations resulting from placing the links at different places in the molecule, as can occur, for instance, in 2F rings. In the case of a binary alloy containing A and B atoms with fugacities \(X_A\) and \(X_B\), the expression for \(c_{m1}^n\) for a molecular constituent containing \(v_A\) A atoms and \(v_B\) B atoms would also include a factor \(X_A^{v_A} X_B^{v_B}\).

\(x_a\) is a parameter which appears in the theory of Refs. 1 and 3, and which becomes important in situations where molecular constituents containing many atoms need to be considered. Its value can be expressed by

\[
x_a = 2c_2/(c_1 + 2c_2 + 3c_3)
\]

When \(c_2 \gg c_1 + c_3\), \(x_a\) is slightly less than 1. But the factor \(x_a^{v_m-1}\) in Eq. 5 causes the distribution of sizes of molecular groups to fall off sharply for \(v_m \gtrsim (1-x_a)^{-1}\).
In extending the theory to molecular constituents, each molecular group is treated as single particle as far as the topology of the polymer molecules is concerned. Thus all the atoms in OF molecules and all but one of the atoms of each attached molecular group are excluded. This effect is expressed in terms of the fraction $\phi$ of "effective" polymer units:

$$\phi = c_1 + c_2 + c_3 = 1 - \sum_{m} c_m - \sum_{m,y} (\nu_m - 1)(c_{1y} + c_{2y} + c_{3y}) \quad . (7)$$

Application to $\text{As}_x \text{Se}_{1-x}$ Alloys.- A start has been made in an investigation of the behavior of $\text{As}_x \text{Se}_{1-x}$ alloys in terms of BET. It seems likely that alloys at compositions near $\text{As}_2\text{Se}_3$ contain complicated molecular structures as exemplified by the molecule $\text{As}_4\text{Se}_6$, which is known to occur in the gaseous phase. It has a cage-like structure containing four rings. A wide variety of analogous multiply-connected structures would need to be considered if large molecular groups are important. As discussed in Ref. 3 for the case of rings, steric constraints limit multiply-connected structures to a minimum number of $\sim 8$ atoms in a ring. Consequently it is a matter of great interest to learn whether $X_3$ is small enough in As-rich alloys to restrict the size of the important molecular groups to the smallest ones consistent with the constraints of the bond angles.

The approach which has been taken is to first study simplified models in the limit of small $x$ ($\leq 0.1$), where only ring constituents need to be considered. A useful first step is to neglect thermally excited bond defects, since their concentrations are apt to be small compared to those of 1F, 2F, and 3F molecular constituents formed from normally bonded As and Se atoms (at least at low $T$).

In Fig. 1, the dependence of $\lambda$, $\phi$, and the concentrations of constituents on alloy composition is presented for a model in which only OF and 1F ring constituents are considered, in addition to 2F Se atoms and 3F As atoms. The parameters determining the ring distributions are the same as in Ref. 3. Each 1F ring has one Se atom replaced by an As atom, so that $c_1 + c_3 = x$. As seen in Fig. 1, $c_1$ is slightly larger than $x/2$ and $c_3$ is slightly smaller, the differences decreasing with $x$ due to the increase in $\lambda$ (also plotted). The concentration of free rings $c_0$ becomes small compared to $c_1$ as $x$ increases since it does not depend on $p_1$, which increases with $x$.

The most significant result in this model is the behavior of the distribution of ring sizes. The concentration of an $n$-atom ring is proportional to $(X_3X_a)^{n-1}$. Since $X_3X_a = c_2$, the density of $n$-atom molecular groups falls off sharply when $n \lesssim (1-c_2)^{-1}$. Fig. 1 includes plots of $c_2$ and the average number of atoms in a ring $\langle n \rangle$. It is seen that $c_2$ becomes small enough at moderate As concentrations so that $\langle n \rangle$ approaches the minimum value 8 set by the model.

This model describes a non-thermal liquid. One expects that thermally excited 1F or 3F bond defects will modify the behavior when their concentrations become comparable to $c_1 - c_3$.

Conclusions.- The groundwork has been laid for an application of BET to the molecular structure of alloys of the type As-Se. The alloy is viewed as simply-connected polymer chains composed of 1F, 2F, and 3F constituents which may be molecular or atomic. Preliminary studies support the conclusion that only molecular groups of the minimum size consistent with steric constraints are important. At low As concentrations considered so far, these would be rings with $\sim 8$ atoms. The premises of the theory require that $c_1 > c_3$. Therefore when the ratio of As/Se atoms becomes larger, rings containing three or more As atoms will become important, and molecular groups would have to be formed with more complicated multiply-connected
structures. The conclusions are consistent with some of the concepts about the structure of As-Se alloys derived from experimental information (4). They are also to be compared with the models developed by Phillips for amorphous chalcogenide alloys (5). Our models agree in the sense that molecular groups are taken to be the basic structure units, but the BET theory leads to an emphasis on chain-like structures composed of small molecular groups rather than layer-like structures.

The present study is based on models which assume random bonding. Spectroscopic and diffraction studies indicate a strong tendency for alternate bonding in amorphous As-Se alloys near the compositions As2Se3, which suggests non-random bonding (4). However the difference in electronegativities of As and Se is small and an empirical formula due to Pauling (6) suggests that a mixed bond has a stabilization energy of only 0.16 eV. Since $kT \approx 0.05$ eV at the glass transition of As2Se3, this would give an appreciable concentration of like bonds. It seems possible that the multiple-connected structures of minimum size, like the As4Se6 cage molecule, require alternate bonding because of steric constraints. Therefore the observed alternate bonding, may be the indirect result of steric constraints in conjunction with the limitation to small molecular units.

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