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ABSTRACT

Bulk recombination in the rate theory of void swelling and irradiation creep is a significant process at low temperatures. The rate of recombination is proportional to the recombination radius which is evaluated in the present paper. The computed radius is in good agreement with measured values for dilute copper alloys at cryogenic temperatures. The theoretical results can therefore be extended to the temperature range for void swelling, and it is found that the recombination radius is about two times the lattice parameter.

1. Introduction

The recombination or mutual annihilation of interstitials and vacancies is an important process which limits the number of point defects absorbed at dislocations and voids. In fact, a substantial fraction of all the Frenkel pairs produced by displacement damage recombine either within the collision cascade or during the long-range migration of the point defects through the crystal lattice. The recombination of a closely spaced Frenkel pair is usually referred to as correlated recombination, whereas distant pairs annihilate by uncorrelated recombination.

Point defects which escape the collision cascade may therefore be annihilated by uncorrelated recombination. If C_V and C_I are the average vacancy and interstitial concentrations per unit volume, respectively, and D_V and D_I their diffusion coefficients, the rate of uncorrelated recombination (UR) is given by [1]

$$UR = 4\pi R_c \, (D_V + D_I) \, C_V C_I \quad . \tag{1}$$

Equation (1) is obtained by solving the diffusion equation for interstitials with vacancies as their sinks [1], assuming that absorption occurs when the two point defects are within the separation distance R_c. This recombination radius R_c depends on the interaction between the vacancy and the interstitial, and its evaluation represents the major purpose of this paper.

This research was motivated by the fact that there is apparently no commonly accepted value for R_c in the rate theory of void swelling and irradiation creep. A cursory survey of the literature published over the last ten years revealed that the number of recombination sites chosen varies from 12, the number of next nearest neighbor sites, to over 2000. This implies that the recombination radius R_c varies by about a factor of 6 among different researchers. The apparent confusion about the value of R_c may originate from two issues. First, measured values of R_c have been obtained only for low temperature irradiations, and their extrapolation to elevated temperatures is uncertain. Second, it is often not appreciated that there are two parameters related to R_c, namely the spontaneous recombination radius R_0, and the capture efficiency.

Spontaneous recombination without the assistance of thermal activation will occur at a distance where the Frenkel pair becomes unstable. At this distance, no activation barrier exists for interstitial migration because of the strong interaction force between the interstitial and the vacancy. However, this interaction force still persists at greater distances, but it merely biases the diffusive jumps. As a result, it increases the mutual capture distance for recombination from R_0 to R_c.

Information about R_0 can be gained from computer simulation studies of close Frenkel pairs and from irradiation experiments with electrons at very low temperatures. The pertinent results of these studies are reviewed in Section 2. Next, for the evaluation of R_c, the mechanical interaction between an interstitial and a vacancy must be known. The various contributions to this interaction are considered in Section 3. Finally, the recombination radius R_c can be computed by solving a diffusion equation with a drift term containing the interaction force. Results of this computation are presented in Section 4, and comparison with available data for copper is made in Section 5.

2. The Spontaneous Recombination Radius

Computer simulation studies of Frenkel pairs [2,3,4] have shown that there exists around the vacancy a region of instability for the interstitial. In general, this region is not of spherical shape, so that the distance of spontaneous recombination depends on the crystallographic direction. Nevertheless, it is possible to define an equivalent recombination sphere, and its radius will be referred to as the spontaneous recombination radius R_0. Schroeder and Eberlein [5] have studied the recombination of Frenkel pairs with a lattice theory of diffusion and with non-spherical recombination regions. They found that the equivalent recombination radius is simply the arithmetic mean of the recombination distances along the various crystallographic directions. Furthermore, the continuous diffusion approximation to the lattice theory gives excellent results when diffusion takes place by nearest neighbor jumps.

As a result, we can evaluate the recombination radius with a spherical diffusion model where the vacancy represents a sink with radius equal to R_0.

The number of lattice sites from which spontaneous recombination takes place varies from 32 [3] to 74 [4] depending on the assumed interatomic potential used in the computer simulation. Measurements of the spontaneous recombination volume, reviewed by Wollenberger [6], gave 125 atomic volumes in the case of copper, 48 for platinum, and 135 for gold. However, these values are uncertain by perhaps a factor of two due to the approximate value of the electrical resistivity of one Frenkel pair. Hence, it can only be concluded that the spontaneous recombination volume comprises of the order of 50 to 150 atomic volumes, and that this agrees as well as can be expected with the computer simulation results.

Fortunately, as will become apparent, the recombination radius R_c depends only weakly on the choice of R_0.

3. The Interaction Energy Between a Vacancy and an Interstitial

Various expressions for the mechanical interaction energy between point defects have been derived in the past. The form of these expressions depends on how the point defects are modeled, and how the elastic distortions around the defects are treated. Each of the derived expressions captures usually one particular aspect of the point defect. Therefore, the total interaction consists of a sum of various contributions which can be identified as follows.

a) The dipole interaction, U^D, in an elastically isotropic and continuous medium requires that at least one point defect is modeled as a dilatation center with a non-isotropic dipole tensor P_{ij}. A vacancy is commonly considered as an isotropic center of dilatation, and its dipole tensor is given by

$$P^V_{ij} = Kv_V\delta_{ij} \tag{2}$$

where δ_{ij} is the Kronecker symbol, K the bulk modulus, and v_V the relaxation volume of the vacancy.

The interstitial in a fcc crystal, however, must be described by a non-isotropic dipole tensor as given by

$$P^I_{ij} = Kv_I \frac{3}{3+\eta}(\delta_{ij} + \eta\delta_{1i}\delta_{1j}) \tag{3}$$

when the dumbbell axis is along the x_1-direction of the cartesian reference frame. Here v_I is the relaxation volume for the interstitial and η

is the dipole anisotropy parameter.

The dipole interaction U^D is then given by [7]

$$U^D(\underset{\sim}{r}) = v_I v_V \frac{\eta}{(3 + \eta)} \frac{\mu}{2\pi} \frac{(1 + \nu)^2}{(1 - \nu)(1 - 2\nu)} \frac{\cos^2\theta - 1/3}{r^3} \tag{4}$$

where θ is the angle between the dumbbell axis and the distance vector $\underset{\sim}{r}$ connecting the vacancy and the interstitial. The shear modulus and Poisson's ratio are denoted by μ and ν, respectively.

As it is well known, the dipole interaction vanishes when both defects are isotropic, i.e, when $\eta = 0$. Furthermore, the angular average of U^D vanishes even when $\eta \neq 0$.

b) The dipole interaction in an elastically anisotropic and continuous medium, U^A, does not vanish even for isotropic point defects. This interaction has been evaluated by various authors [8,9,10]. When the elastic anisotropy constant

$$A = C_{11} - C_{12} - 2C_{44} \tag{5}$$

is small in comparison to the elastic constants C_{11}, C_{12}, and C_{44} of the cubic crystal, the interaction U^A can be expanded in powers of A [9]. The first-order term can be written as [8]

$$U^A(\underset{\sim}{r}) = v_I v_V \frac{5A}{24\pi} \left(\frac{1 + \nu}{1 - \nu}\right)^2 \frac{3/5 - f_4}{r^3} \tag{6}$$

where

$$f_4 = (x_1^4 + x_2^4 + x_3^4)/r^4 \qquad (7)$$

and x_1, x_2, and x_3 are the components of $\underset{\sim}{r}$ along the cubic axis of the elementary cell. Again, as in the case of $U^D(\underset{\sim}{r})$, the angular average of $U^A(\underset{\sim}{r})$ vanishes. The higher order terms for $U^A(\underset{\sim}{r})$, being nonlinear in A, exhibit a more complicated angular dependence but retain the same radial dependence as the first order term [9]. The angular average of these higher order terms vanishes also. Since we will be able to replace the angular variation by a constant in later computations, Eq. (6) will suffice as an adequate approximation even when the elastic anisotropy constant is not small in comparison to the elastic constants.

c) The dipole interaction in a crystalline medium requires further corrections. First, the dipole tensor characterizes a point defect as a set of three orthogonal double forces attached to a singular point. In reality, an interstitial atom, for example, exerts forces on its neighboring atoms attached to their centers rather than to one singular point. To characterize this finite separation of the forces requires multipoles in addition to the dipole tensor [7]. Second, the elastic Green's function of the continuum theory also requires lattice corrections when applied to small separation distances between the point defects [7]. These corrections were first discovered in the lattice statics work of Hardy and Bullough [11]. As shown by Siems [7], the Hardy-Bullough interaction in an isotropic elastic medium can be written as

$$U^{HB}(\underset{\sim}{r}) = v_I v_V \frac{35\ a^2 \mu}{192\pi} \frac{(1 + \nu)^2}{(1 - \nu)(1 - 2\nu)} \frac{(3/5 - f_4)}{r^5} \qquad (8)$$

where a is the lattice parameter. For the fcc lattice, the lattice parameter is related to the atomic volume by $\Omega = a^3/4$.

d) The interaction energies discussed so far are based on the assumption that the entire crystal, including the regions occupied by point defects, can be treated as a medium with uniform elastic properties. Due to the large distortions close to the point defect, however, the elastic properties of the region around the point defect are substantially different than in the perfect crystal. If the point defect is therefore modeled as an inhomogeneous inclusion, an additional interaction arises [12]. This so called modulus interaction between an interstitial and a spherical cavity was derived previously by Wolfer and Ashkin [13], and it can be written as

$$U^M = \frac{9}{8}\, \alpha_I^G \left(\frac{r_o}{r}\right)^6 \left(\frac{2\gamma}{\mu r_o}\right)^2 \quad . \tag{9}$$

Here, r_0 is the cavity radius, γ the surface stress, and α_I^G is the shear polarizability of an interstitial. The surface tension $2\gamma/r_0$ of the cavity produces a spherically symmetric strain field which is equivalent to the strain field of an inclusion with appropriately chosen misfit or relaxation volume. In fact, as shown by Eshelby [12], the equivalent relaxation volume is given by

$$v/\Omega = -3 \left(\frac{1 - \nu}{1 + \nu}\right)\left(\frac{2\gamma}{\mu r_0}\right) \quad . \tag{10}$$

If we choose the cavity radius for a vacancy according to $4\pi r_0^3/3 = \Omega$, we obtain

$$U^M = \frac{1}{2} \left(\frac{3}{8\pi}\right)^2 \left(\frac{1 + \nu}{1 - \nu}\right)^2 \alpha_I^G \, v_V^2 \, r^{-6}$$

for the modulus interaction of an interstitial in the strain field of a vacancy. Since the vacancy also possesses a shear polarizability α_V^G, we must add the modulus interaction of the vacancy in the strain field of the interstitial. The total modulus interaction is therefore

$$U^M = \frac{1}{2} \left(\frac{3}{8\pi}\right)^2 \left(\frac{1 + \nu}{1 - \nu}\right)^2 (\alpha_I^G \, v_V^2 + \alpha_V^G \, v_I^2) \, r^{-6} \quad . \tag{11}$$

It should be noted that the modulus interaction in an isotropic medium has no angular dependence. In a cubic lattice, however, the shear polarizability tensor has two different components. As shown by Trinkaus [14], the modulus interaction does then depend on the orientation of the separation vector $\underset{\sim}{r}$ with regard to the cubic axis when the two shear polarizabilities are different. But for equal shear polarizabilities, his expression closely agrees with ours, except that his numerical factor is larger by about 18%. This difference appears to be the result of modeling the point defect as an inhomogeneous spherical inclusion in our case, and by a set of induced double forces in his case. Considering the dissimilarity of the model assumptions, the close agreement of the results is remarkable. In any case, the numerical difference is of little consequence for the present application.

The total interaction energy consists now of the sum of all the above contributions, i.e.

$$U(\underset{\sim}{r}) = U^D + U^A + U^{HB} + U^M \quad . \tag{12}$$

The various contributions can be evaluated with the physical parameters given in Table 1 for copper. The radial dependencies of the interaction energies are shown in Fig. 1 for the case of copper. It is seen that the dipole interaction U^D and its lattice correction, the Hardy-Bullough interaction U^{HB}, are both negligible compared to the modulus interaction U^M and the dipole interaction U^A due to the elastic anisotropy of the lattice.

4. The Recombination Radius

If the interaction energy is only dependent on the radial distance between the interstitial and the vacancy, then the recombination radius is given by [20,21]

$$R_c/b = \{\int_0^{b/R_0} d(b/r)\ \exp\,[U(r)/kT]\}^{-1} \qquad (13)$$

where b is the Burgers vector or the next nearest neighbor distance, k is the Boltzmann constant, and T the absolute temperature. In order to use Eq. (13) with the interaction energy as given by Eq. (12), an angular independent average for $U(\underset{\sim}{r})$ must be chosen. Profant and Wollenberger [22] have performed an extensive numerical computation to evaluate R_c. However, they employed only the angular dependent interaction $U^A(\underset{\sim}{r})$, and compared the exact result with the approximate result when the angular variation of $U^A(\underset{\sim}{r})$ was neglected. They found that the exact recombination radius R_c is 63% of the approximate one. The two results can be made to agree, however, if the angular factor in $U^A(\underset{\sim}{r})$ is replaced by a constant factor of 0.25. The physical meaning of this constant factor is that the interstitial has access to the vacancy only within a cone extending over one quarter of the entire solid angle. In

Table 1

Physical Parameters for Copper, Nickel, and Austenitic Stainless Steels

Physical Property	Symbol	Cu	Ni	Stainless Steels 18% Cr, 14% Ni	Stainless Steels 17.5% Cr, 12% Ni
Shear Modulus, x 10^{10} Pa	μ	5.47	9.47	8.78	9.16
Poisson's Ratio	ν	0.324	0.277	0.254	0.270
Anisotropy Ratio	$\|A\|/\mu$	1.89	1.59	1.94	2.03
Relaxation Volume for					
Interstitial	v_I/Ω	1.45(a)	1.4(b)	1.4(b)	1.4(b)
Vacancy	v_V/Ω	-0.40(a)	-0.2(c)	-0.2(c)	-0.2(c)
Dipole Anisotropy Parameter for Interstitial	η	0.053	0.053	0.053	0.053
Shear Polarizability for					
Interstitial, x 10^{-17} J	α_I^G	-2.73(d)	-2.73	-2.73	-2.73
Vacancy, x 10^{-17} J	α_V^G	-0.27(d)	-0.27	-0.27	-0.27
Lattice Parameter x 10^{-10} m	a	3.615	3.524	3.582	3.582

[a] Values from Ref. [15].

[b] Assumed values.

[c] Typical value in fcc metals according to estimates by Sherby, Robbins, and Goldert [16].

[d] Values are close to those measured [17,18] and theoretically predicted [19] for copper.

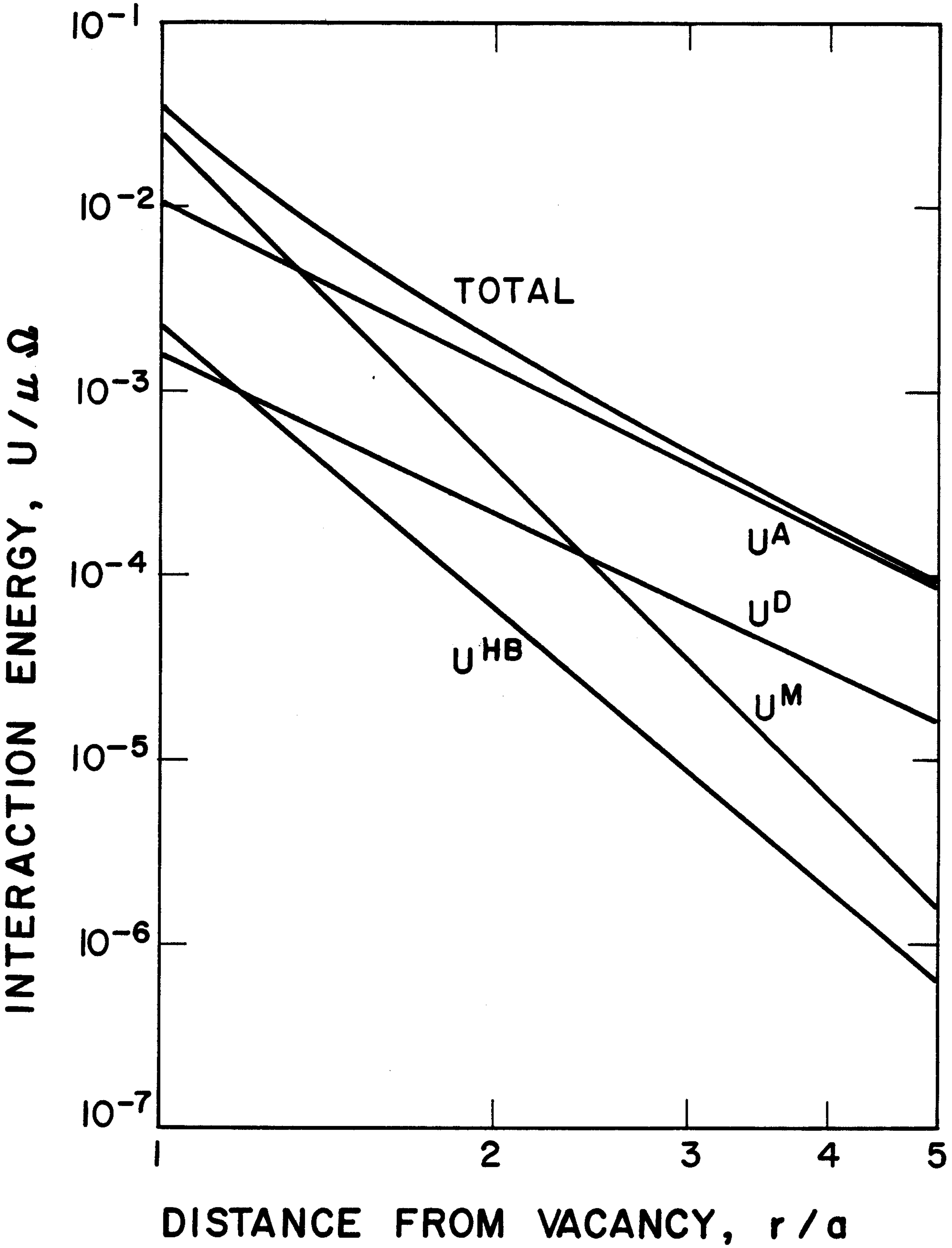

Fig. 1 Interaction Energies between a Vacancy and an Interstitial in Copper.

directions outside this cone, the interaction $U^A(\underset{\sim}{r})$ exerts a repulsive force on the interstitial migration.

In our case, the total interaction is the sum of U^A and U^M. Since the latter is attractive in all directions, the accessible solid angle is expected to be somewhat larger than π. Accordingly, the constant factor which replaces the angular factor of $U^A(\underset{\sim}{r})$ can be treated as an adjustable parameter when experimentally derived recombination radii are available.

5. Results

For dilute copper alloys, Lennartz et al. [23] have determined experimentally the recombination radius R_c in the temperature range from 50 K to 105 K. Their data are shown in Fig. 2 together with our numerical results obtained from Eq. (12). These results are drawn as solid lines, and the best fit with the data is achieved when replacing the angular factor of $U^A(\underset{\sim}{r})$ with a constant of 0.3. This is only slightly larger than 0.25, the appropriate constant if the modulus interaction U^M were not included. The dashed line in Fig. 2 represents the empirical fit of Lennartz et al. [23] to their own data.

Considering the large error bars associated with the data, our fit is as satisfactory within the data range as is the dashed line. However, our results show that a straight line extrapolation to higher temperatures would not be correct.

The various solid curves shown in Fig. 2 represent the computed recombination radii R_c for different values of the spontaneous recombination radius R_0. Whereas R_c is independent of the choice of R_0 in the low temperature range, at least within the range of possible values discussed in Section 2, it increased with increasing R_0 in the high-temperature range for void swelling and irradiation creep. The reason for this dependence is simply that R_c must

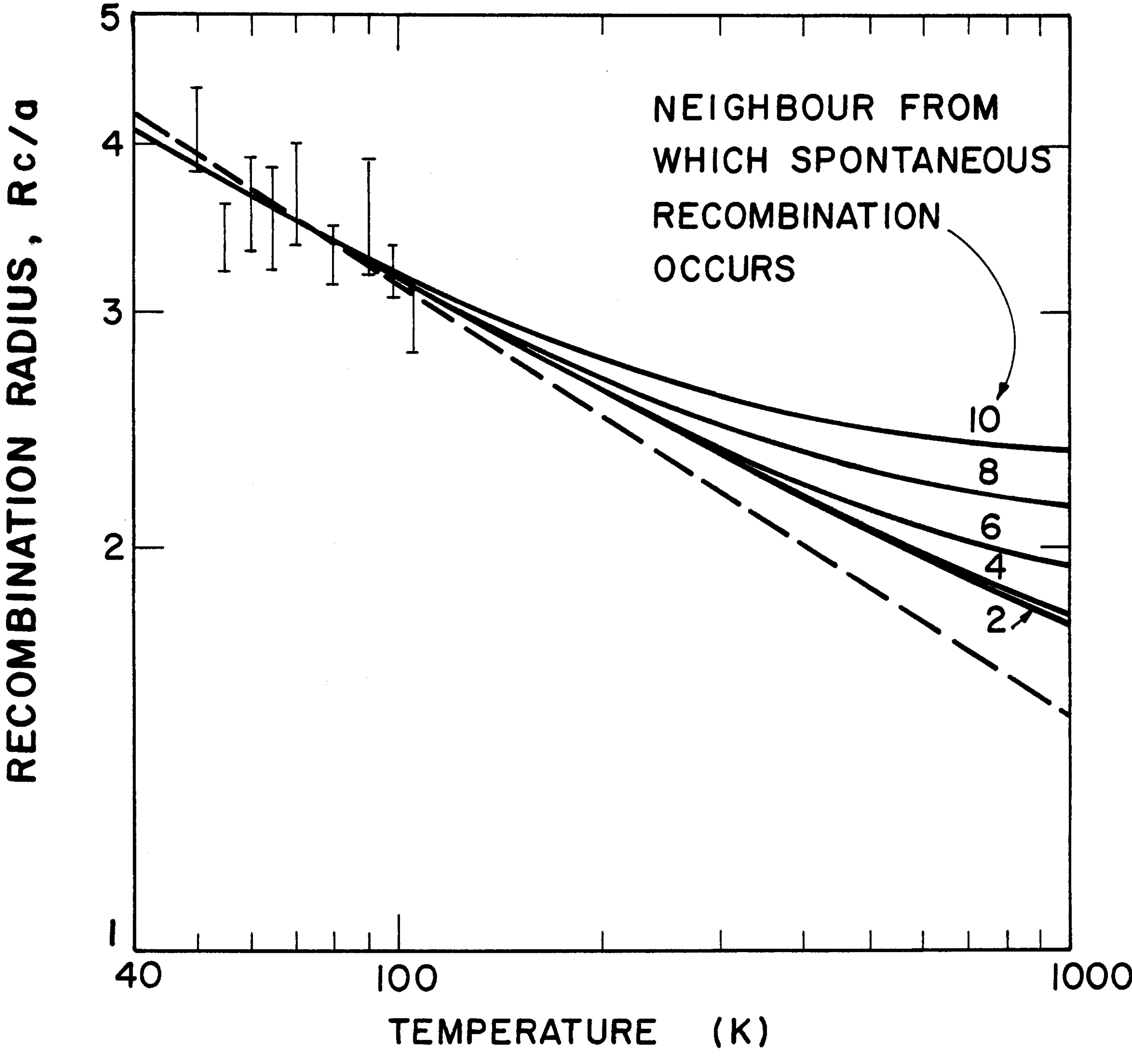

Fig. 2 Recombination Radius for Copper.

approach R_0 asymptotically with increasing temperature. According to both computer simulation studies and experiments, the radius of spontaneous recombination is found to be between the fourth and eighth neighbor distance, i.e. comprising 54 to 140 lattice sites according to Table 2. As our analysis shows, the recombination radius R_c at elevated temperatures is only slightly larger than R_0.

It is unfortunate that point defect parameters for nickel or austenitic stainless steels are not known. Assuming, however, that they are similar to the point defect parameters in copper, as indicated in Table 1, the recombination radius R_c has been computed for nickel and for two steels whose chromium and nickel contents fall within the specifications of type 316 stainless steels. The results are shown in Fig. 3 for a spontaneous recombination radius of $R_0 = a$ and $R_0 = 2a$, respectively. The differences between the three materials are due to variations in the elastic constants. Their effect on the recombination radius R_c is seen to be minor.

In order to assess the variation of the recombination radius with the point defect properties, we examined two additional cases for the 18% Cr - 14% Ni stainless steel. For the "upper estimate" shown in Figure 4, the relaxation volume of the interstitial is assumed to be $v_I = 2\ \Omega$, and the shear polarizabilities are increased by a factor of two compared to the "nominal estimates" given in Table 1. For the "lower estimate", the relaxation volume of an interstitial is chosen as $v_I = 1\ \Omega$, and the shear polarizabilities are assumed to vanish. In this case, $U^M = 0$. As shown in Figure 4, all three cases give very similar results at high temperatures and for a spontaneous recombination radius of $R_0 = 2a$. Differences are significant only when

Table 2

Near-Neighbor Distances for the FCC Lattice

Order of Neighbor	Distance in Units of b[a]	Distance in Units of a	Total Number of Enclosed Sites
1	1.000	0.708	12
2	1.412	1.000	18
3	1.732	1.226	42
4	2.000	1.416	54
5	2.236	1.583	78
6	2.540	1.734	86
7	2.646	1.873	134
8	2.828	2.000	140
9	3.000	2.124	176
10	3.162	2.239	200

(a)b is the Burgers vector.

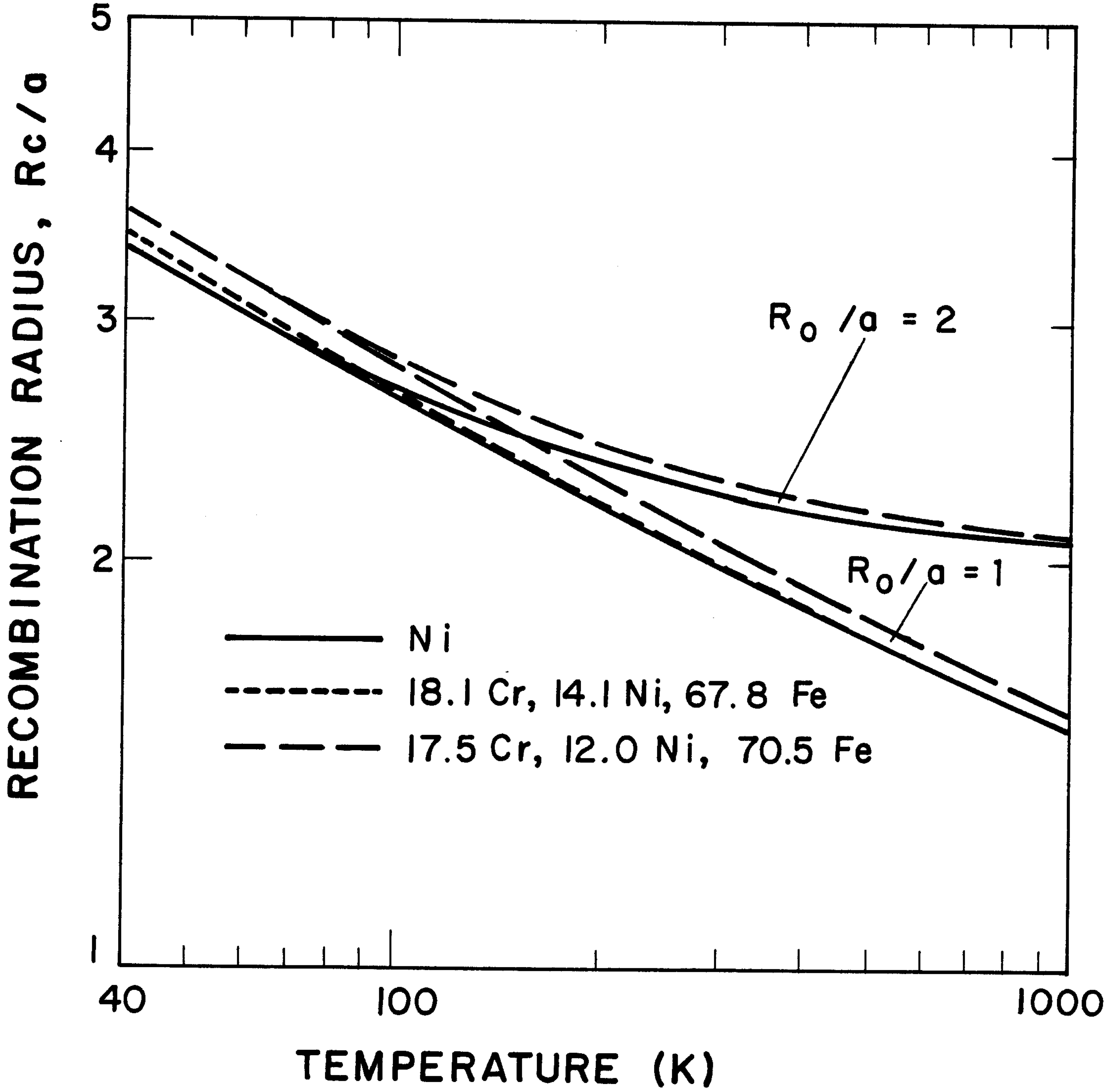

Fig. 3 Recombination Radius for Nickel and Stainless Steels for Nominal Point Defect Parameters.

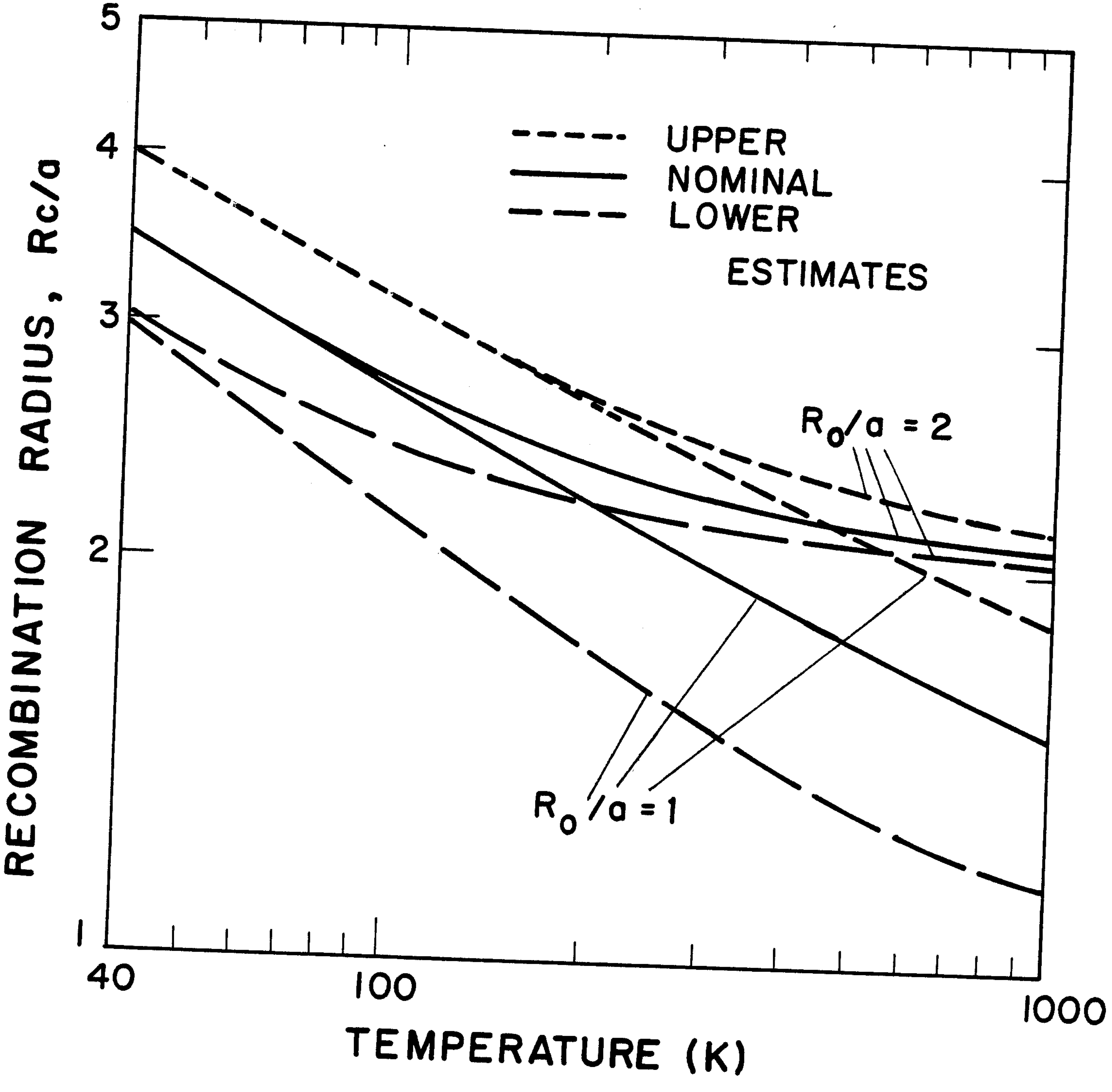

Fig. 4 Recombination Radius for Stainless Steel and for Upper and Lower Estimates of the Point Defect Parameters.

$R_0 = a$. Nevertheless, the recombination radii obtained for the lower and upper estimate differ by no more than a factor of 1.5 even for this case.

6. Conclusions

The radius R_c for bulk recombination of vacancies and interstitials has been computed based on the long-range mechanical interaction between point defects. For copper, where experimental results are available for both the essential point defect parameters as well as the recombination radius at low temperatures, excellent agreement can be obtained between computed and measured values for R_c. Although the recombination radius R_c depends on the spontaneous recombination radius R_0 at high temperatures, the possible values of R_c are very close to about 2a, where a is the lattice parameter. In fact, the remaining uncertainty is substantially less than the spread of values for R_c used in the literature.

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