The Effect of Temperature Gradients on Diffusion in Crystals

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(Received December 3, 1953)

It has been proposed by Shockley[1] that it may be possible to distinguish experimentally between the vacancy and interstitial diffusion mechanisms by observing mass transfer as the result of a temperature gradient. In particular, it was stated that the temperature gradient should give rise to a diffusion current of defects under steady state conditions and that this current should produce mass transport toward high temperature for vacancies and toward low temperature for interstitial atoms. It is the purpose of the present note to show that this is true only for vacancies in case the formation energy of vacancies, E_f, exceeds the activation energy for their migration, E_m, whereas if the reverse is true, the direction of mass flow should be reversed. Thus, the experiments proposed by Shockley may prove of value in determining which energy, E_m or E_f, is the larger for materials in which the diffusion mechanism is known to be vacancy migration, rather than in determining whether an interstitial or vacancy migration mechanism is responsible for diffusion.

Consider two parallel neighboring planes of atoms perpendicular to the temperature gradient in the material, the first at a temperature T, and the second at $T+\Delta T$, as in Fig. 1. The flow of vacancies across a representative pair of atom sites, a and b, will be calculated. In order for a vacancy to flow toward higher temperature via this pair, (1) a must first be vacant and (2) the atom on b must jump the energy barrier, E_m, representing the activation energy for vacancy migration. The probability of (1) can be written:

$$Ae^{-E_f/kT},$$

assuming that the thermal equilibrium concentration is maintained in each plane, and the probability of (2):

$$Be^{-E_m/k(T+\Delta T)},$$

where both the entropy factor, A, and the frequency factor, B, are temperature independent. Thus, the vacancy flow to the right is:

$$ABe^{-E_f/kT}e^{-E_m/k(T+\Delta T)}.$$

Similarly, the vacancy flow to the left is:

$$ABe^{-E_f/k(T+\Delta T)}e^{-E_m/kT}.$$

The net flow of vacancies to the right is:

$$ABe^{-(E_m+E_f)/kT}[\exp(E_m\Delta T/kT^2)-\exp(E_f\Delta T/kT^2)],$$

if all terms higher than first order in $\Delta T/T$ are neglected. Thus, the net flow of vacancies is toward higher vacancy concentrations if $E_m>E_f$ and toward lower concentrations if $E_m<E_f$, whereas there should be no net flow if $E_m=E_f$. Recent work[2] indicates that $E_m>E_f$ for face-centered cubic metals, implying that the mass flow should be opposite in direction to that assumed by Shockley.

The geometry associated with interstitial migration is more complex, and the conditions under which mass transfer should be toward lower or higher temperatures cannot be calculated easily in an analogous manner.

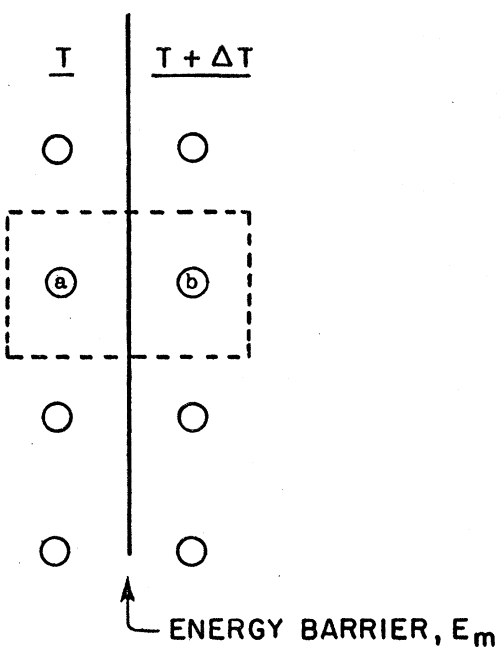

Fig. 1. Two neighboring planes of atoms in a crystal, each perpendicular to the temperature gradient.

[1] W. Shockley, Phys. Rev. **91**, 1563 (1953).
[2] A. D. LeClaire, Acta Metallurgica **1**, 438 (1953).

Some Predicted Effects of Temperature Gradients on Diffusion in Crystals

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(Received November 27, 1953)

The writer is entirely in agreement with the conclusion reached by LeClaire[1] and Brinkman[2] that one of the major mechanisms was unwarrantably disregarded in his first publication.[3]

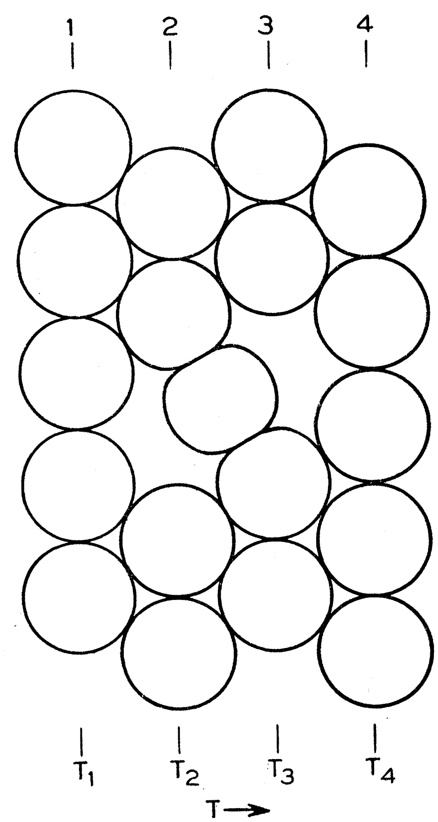

Fig. 1. Schematic representation of how the activation energy for jumping is furnished in part by neighbors of a jumping atom.