The Effect of Temperature Gradients on Diffusion in Crystals

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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
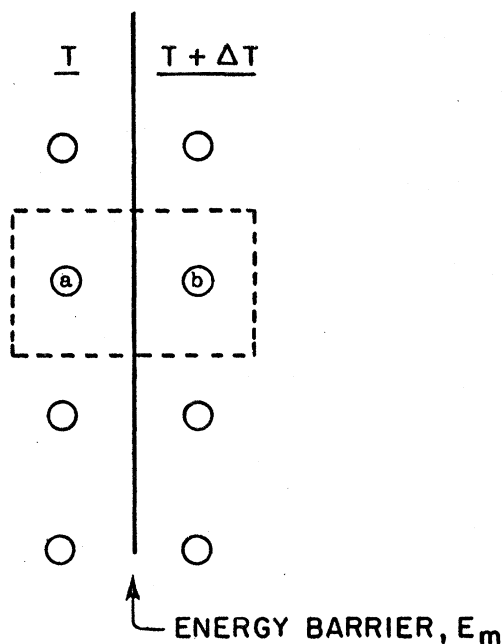

FIG. 1. Two neighboring planes of atoms in a crystal, each perpendicular to the temperature gradient.

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:

$$A e^{-E_f/kT},$$

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

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

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

right is:

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

Similarly, the vacancy flow to the left is:

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

The net flow of vacancies to the right is:

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

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.

[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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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]
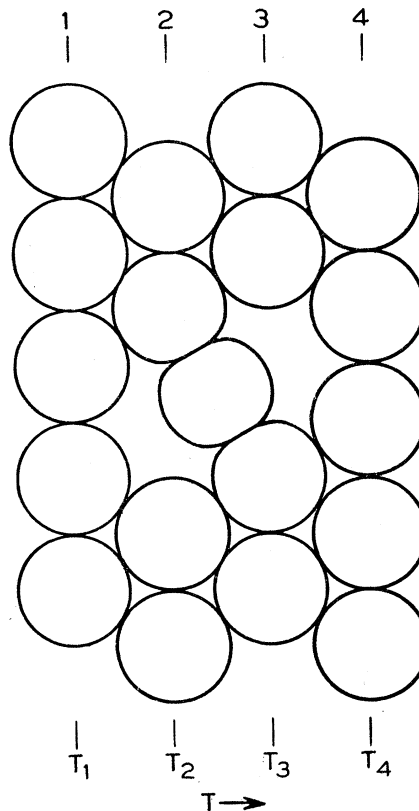

FIG. 1. Schematic representation of how the activation energy for jumping is furnished in part by neighbors of a jumping atom.

On the other hand, it appears to the writer that both LeClaire and Brinkman have rather oversimplified the problem with the result that they have overestimated the effect of jump activation energy. This may be illustrated for the case of vacancy diffusion in a two-dimensional hexagonal lattice as shown in Fig. 1. This figure represents a vacancy midway between planes 2 and 3, a situation produced by an atom that has jumped halfway from one plane into a vacancy on the other.

Evidently some of the energy Q for jumping will be stored in the interactions between the neighbors and next neighbors of the jumping atom. This energy would appear to be furnished thermally from a source at temperature of $T_{2.5}$, about midway between that on planes 2 and 3, regardless of the jump direction. Only a fraction of the activation energy Q will be furnished by the jumping atom itself.

This reasoning suggests that driving force for thermal diffusion will be smaller than that estimated from Q and, hence, that the domination of mass transport by the concentration gradient, as originally predicted by the writer, will be greater than LeClaire and Brinkman conclude. The effects they discuss will play an important role, but it is difficult to see how a quantitative theory can be developed.

In the case of germanium, it may be remarked, there appears to be a good possibility[4] of measuring both the energy of formation of centers U and jump energy Q. If Q turns out to be less than U, a unique determination of the nature of the heat centers may be possible.

[1] A. D. LeClaire, this issue [Phys. Rev. 93, 344 (1954)].
[2] J. A. Brinkman, preceding Letter [Phys. Rev. 93, 345 (1954)].
[3] W. Shockley, Phys. Rev. 91, 1563 (1953).
[4] R. A. Logan, Phys. Rev. 91, 757–758 (1953).

Water Vapor and the "Channel" Effect in n-p-n Junction Transistors*

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BROWN[1] has proposed two possible mechanisms for the formation of a "channel" or n-type conductivity layer on the normally p-type base region of an n-p-n transistor. These are (1) the accumulation of positive ions over the base region resulting from the electric field at the junctions, and (2) the ionization of neutral impurities on the surface due to the departure from equilibrium of the underlying semiconductor. These effects are generally attributed to small amounts of water vapor deposited on the surface although other contaminants have not been ruled out. Brown's observations on encapsuled units indicated that it takes several minutes to an hour to establish a channel after applying bias whereas recent work here indicates that this conditioning time decreases continuously with increasing water-vapor pressure to a value less than a millisecond near 100 percent relative humidity.

To examine further the effects of water vapor on "channel" formation, conductance, G, from emitter to collector was measured as a function of water-vapor pressure and applied reverse bias. The data shown in Fig. 1 were obtained on an etched[2] n-p-n bar having the same dimensions as that used by Brown and a p-type base resistivity of approximately 10 ohm-cm. The temperature was 25°C, and the ambient gas was nitrogen in all cases. Since Brown immersed his sample in liquid nitrogen after establishing a "channel," the surface charge was "frozen" at a fixed value; however, the present data indicate that the charge is increasing with applied bias since no "pinch-off" is observed. Furthermore, the apparent $1/V$ relationship (as indicated by the solid lines) points to the following explanation of the effect.
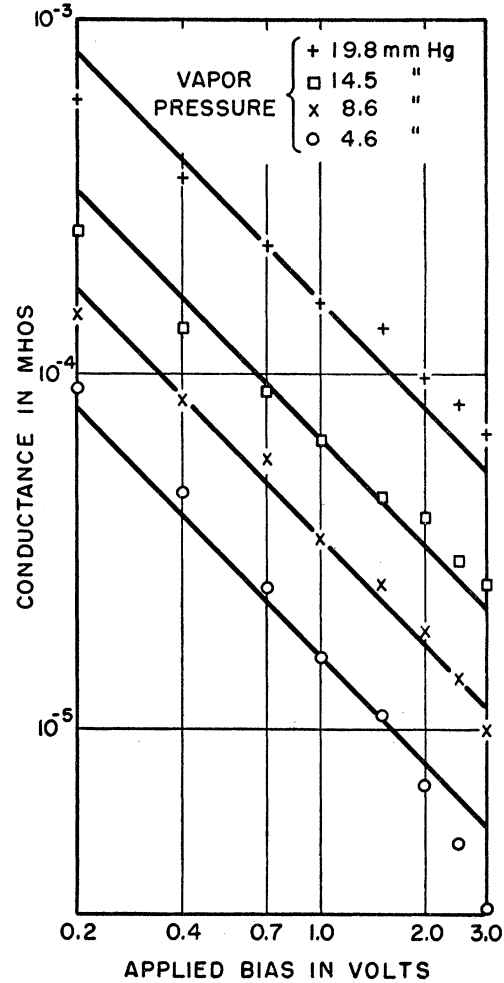

FIG. 1. Channel conductance *versus* applied bias at several values of water-vapor pressure.

On the basis of the second mechanism proposed by Brown, N_s ionizable impurities per cm^2 are assumed to be on the surface, having an excitation energy, ψ_D, as shown in Fig. 2. These impurities are of donor type, and their density is assumed to increase with increasing vapor pressure. The net positive surface charge may then be written

$$Q_s = qN_s \exp[-q(\psi_s + \psi_D - \phi_n)/kT]; \quad (1)$$

and by use of Eq. (6), reference 1, with the notation of Fig. 2, the conductance is found to be

$$G \propto \left\{ V_A - 2\psi_p + \frac{kT}{q}\left[\exp\left(\frac{q(\psi_s - \psi_p - \phi_n)}{kT}\right) - 1\right]\right\}^{\frac{1}{2}} - (V_A - 2\psi_p)^{\frac{1}{2}}, \quad (2)$$

since G is proportional to the number of conduction electrons, which is, in turn, proportional to the difference between the total field at the surface and that due to the acceptor ions alone. For most of the data considered, V_A is much greater than any of the other terms under the radicals in Eq. (2); therefore,

$$Q_s \propto \sqrt{V_A}, \quad (3)$$

since the first term in Eq. (2) represents the total field at the surface. Furthermore, the exponential in Eq. (2) is much greater than unity and is inversely proportional to Q_s/N_s from Eq. (1).