CONF-900936--3

The effect of defect clusters formed in cascades on the sink strength in irradiated materials*

Hartmut Wiedersich
Materials Science Division
Argonne National Laboratory
Argonne IL 60439

CONF-900936--3

DE90 017815

September 1990

Submitted to the Seventh International Conference on Ion Beam Modification of Materials (IBMM 90), September 9-14, 1990, Knoxville, TN.

*Work supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

The effect of defect clusters formed in cascades on the sink strength in irradiated materials*

Hartmut Wiedersich
Materials Science Division
Argonne National Laboratory, Argonne IL 60439

Defects produced by irradiation with energetic particles are most often spatially strongly correlated. Energetic primary recoil atoms produce generally more or less dense cascades in which vacant lattice sites predominate in the central regions, and interstitial atoms are deposited at the periphery. In fact, in many cases a fraction of the defects produced in the cascades form clusters during the cascade event. In this paper we examine the role of these clusters as defect sinks during high dose irradiations at moderate temperatures. It is shown that a steady state population of vacancy and interstitial clusters evolves during irradiation which significantly contributes to the overall sink density in the material. At sufficiently low temperature, i. e., at which thermal evaporation from vacancy clusters can be neglected, the steady state cluster density is characteristic of the primary recoil spectrum, but does not depend on temperature or dose rate. Consequently, contributions by migrating defects to irradiation-enhanced diffusion or to ion-beam mixing should also be temperature and dose-rate independent. When thermal evaporation of vacancies from small defect clusters becomes competitive with absorption of excess interstitials, the cluster population becomes temperature and rate dependent.

*Work supported by the U. S. Department of Energy, Basic Energy Sciences-Materials Sciences under Contract #W-31-109-ENG-8

1. Introduction

Since a number of years it has been recognized that the defect production calculated from codes based on straight forward binary collision approximations and the Kinchin and Pease formula overestimates the number of individual point defects produced by energetic particle bombardment see, e. g., references [1-4]. Even if one takes spontaneous recombination of defects produced in close proximity to each other into account, the calculated number of surviving defects exceeds significantly the experimentally observable numbers especially for irradiations with heavy ions and with high energy neutrons. [5,6] The knowledge of the fraction of defects that survive and undergo long range migration is of particular importance to the interpretation and prediction of microstructural changes occurring in materials during irradiations with neutron and energetic charged particles, since a number of these changes, such as radiation-induced precipitation and void swelling, require the migration of alloying elements and/or defects over considerable distances.

Transmission electron microscopic observations have shown that a large fraction of the defects produced in energetic cascade events are observed as clusters in the form of vacancy dislocation loops, stacking fault tetrahedra, and other three-dimensional clusters, and, to a minor extent, as interstitial dislocation loops see, e. g., [7], [8]. A number of treatments concerned with the survival of individual or "free" defects, potentially undergoing long range migration, have dealt with these clusters in more or less heuristic manner, e. g., [9], [10].

In this paper we present a treatment for the concentration of these clusters and their effects on the sink strength and, hence, on "free" defects in the framework of rate theory. [11] Bullough et al. have proposed a way of including the effects of small vacancy loops on void swelling. [12],[13] However, this approach has been largely ignored in the general treatments of microstructural changes, probably, because of the complexity of the model which includes the varying bias effects of several sink types.

Recently, Woo and Singh pointed out that clustering of interstitials can lead to a "production-bias" term and to an anomalously large void swelling rate if vacancy clusters are highly unstable. [14] The present treatment focuses on situations where vacancy clusters are thermally stable or moderately stable. It ignores bias effects since it is meant to be applied to phenomena such as radiation-induced segregation and radiation-enhanced diffusion, where bias effects are not central.

2. Model description

Irradiation with energetic particles almost invariable produces a significant fraction of defects in the form of clusters of closely spaced defects in cascades. In fact, the majority of defects is created in cascades in the case of irradiations with heavy ions and, even more so, with high energy neutrons. As a consequence, a significant fraction of the point defects created in cascades are lost by mutual recombination or form clusters of like defects during the cascade life-time ($\sim 10^{-12}$ s). It has been established experimentally that vacancies form clusters, dislocation loops and stacking fault tetrahedra, see, e. g., [7], [8]. Molecular dynamics simulations indicate that vacancies cluster predominantly in the central regions of cascades, whereas interstitials form clusters at the periphery, see, e. g.,[15], [16].

For the present purpose we will assume that the primary knock-on spectrum produces clusters at a rate $K_{icl,vcl}$ containing $n_{io,vo}$ interstitials (subscript i) or vacancies (subscript v). In reality there will be a distribution of cluster sizes, but for simplicity we will assume here that they are all of the same, average size. Both K and n will be different for interstitials and for vacancies. The clusters will shrink or grow depending on the net condensation rate of defects on clusters which, in turn, will be determined by the effective medium concentration [17] of interstitials, c_i, and vacancies, c_v, and by the cluster size dependent evaporation rate of defects. The cluster type that experiences shrinkage will tend towards a steady state cluster concentration; the type that grows will become ultimately a part of the "network" dislocation density. We note here that it is not inconceivable that both types of clusters shrink, e. g., at sufficiently high temperatures, when evaporation of defects from small clusters may be dominant even for interstitial clusters.

At temperatures of interest here, i. e., at which both types of point defects are mobile, one can expect that the material under irradiation approaches a quasi-steady-state. The relaxation times for approaching such a quasi-steady-state for a species depend on the species of interest. Although the microstructure as a whole continues to evolve, and, hence, the quasi-steady-state for every species changes with the microstructure, the concept of a quasi-steady-state is quite useful for species with short relaxation times. Generally, we can expect that quasi-steady-states are reached in sequence for interstitials, for vacancies, for cascade produced defect clusters that shrink followed by those clusters which get incorporated into the dislocation network and the network itself.

Our approach will be to determine the steady state concentrations of mobile vacancies and interstitials in the effective medium by a set of rate equations which takes into account that rate of freely migrating defects is reduced from the number of initially produced defects (displacements per atom) not only by mutual annihilation, but also by clustering of like defects during the cascade event. Furthermore, small clusters will be redissolved if entirely located within a central region of an energetic cascade and the resulting defects join the defects produced in the cascade. This region can be taken to be the equivalent to the "molten zone" [16] or region in which the deposited energy density during the collisional phase exceeds, say, the latent heat of melting. The production rate for vacancies, K_v, and that for interstitials, K_i, become different because the population of vacancy clusters differs from that of interstitial clusters. Therefore, we introduce separate rates of defect production for vacancies and interstitials: $K_v = K + K_{vcas}$ and $K_i = K + K_{icas}$ with K as the conventional production rate.

Of the defects formed and dissolved during a cascade event, N_v and N_i, fractions f_v and f_i will escape from the immediate vicinity of the cascades and will enter the effective medium as mobile defects. The remainder will either recombine, fractions f_{vr} and f_{ir}, or form clusters, fractions f_{vcl} and f_{icl} for vacancies and interstitials, respectively. We note here that only three of the six fractions are independent since the relations $1 = f_v + f_{vcl} +$

f_{vr}, $1 = f_i + f_{icl} + f_{ir}$ and $N_v f_{vr} = N_i f_{ir}$ must hold. The clusters themselves are considered as immobile.

With these definitions, the standard rate equations [11, 18] for the steady state concentrations of vacancies and interstitials c_v and c_i are:

$$\frac{\partial c_v}{\partial t} = 0 = K_v f_v + K_v^{th} - A c_i c_v - p_v \nu_v c_v \tag{1}$$

and

$$\frac{\partial c_i}{\partial t} = 0 = K_i f_i + K_i^{th} - A c_i c_v - p_i \nu_i c_i \tag{2}$$

In eqs. (1) and (2) $K_v f_v$ and $K_i f_i$ are the rates of release of vacancies and interstitials, respectively, from cascades into the medium. These terms take the place of the conventional production rate, K. K_v^{th} and K_i^{th} are the thermal emission rates of vacancies and interstitials, respectively, from all sources including the clusters. A is the recombination coefficient containing the jump frequencies ν_v and ν_i for vacancies and interstitials, and geometrical factors. The sink strengths p_v and p_i include those of the clusters; they are the probability per jump that the defect is annihilated at a sink. We will use throughout this paper "atomic units", i. e., the concentrations are atomic fractions and the production rates numbers of defects/atom/s. It should be pointed out, that the sink terms are frequently expressed [18] as Dk^2c with k^2 referred to as "sink strength" instead of $p\nu c$. Since the diffusion coefficient D equals $\nu b^2/6$ with b the jump or nearest neighbor distance, $k^2 = 6p/b^2$. The meaning of k^2 is an inverse reaction cross section for defect annihilation per unit time, whereas p is the probability that a defect is annihilated after its next jump.

The cluster size distributions are calculated from the rates at which clusters of a given size are formed and are lost either directly in cascades, or by shrinkage (or growth) of clusters of adjacent sizes. The latter rates are calculated from the "net flux" of defects in the medium:

$$\Delta j = \nu_i c_i - \nu_v c_v \qquad (3)$$

Neglecting bias effects for simplicity ($p_v = p_i = p$), we obtain from the rate equations (1) and (2):

$$\Delta j = (K_i f_i - K_v f_v)/p + (K_i^{th} - K_v^{th})/p \qquad (4)$$

The growth or shrinkage rate of clusters [in number of defects/s] is obtained from the approximate solution of the diffusion equation for a spherical cluster of radius r_n of n defects in the effective medium

$$J(r_n) = \frac{2\pi b^2}{3\Omega} r_n \{(K_i f_i - K_v f_v)/p + (K_i^{th} - K_v^{th})/p - (\nu_i c_i^{th}(r_n) - \nu_v c_v^{th}(r_n))\} \qquad (5)$$

Ω is the atomic volume, $c_v^{th}(r_n)$ and $c_i^{th}(r_n)$ are the thermal equilibrium concentrations of vacancies and interstitials, respectively, at the surface of the cluster of n defects. The first term in the curly bracket of eq. (5) arises from the excess of mobile interstitials (over vacancies) escaping from cascades; the second term comes from the thermal emission of defects from all other sinks including clusters and from clusters becoming unstable by shrinkage; and the last term is the net defect loss by evaporation from the cluster of radius r_n under consideration.

As we have discussed before, more interstitials than vacancies are likely to escape from clustering in cascades, making the first term in curly brackets of eq. (6) positive; the second term is, generally, negative, but smaller than the first; and the third term gives a positive contribution because interstitial evaporation is likely to be negligible. Hence, $J > 0$, and vacancy vacancy clusters shrink. The differential equation for the cluster size distribution for vacancies, $m_{vcl}(n)$, are

$$\frac{\partial m_{vcl}(n)}{\partial t} = 0 = K_{vcl}(n) + J(n+1)m_{vcl}(n+1) - [J(n) + N_{dis}(n)K_{cas}]m_{vcl}(n) \tag{6}$$

For $J > 0$ interstitial clusters grow, hence:

$$\frac{\partial m_{icl}(n)}{\partial t} = 0 = K_{icl}(n) + J(n-1)m_{icl}(n-1) - [J(n) + N_{dis}(n)K_{cas}]m_{icl}(n) \tag{7}$$

$K_{vcl}(n)$ and $K_{icl}(n)$ are the rates at which vacancy and interstitial clusters of size n, respectively, are produced directly by cascades; $N_{dis}(n)$ is the number of sites within the cascade upon which a cluster of size n can be centered and still be entirely within the "molten zone" of size N_{cas}; and K_{cas} is the rate of cascade formation. The second term on the right-hand side is the gain of vacancy (interstitial) clusters of size n by shrinkage (growth) of clusters of the next larger (smaller) size. The third term represents the losses by shrinkage (growth) and by cascade dissolution.

The differential equations for the cluster size distributions can be solved for steady state by recursion, i. e., by solving for $m_{vcl}(n)$ in terms of $m_{vcl}(n+1)$ and for $m_{icl}(n)$ in terms of $m_{icl}(n-1)$ for any given set of cluster formation rates, $K_{vcl}(n)$and $K_{icl}(n)$, total sink strength, p, [implicit in J(n)] and and an appropriate equation for $N_{dis}(n)$. The sink strength, p, must be recalculated to include the current cluster distributions, and by iteration self-consistent, quasi-steady state solutions can be obtained.

3. Assumptions and input parameters for model calculations

To get some physical insights, calculations under a number of simplifying assumptions have been made:

1) All defects are produced by a single size of cascades characterized by the following quantities: the number of defect pairs produced by collisions, N_0; the size of the "molten" region in which existing defect clusters are dispersed (expressed as number of sites affected, N_{cas}); the fractions of the total number of vacancies, f_v, and interstitials, f_i, that escape from the cascade and the fraction, f_{ir}, of interstitials that recombine with vacancies; the remaining vacancies cluster into a single vacancy cluster of size n_{vo}; the remaining interstitials form interstitial clusters of a single, small size n_{io}. With these assumptions and the conventional displacement rate, K, we have: $K_{cas} = K/N_0$, $n_{vo} = f_{vcl}\, N_v$, $K_{vcl}(n_{vo}) = K_{cas}$ and $K_{icl}(nio) =$ $K_{cas} f_{icl} N_i / n_{io}$; all other $K_{v,icl}(n) = 0$.

2) For cascade dissolution, the clusters are assumed to be circular dislocation loops with stacking faults. For fcc lattices we obtain the following expression:

$$N_{dis}(n) = N_{cas}\{1-(4/\sqrt{3}p)^{1/6}n^{1/2}/N_{cas}^{1/3}\}^3 \quad (8)$$

3) The maximum size of interstitial loops subject to dissolution is determined from eq. (8) by $N_{dis}(n_{imax}) = 0$. Interstitial loops that grow beyond that size are considered to become part of the dislocation network.

4) Vacancy loops that shrink below a size n_{vmin} are assumed to dissolve spontaneously and the resulting vacancies are added to the thermal production rate of vacancies.

5) The sink strength contributions of the clusters are calculated in the approximation of spherical sinks in an effective medium. Sink strengths for vacancy and interstitial clusters, and that of the matrix are not corrected for the presence of the other sinks.

6) Thermal evaporation of defects from clusters are neglected. This has the advantage that all quantities calculated do not depend explicitly on the displacement rate when compared on basis of dose. It should be noted, however, that the effects of thermal instability of small vacancy clusters can be explored by adjusting the minimum stable vacancy cluster size, n_{vmin}.

For the calculations, a set of reference values for the input parameters has been used. The values of several of them are rather uncertain; therefore, the sensitivity of the results to the choices were explored. Most of the reference parameter values were chosen to be consistent with values derived by Heinisch [9] from Marlowe type binary collision simulations of cascades in copper with subsequent "quenching" and "short term annealing": The numbers of defects, N_0 = 800, 400, 200, 100, 50, corresponds to cascades with 60, 30, 15, 7.5 and 3.75 keV of damage energy; the values of the fraction of vacancies escaping from cascades, f_v = 0.01, and that of defects recombining, f_r = 0.77, are those of Heinisch. The value for f_i has been increased from the Heinisch value of 0.04 to 0.1 corresponding to a minimum stable and immobile interstitial cluster size of 5 at elevated temperatures which appears more consistent with significant growth of interstitial clusters during stage II annealing [19]. The assumption of one big, immobile vacancy cluster, instead of many small clusters observed in the simulations has been made on the basis of TEM observations [7], [8] and molecular dynamics simulations of cascades [16]. The choice for the volume of the "molten" zone, N_{cas} = 10 N_0, is rather uncertain, but seems reasonable in the light of scarce existing results from molecular dynamics simulations. As sink strength for the matrix p_0 = 0.001 was chosen as reference value; this sink strength is rather high, and corresponds to a dislocation density of approximately 10^{12} /cm^2. The minimum stable and immobile vacancy cluster size for the reference set is n_{v0} = 3; as will be seen from the calculation, the exact value of n_{v0} has little bearing on the results. The exact choice for the size of interstitial clusters at formation, n_{i0} = 5, again has little effect. Although the calculations were performed with a displacement rate of K = 10^{-3} dpa/s , the results are independent of the rate as long as thermal processes are not explicitly taken into account and states are compared on the basis of dose rather than time.

All calculations were done with $f_i > f_v$, i. e., a larger fraction of mobile interstitials escapes from cascades at formation than vacancies. This implies that the fraction of interstitials that form in clusters in cascades is smaller than the corresponding fraction for vacancies, $f_{icl} < f_{vcl}$.

4. Results of model calculations

Figure 1 shows the steady-state size distributions for vacancy and the interstitial clusters obtained with the reference values of the input parameters just discussed. The maxima in the cluster concentrations occur at sizes of formation for both the vacancy and the interstitial clusters. This is a consequence of cascade dissolution: longer times are required to shrink a vacancy cluster to smaller sizes (or grow interstitial clusters to larger sizes), hence, the more of these clusters have been lost by cascade dissolution. The character of the distributions are similar for different cascade sizes indicated by the number, N_0, of defect pairs produced by collisions within the cascades. The sink strength for the cluster distributions are dominated the high concentrations of clusters near their size of formation.

The total sink strength, and those arising from the interstitial and vacancy clusters are shown in Fig. 2 as a function of the size of the vacancy clusters at formation (which is approximately proportional to cascade sizes). The sink strength is only weakly dependent on the size at larger cascade sizes and increases towards small cascade sizes. It must be emphasized that the matrix sink strength, $p_o = 0.001$, although chosen to be very high, contributes very little to the total sink strength. The largest contribution comes from the small interstitial clusters, and only around a third arises from vacancy clusters.

The dose required to shrink vacancy clusters from the formation to the chosen minimum size, n_{vmin} =3, is illustrated in fig. 3 as function of their size at formation. This dose is independent of the displacement rate under the present assumption of neglecting thermal evaporation; this dose is required to approach steady state for the entire size distributions. However, since small vacancy clusters (and large interstitial clusters) contribute little to the sink strength, we expect most of the sink strength attributable to clusters to develop at smaller doses.

Variations of the input parameters affect the details of the calculated cluster distributions and sink strengths. However, the general features are surprisingly robust for variations of the input parameters over the entire reasonable range. For example, the total sink strength changes only significantly for matrix sink strengths exceeding p_0 = 0.01 corresponding to unrealistically high dislocation densities of $10^{13}/cm^2$. This insensitivity to the background sink strength results from the high effectiveness of the small defect clusters.

A change of f_i from 0.1 to 0.04 (the Heinisch value) increases the total sink strengths by about 0.005 for all cascade sizes shown in fig. 2. At the other extreme, f_i = 0.2, the sink strengths drop by about 0.01 because only 1% of the interstitials formed in the cascades are available to form clusters.

The effect of increasing the minimum stable vacancy cluster size becomes only significant for n_{vmin} above about 80% of the vacancy cluster size at formation in the cascades , n_{vo}.

Summary and conclusions

Cluster formed in cascades develop under most circumstances to the dominant sinks for mobile point defects.

Dissolution of clusters by cascades is important in attaining quasi-steady-state cluster populations. As a consequence, the distribution of cluster sizes peak the size of formation, i. e., for vacancy clusters at the large end and for interstitial clusters at the small end. This leads to important secondary consequences: (a) the thermal dissolution of vacancy clusters contributes negligibly to the mobile vacancy concentration except when the size of instability approaches the size of formation. (b) the rate of production of interstitial dislocation loops exceeding the dissolution size by cascades is rather low. Although a smaller fraction of interstitials cluster, interstitial clusters contribute generally more to the sink strength than vacancy clusters.

As a consequence of the large sink strength of defect clusters produced under irradiation conditions in which significant numbers of large cascades occur, the steady state concentration of defects is reduced significantly below that in which few or no stable defect clusters are produced. Therefore, rate theory predictions neglecting the presence of defect clusters formed in cascades grossly overestimate, e. g., radiation-enhanced diffusion or radiation-induced segregation.

Acknowledgement

The author thanks L. J. Thompson for his help in developing a highly efficient program for the computations.

References

[1] W. Schilling, G. Burger, K. Isebeck and H. Wenzel in: Vacancies and Interstitials in Metals, A. Seeger, D. Schumacher, W. Schilling and J. Diehl, eds., North Holland, Amsterdam, 1970, p.255.

[2] R. S. Averback, R. Benedek and K. L. Merkle, Phys. Rev. B 18 (1978) 4156.

[3] L. E. Rehn, P. R. Okamoto and R. S. Averback, Phys. Rev. B30(1984)3073.

[4] M.-P. Macht, A. Müller, V. Naundorf and H. Wollenberger Nucl. Instr. and Meth. B 16 (1986) 148.

[5] L. E. Rehn and P. R. Okamoto, Materials Science Forum 15-18 (1987) 985.

[6] A. Müller, M.-P. Macht and V. Naundorf, J. Nucl. Mater. 103/104 (1981) 1487, J. Nucl. Mater. (1990) in press (Proc. ICFRM-4, Kyoto, 1989).

[7] J. Black, M. L. Jenkins, C. A. English and M.A. Kirk , Proc. R. Soc. Lond. A409 (1987) 177.

[8] M. Kiritani, T. Yoshiie, S. Kojima and Y. Satoh, Rad. Eff. Def. Sol.113(1990)75, M. Kiritani, Materials Science Forum, 15-18 (1987) 1023.

[9] H. L. Heinisch, Rad. Eff. Def. Sol.113 (1990) 53.

[10] H. Wiedersich, Rad. Eff. Def. Sol. 113 (1990) 97, J. Nucl. Mater. (1990) in press (Proc. ICFRM-4, Kyoto, 1989).

[11] H. Wiedersich, Rad. Effects 12 (1972) 111.

[12] R. Bullough, B. L. Eyre and K. Krishan, Proc. Royal Soc. A346(1975)81.

[13] R. Bullough and T. M. Quigley, J. Nucl, Mater. 113 (1983) 179.

[14] C. H. Woo and B. N. Singh, phys. stat. sol. (b) 159 (1990) 609.

[15] M. W. Guinan and J. H. Kinney, J. Nucl. Mater. 103/104 (1981) 1319.

[16] T. Diaz de la Rubia, R. S. Averback, R. Benedek and I. M. Robertson, Rad. Eff. Def. Sol.113 (1990) 39.

[17] A. D. Brailsford and R. Bullough, Phil. Trans. Royal Soc. London 302 (1981) 87.

[18] A. D. Brailsford and R. Bullough, J. Nucl. Mater. 44 (1972) 121.

[19] P. Ehrhart, K. H. Robrock and H. R. Schober, in Physics of Radiation Effects in Crystals, R. A. Johnson and A. N. Orlov, eds., North-Holland, Amsterdam, Oxford, New York, Tokyo, 1986, pp. 3-115.

Figure Captions.

Fig. 1. Size distributions of vacancy and interstitial clusters at quasi-steady state for cascades producing N_0 = 50, 100, 200, 400 and 800 defect pairs in collision events, respectively. The reference input parameters are: N_{cas} = 10, p_0=0.001, f_v =0.01, f_i = 0.1, f_{ir} = 0.77, n_{vmin} = 3 and n_{imin} = 5. The size interval is d_n = 1.

Fig. 2. Total sink strength and the contributions from interstitial and vacancy clusters of the distributions, shown in fig. 1, as function of the number of vacancies in the clusters at formation.

Fig. 3. Dose required to shrink vacancy clusters from size at formation, n_{vo}, to the minimum stable size, n_{vmin} = 3 for the vacancy clusters distributions shown in fig. 1.

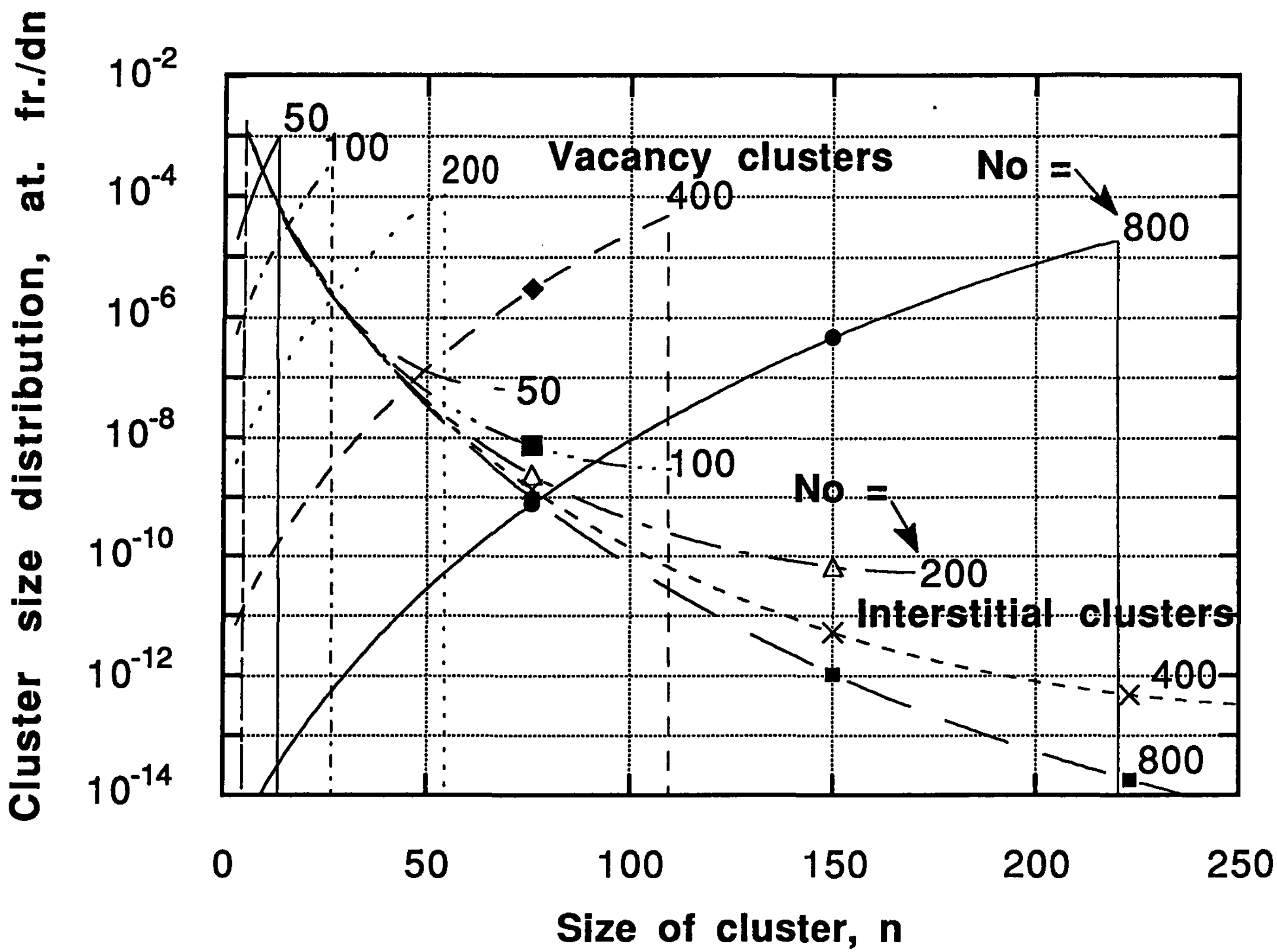

Fig. 1. Wiedersich

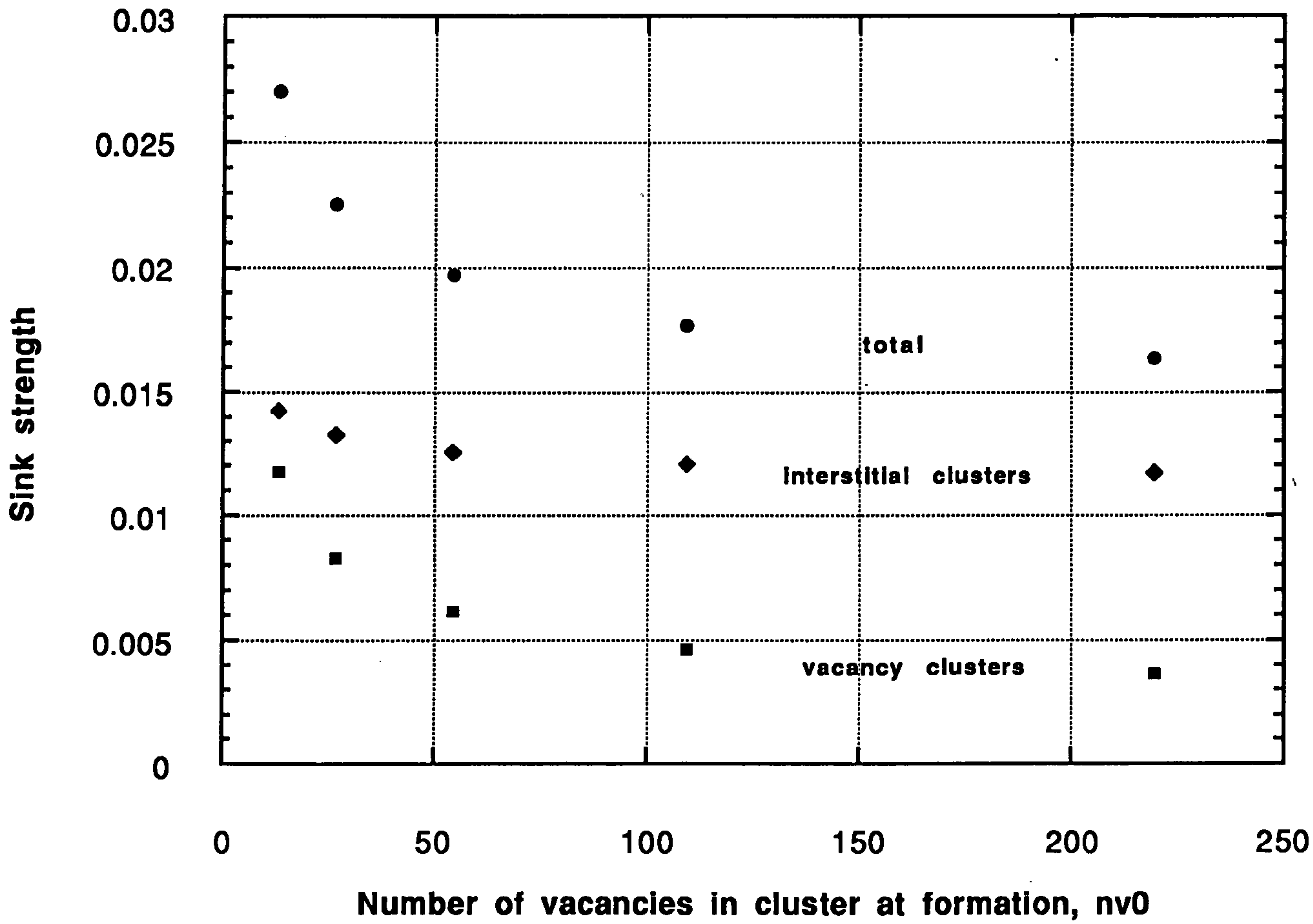

Fig. 2 Wiedersich

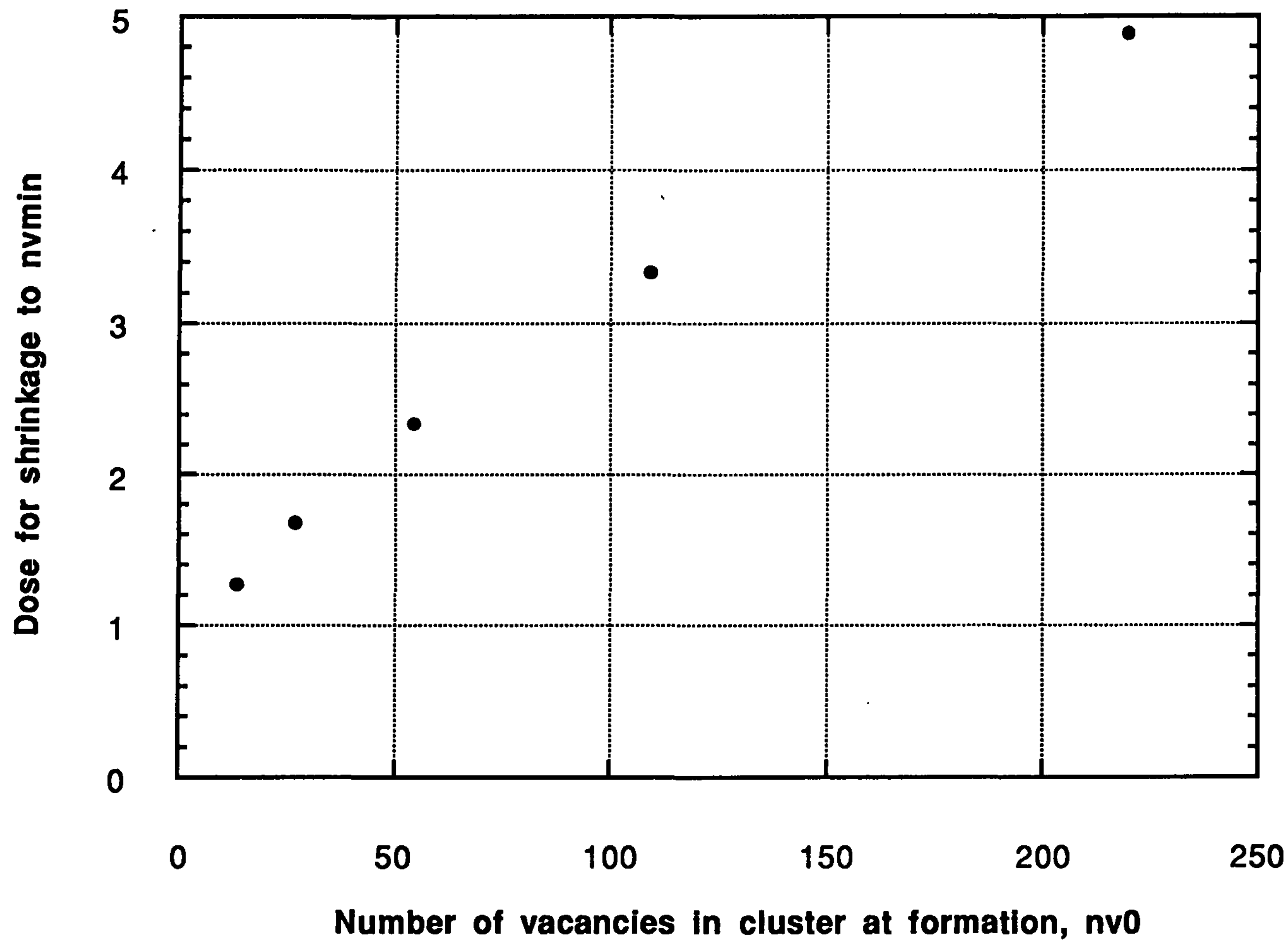

Fig. 3 Wiedersich