Letters to the Editor

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Vacancy Diffusion Mechanism in Ordered Alloys

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IT has been suggested[1] that for binary ordered alloys of type AB, in which every A (B) atom is surrounded only by $B(A)$ atoms, a direct experimental decision can be made between the vacancy and the interstitial diffusion mechanisms. It is assumed that vacancies can move only by nearest neighbor jumps: then in the course of N vacancy jumps through an ordered lattice, $\frac{1}{2}NA$ atoms are displaced and $\frac{1}{2}NB$ atoms are displaced; hence, it is argued, the self-diffusion coefficients of A and B are equal. With the interstitial mechanism there need be no such equality. In our view this argument is incomplete and a vacancy mechanism with nearest neighbor jumps does not necessarily lead to equality of the two diffusion coefficients. This is shown by supplementing the above geometrical argument with the condition that the alloy must be in thermodynamic equilibrium. The formula advanced by Slifkin and Tomizuka for the ratio of self-diffusion coefficients in a partially ordered alloy is inadmissible because it is inconsistent with this condition.

We divide the lattice into two sublattices α and β such that in the completely ordered state only α sites are occupied by A atoms and only β sites by B atoms. Let $w_A(\alpha\rightarrow\beta)$ be the average jump frequency for a particular A atom on an α site going into an adjacent β vacancy; let there be other jump frequencies $w_A(\beta\rightarrow\alpha)$, $w_B(\alpha\rightarrow\beta)$ and $w_B(\beta\rightarrow\alpha)$ with corresponding definitions. The probability that any given α site is occupied by an A atom is, in terms of the long-range order parameter s, $(1+s)/2$; the probability that it is occupied by a B atom is $(1-s)/2$. Conversely for β sites. It follows that the average number of A atoms moved in every $\beta\rightarrow\alpha$ *vacancy* jump is

$$\frac{(1+s)w_A(\alpha\rightarrow\beta)}{(1+s)w_A(\alpha\rightarrow\beta)+(1-s)w_B(\alpha\rightarrow\beta)}. \quad (A) \qquad (1)$$

Likewise the average number of B atoms moved in every $\beta\rightarrow\alpha$ vacancy jump is

$$\frac{(1-s)w_B(\alpha\rightarrow\beta)}{(1+s)w_A(\alpha\rightarrow\beta)+(1-s)w_B(\alpha\rightarrow\beta)}. \quad (B) \qquad (2)$$

The corresponding quantities for the $\alpha\rightarrow\beta$ vacancy jumps are

$$\frac{(1-s)w_A(\beta\rightarrow\alpha)}{(1-s)w_A(\beta\rightarrow\alpha)+(1+s)w_B(\beta\rightarrow\alpha)}, \quad (A) \qquad (3)$$

and

$$\frac{(1+s)w_B(\beta\rightarrow\alpha)}{(1-s)w_A(\beta\rightarrow\alpha)+(1+s)w_B(\beta\rightarrow\alpha)}. \quad (B) \qquad (4)$$

Since the number of vacancies jumping from α to β is equal to the number jumping from β to α, the ratio of the self-diffusion coefficients $D_B/D_A\equiv G$ is $[(2)+(4)]/[(1)+(3)]$. To obtain the formula given by Slifkin and Tomizuka, we must set

$$w_B(\alpha\rightarrow\beta)/w_A(\alpha\rightarrow\beta)\equiv J\equiv w_B(\beta\rightarrow\alpha)/w_A(\beta\rightarrow\alpha). \quad (5)$$

However, this assumption is inconsistent with the condition of thermodynamic equilibrium. For the number of $A(B)$ atoms jumping from α to β must equal the number jumping from β to α, otherwise the equilibrium degree of order is not established. If one introduces vacancy concentrations n_α and n_β for the two sublattices, these requirements give the two relations

$$\begin{aligned} n_\beta(1+s)w_A(\alpha\rightarrow\beta)&=n_\alpha(1-s)w_A(\beta\rightarrow\alpha),\\ n_\beta(1-s)w_B(\alpha\rightarrow\beta)&=n_\alpha(1+s)w_B(\beta\rightarrow\alpha). \end{aligned} \quad (6)$$

Hence

$$\frac{w_B(\alpha\rightarrow\beta)}{w_A(\alpha\rightarrow\beta)}\cdot\frac{w_A(\beta\rightarrow\alpha)}{w_B(\beta\rightarrow\alpha)}=\left(\frac{1+s}{1-s}\right)^2, \quad (7)$$

which is consistent with (5) only in the absence of long-range order. From (6), we can also obtain the following alternative expressions for G:

$$\begin{aligned} G\equiv\frac{D_B}{D_A}&=\left(\frac{1-s}{1+s}\right)\frac{w_B(\alpha\rightarrow\beta)}{w_A(\alpha\rightarrow\beta)}=\left(\frac{1+s}{1-s}\right)\frac{w_B(\beta\rightarrow\alpha)}{w_A(\beta\rightarrow\alpha)}\\ &=\left(\frac{n_\alpha}{n_\beta}\right)\frac{w_B(\beta\rightarrow\alpha)}{w_A(\alpha\rightarrow\beta)}=\left(\frac{n_\beta}{n_\alpha}\right)\frac{w_B(\alpha\rightarrow\beta)}{w_A(\beta\rightarrow\alpha)}. \end{aligned} \quad (8)$$

To establish the dependence of G on s, it appears necessary to have detailed information about the jump frequencies, and this necessity cannot be circumvented in the way tried by Slifkin and Tomizuka. Summarizing, we may say that there seems no reason to suppose that $G\rightarrow1$ as $s\rightarrow1$ for the vacancy mechanism any more than for the interstitial mechanism.

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[1] L. Slifkin and C. T. Tomizuka, Phys. Rev. **97**, 836 (1955); **104**, 1803 (1956).