"Uphill" diffusion of vacancies and the instability of irradiated materials

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A mechanism is proposed for the "uphill" diffusion of vacancies against the gradient of a substitutional impurity. The influence of this diffusion mechanism is manifested in the possibility of unstable behavior arising in the irradiated material.

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During prolonged exposure of a material to ionizing radiation at an energy sufficient to produce vacancies (V), certain manifestations of unstable behavior on the part of the irradiated material are observed in experiments, including the formation of vacancy pores and segregations of other phases. It is natural to believe that the instability is a consequence of the appearance of mobile point defects in the system. However, in the existing theory the instability is introduced phenomenologically,[1] since the kinetic equations used to describe the mobile point defects[2] do not give rise to unstable solutions for the densities of point defects.

The principal mechanism governing the behavior of point defects are the diffusion, annihilation, formation, and decay of complexes of point defects, the simplest complex being a substitutional impurity—a foreign atom in a vacant lattice site. The

kinetic equations incorporating these mechanisms have only stable solutions in the region of low defect densities if the "uphill" diffusion of vacancies against the gradient of the substitutional impurity is ignored. This last mechanism arises because the complexes (the substitutional impurity), with an overwhelming probability, move only via vacancies, and their motion is accompanied by a counterflow of vacancies. Thus the presence of a nonuniform distribution of complexes in the system automatically leads to the motion of vacancies, even if the initial distribution of the vacancies is uniform. This motion of vacancies is not due to their concentration gradient, and amounts to an "uphill" diffusion of the vacancies. This mechanism (which was introduced by Kurata *et al.*[3] to describe impurity profiles), together with the "uphill" diffusion of the impurity via vacancies, automatically gives rise to instabilities in an irradiated material.

To elucidate the mechanism giving rise to the instabilities, it is sufficient to retain only two equations from the general system of kinetic equations describing the behavior of point defects in an irradiated material—the kinetic equations for the density n_V of vacancies and for the density n_m of complexes (the substitutional impurity):

$$\frac{\partial n_V}{\partial t} = D_V \Delta n_V - d_0 n_V \Delta n_m + (d_1 - d_0)(\nabla n_V, \nabla n_m) - \alpha n_V n_I - \beta n_V n_p + \gamma n_0 n_m + Q, \tag{1}$$

$$\frac{\partial n_m}{\partial t} = d_0 n_V \Delta n_m - d_1 n_m \Delta n_V + (d_0 - d_1)(\nabla n_V, \nabla n_m) + \beta n_V n_p - \gamma n_0 n_m + Q_m . \tag{2}$$

Here n_I and n_p are the densities of interstitial atoms of the matrix and impurity; D_V is the coefficient of diffusion of vacancies along their concentration gradient; Q is a source of vacancies; Q_m is an effective source of complexes; α, β, and γ are the coefficients of annihilation, decay, and formation of the point defects mentioned; and n_0 is the density of lattice sites in the medium. The term $d_0 n_V \Delta n_m$ in Eq. (1) corresponds to the proposed mechanism of diffusion of vacancies against the concentration gradient of the complexes. The term $d_1 n_m \Delta n_V$ in (2) describes the diffusion of complexes against the concentration gradient of the vacancies.[3] The coefficients d_0 and d_1 are generally different, in contrast to the treatment of Ref. 3. In Eqs. (1) and (2) we have dropped the terms describing the formation and decay of more complex formations of point defects.

Let us assume that the sources of point defects are such that there exist homogeneous and quasistationary solutions for the densities of point defects $n_l^{(0)}$ ($l = V, I, p, m$). If the deviations from the quasistationary solutions are small, we can linearly analyze Eqs. (1) and (2), seeking a solution of the following form, which corresponds to a variation of the density of vacancies:

$$n_m = n_m^{(0)} \equiv Q_m t; \quad n_V = n_V^{(0)} + \delta n_V = \frac{Q}{\alpha n_I^{(0)}} + \sum_{\mathbf{k}} \delta n_V(\mathbf{k})\, e^{\lambda(\mathbf{k})\, t}\, \phi_{\mathbf{k}}(\mathbf{r}), \tag{3}$$

where $\Delta \phi_{\mathbf{k}}(\mathbf{r}) = -k^2 \phi_{\mathbf{k}}(\mathbf{r})$, and t is the irradiation time. Combining Eqs. (1) and (2) and using Eq. (3), we obtain a kinetic equation for the variation of the vacancy density:

$$\frac{\partial \delta n_V}{\partial t} = (D_V - d_1 n_m^{(0)}) \Delta \delta n_V - \alpha n_I^{(0)} \delta n_V . \tag{4}$$

The condition of instability ($\lambda \geqslant 0$) is of the form

$$d_1 n_m^{(0)} \geqslant D_V + \frac{\alpha n_I^{(0)}}{k^2} . \tag{5}$$

The method of obtaining Eq. (4) reflects the compensational nature of the mechanism for the instability under study: The "uphill" diffusion of vacancies compensates the diffusion of complexes along their concentration gradient. Here the quantity $(D_V - d_1 n_m^{(0)})$ plays the role of an effective diffusion coefficient, and the onset of instability is in fact equivalent to a local change of the sign of this coefficient. Since the quantity on the left-hand side of condition (5) is proportional to the irradiation time [see Eq. (3)], the condition for the appearance of the instability can certainly be satisfied. Condition (5) implies that the instability arises at finite dimensions: $0 < k < a^{-1}$. The lower limit on k comes directly from condition (5), and the upper limit is due to the presence of a minimum dimensions in a crystal—the lattice constant a.

We note that Eq. (4) is rather general, since it can be obtained by summing the total system of kinetic equations describing the behavior of point defects in the medium. In the summation of these equations the terms describing the various processes involving point defects cancel out each other, since the kinetic equations are equations of local balance. The contribution to Eq. (4) from complexes higher than the substitutional impurity can be ignored: Their diffusion is small because of their large effective mass. The use of the entire set of kinetic equations in obtaining the instability condition leads to a renormalization of the last term in Eq. (4) and, hence, to a refinement of instability condition (5). Thus, in a system containing only four types of defects—vacancies, interstitial atoms, complexes, and impurity atoms in interstitial positions—the instability condition is of the form

$$d_1 n_m^{(0)} \geqslant D_V + \frac{D_I}{D_I k^2 + \alpha n_V^{(0)}} \alpha n_I^{(0)}, \tag{6}$$

where D_I is the diffusion coefficient of the interstitial atoms of the matrix;

$$n_V^{(0)} = \sqrt{\frac{Q}{\alpha (1+z)}} ; \; n_I^{(0)} = \sqrt{\frac{Q}{\alpha} (1+z)} ; \; n_m^{(0)} = z n_V^{(0)}; \; z = \frac{\beta}{\gamma n_0} \int_0^t Q_p \, d\tau \tag{7}$$

and Q_p is a uniform source of impurity atoms. Such a system can be considered a model of a medium which is homogeneously and uniformly bombarded by impurity atoms. In this case the solutions for the interstitial atoms of the matrix and of the impurities are quasistationary: $n_p = n_p^{(0)}$, $n_I = n_I^{(0)}$, and the solutions for the vacancies and complexes are (for $\lambda = 0$):

$$n_V = n_V^{(0)} + \frac{\delta n_V}{\sqrt{1 + d_V/d_n}} \phi_{\mathbf{k}_c}(\mathbf{r}) ; \; n_m = n_m^{(0)} + \frac{\delta n_V}{\sqrt{1 + d_V/d_n}} \frac{d_V}{d_n} \phi_{\mathbf{k}_c}(\mathbf{r}) , \tag{8}$$

where

$$d_V \equiv D_V k_c^2 + \alpha n_I^{(0)} + \beta n_p^{(0)}; \; d_n \equiv \gamma n_0 + d_0 n_V^{(0)} k_c^2; \; n_p^{(0)} = \int_0^t Q_p \, d\tau . \tag{9}$$

It follows from the solutions of (8) that two types of instability are possible in this model: In the case $d_V \ll d_n$ the solution for the complexes coincides with the quaistationary solution, whereas the variation of the vacancy density does not dissipate ($\lambda = 0$): $n_V = n_V^{(0)} + \delta n_V \phi_{\mathbf{k}_c}(\mathbf{r})$, and beyond the point of instability ($\lambda > 0$) the local change in the vacancy density increases. In the opposite case, $d_V \gg d_n$, the initial variation of the density of vacancies leads to the growth (for $\lambda > 0$) of the local density of complexes:

$$n_m = n_m^{(0)} + \sqrt{\frac{d_V}{d_n}} \delta n_V \phi_{\mathbf{k}_c}(\mathbf{r}) .$$

By analyzing the behavior of an irradiated medium near the point of instability without assuming that the deviations from the quasistationary solutions are small, one can study the structure of incipient instabilities. For example, in the case $d_V \ll d_n$, vacancy pores arise in the medium, with a size distribution that is close to that which is obtained phenomenologically.[1]

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