

Letters to the Editor

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Some Predicted Effects of Temperature Gradients on Diffusion in Crystals

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SHOCKLEY has recently proposed¹ that a continuous flow of defects will occur in a crystal in which there exists a temperature gradient, on account of the gradient of defect concentration which exists if the density of defects at any point has the equilibrium value characteristic of the local temperature at that point. Such a flow of defects, he suggests, will produce a mass transport through the lattice towards regions of higher temperature for vacancies and towards regions of lower temperature for interstitials and will be continuous except for limitation imposed by stresses that may be set up by the mass flow. Observations on the direction of such a mass transport, he then proposes, may provide a means of distinguishing between vacancies and interstitials.

It is the purpose of this note to point out that a flow of defects may occur as a direct result of the temperature gradient as well as indirectly through the gradient of local equilibrium concentrations. We shall consider first the more interesting case of vacancies. Figure 1 represents two adjacent lattice planes normal to the direction of the temperature gradient. n and T are, respectively, the numbers of vacancies per unit area and the temperature at plane (1), and $n+\Delta n$ and $T+\Delta T$ are the corresponding quantities for plane (2). In order that a vacancy on plane (1) may move to plane (2), an atom on plane (2) must acquire at temperature $T+\Delta T$ an activation energy Q . The rate of flow of vacancies from plane (1) to (2) is therefore:

$$J_{12} = n\nu \exp[-Q/R(T+\Delta T)],$$

where ν is the vibration frequency of the atoms. Similarly, the rate of flow of vacancies from plane (2) to (1) is:

$$J_{21} = (n+\Delta n)\nu \exp(-Q/RT).$$

The net flow of vacancies from plane (1) to (2) is therefore, for small dT/T ,

$$J = J_{12} - J_{21} = \frac{Q(\Delta T)}{RT^2} n\nu \exp(-Q/RT) - \frac{\Delta n}{n} n\nu \exp(-Q/RT).$$

The second term gives the diffusion flow arising from the concentration gradient and is of course proportional to the gradient and directed towards regions of lower concentrations. The first term

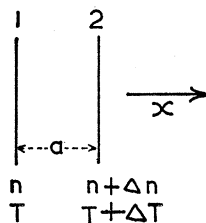


FIG. 1

gives the "thermal diffusion" flow and is directed towards regions of higher temperature.

Now, if we assume with Shockley that the concentration of vacancies is and remains, at each point in the crystal, equal to that which would be found in equilibrium in a crystal at a uniform temperature the same as at that point, then we shall have $\Delta n/n = (U/RT^2)dT$, where U is the energy of formation of a vacancy. Thus n increases in the same direction as does the temperature, and the normal diffusion flow is in a direction opposite to that of the thermal diffusion flow. If $Q=U$, then there will be no flow of vacancies at all. If $Q \neq U$, the net flow of vacancies will be towards the region of higher temperature when $Q > U$ and towards regions of lower temperature when $Q < U$.

In the case of interstitial diffusion, we find by reasoning similar to the above that the net flow of interstitials from plane (1) to (2) is

$$J = -\frac{Q(\Delta T)}{RT^2} \nu n \exp(-Q/RT) - \frac{\Delta n}{n} \nu n \exp(-Q/RT),$$

where Q is the activation energy for the jump of an interstitial, which in this case is to be acquired at the temperature of the plane on which the interstitial is situated. n is the number of interstitials and ν their vibrational frequency.

If again we assume that the concentration of interstitials at any point is that corresponding to thermodynamic equilibrium at the temperature at that point, then n increases in the same direction as does the temperature and the normal diffusion and the thermal diffusion flows are in the same direction, towards regions of lower temperature, and together equal $-\nu \exp(-Q/RT) \times \{(Q+U)/RT^2\} a \cdot dT/dx$, U now being the energy of formation of an interstitial.

We see then that, under the assumptions made, the mass flow accompanying the diffusion of interstitials is always towards the lower temperature regions whereas that accompanying the diffusion of vacancies may be towards either the lower or the higher temperature regions depending on the relative magnitude of Q and U . Observations on the direction of the mass flow will not then necessarily give an unambiguous indication of the type of defect responsible for it.

A detailed analysis of the diffusion of defects in a temperature gradient would have to take account not only of the flux of vacancies but also of the rates at which they are created and annihilated and the variation of these rates with temperature. Two extreme but simple cases can be distinguished. We may suppose that the rates of creation and annihilation of defects are sufficiently rapid to maintain at each point a concentration corresponding to isothermal equilibrium at the local temperature. A continuous flow of defects will then occur as here described. On the other hand, we may consider the case where the rates of creation and annihilation of defects are very slow compared to the diffusion flux. (This might be true for a time for regions well inside a single crystal if defects were generated only at the crystal surfaces.) The total number of defects present at the moment the temperature gradient was imposed would then diffuse until a quasi-stationary state was established where the normal diffusion flow exactly balances the thermal diffusion flow. The concentration of defects at any point would then remain constant but change with distance so that $d \log n/dx = (Q/RT^2)(dT/dx)$ for vacancies and $d \log n/dx = -(Q/RT^2)(dT/dx)$ for interstitials; i.e., the concentration of defects increases towards higher temperature for vacancies but towards lower temperature for interstitials. Such a creation of a concentration gradient by the action of a temperature gradient is, of course, an example of the Soret effect, and these same results may be obtained by the methods of irreversible thermodynamics if we put for the "heat of transport"² the activation energy Q for the motion of defects; the difference in sign arises because the transport of heat is in the same direction as the movement of interstitials but in the opposite direction to the movement of vacancies.

¹ W. Shockley, Phys. Rev. **91**, 1563 (1953).

² K. G. Denbigh, *Thermodynamics of the Steady State* (Methuen, London, 1951).