

Impurities
and Imperfections

1955

IMPURITIES AND IMPERFECTIONS



A SEMINAR ON IMPURITIES AND IMPERFECTIONS HELD DURING THE THIRTY-SIXTH NATIONAL METAL CONGRESS AND EXPOSITION, CHICAGO, OCTOBER 30 TO NOVEMBER 5, 1955, SPONSORED BY THE AMERICAN SOCIETY FOR METALS

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FOREWORD

Metallurgists have long had an interest in the effects of impurities and imperfections on the properties of metals and alloys. Variations in properties between similar lots of metals have frequently been attributed to small differences in chemistry and in many instances such differences have been found. Not infrequently, however, the differences could not be accounted for by chemistry, at least by regular chemical analysis procedures. Recently techniques have been developed that enable the determination of exceedingly small amounts of impurities and these have confirmed that very pronounced effects can result from impurities present in amounts of parts per million. An important factor in bringing this about has been the development of semiconductor devices, such as the transistor, which depend for their operation upon controlled impurities present in exceedingly small quantities. Also well recognized but not as definitely confirmed quantitatively because of experimental difficulties are the effects of fine structural imperfections. The advances being made in this field are very rapid and significant, and it was therefore selected as the topic for the 1954 American Society for Metals Seminar.

The Committee responsible for arranging the program consisted of D. Turnbull, Chairman, P. A. Beck, H. Brooks, B. Chalmers, R. L. Cunningham, E. Jette, L. K. Jetter, E. S. Machlin, R. Maddin, O. T. Marzke, A. S. Nowick and F. Seitz. The members offered many helpful comments and suggestions on topics, speakers, and general arrangements.

Background information on the three major types of imperfections—point (lattice vacancies and interstitials), line (dislocations), and surface (grain and sub-grain boundaries)—is first presented. This is followed by discussions of the effects of both impurities and imperfections on metallurgical reactions (grain growth, diffusion, and transformation) and on properties (mechanical, electrical, and chemical). Finally, papers on semiconductors, ionic crystals, and radiation effects are given because of the very significant contributions to this general field by physicists working on these materials.

O. T. MARZKE
Seminar Coordinator

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Table of Contents

	Page
Lattice Vacancies and Interstitials in Metals—	
By Harvey Brooks, Gordon McKay, professor of applied physics, Harvard University, Cambridge, Mass.	1
Dislocations—	
By John C. Fisher, Research Laboratory, General Electric Co., Sche- nectady, N. Y.	28
Grain Boundaries, Substructures and Impurities—	
By R. W. Cahn, University of Birmingham, Birmingham, England....	41
Effects of Impurities and Imperfections on Crystal Growth—	
By Bruce Chalmers, professor of metallurgy, Division of Applied Science, Harvard University, Cambridge, Mass.	84
Impurities and Imperfections in Metallic Diffusion—	
By David Lazarus, Department of Physics, University of Illinois, Urbana, Ill.	107
Role of Structural Impurities in Phase Transformations—	
By David Turnbull, research associate, General Electric Co., Research Laboratory, Schenectady, N. Y.	121
Effects of Impurities and Imperfections on Mechanical Properties—	
By Earl R. Parker, professor of metallurgy, and Jack Washburn, as- sistant professor of metallurgy, University of California, Berkeley, Cal.	145
Influence of Impurities and Imperfections on the Electrical Properties of Metals—	
By J. S. Koehler, Department of Physics, University of Illinois, Ur- bana, Ill.	162
Structure Dependent Chemistry of Metal Surfaces—	
By W. D. Robertson, Hammond Metallurgical Laboratory, Yale Uni- versity, New Haven, Conn.	170
Effects of Impurities and Imperfections in Semiconductors—	
By J. A. Burton, Bell Telephone Laboratories, Murray Hill, N. J.	186
Vacancies and Alkali Halide Crystals—	
By Robert Maurer, Department of Physics, University of Illinois, Urbana, Ill.	200
Radiation Disarrangement of Crystals—	
By Frederick Seitz and J. S. Koehler, University of Illinois, Depart- ment of Physics, Urbana, Ill.	213

LATTICE VACANCIES AND INTERSTITIALS IN METALS

BY HARVEY BROOKS

1. INTRODUCTION

IT IS convenient to classify imperfections in crystals according to their dimensionality: point or atomic imperfections, line imperfections, and surface imperfections.

Surface imperfections include grain boundaries, mosaic boundaries, twin boundaries, boundaries between solid phases, and free surfaces. Line imperfections are called dislocations. Both surface and line imperfections are characterized by the fact that they do not, in general, exist in thermal equilibrium below the melting point of a solid. They are usually metastable structures which result from incidents of growth, mechanical deformation, or thermal history (1).¹

Atomic imperfections are characterized by the fact that they can exist in thermodynamic equilibrium in a crystal at finite temperature. They consist of localized groups of misplaced or missing atoms. This classification includes lattice vacancies, interstitials, substitutional impurities, and various associations of these such as clusters of vacancies and interstitials in the form of subcritical nuclei or "embryos." A lattice vacancy, for example, is an atom site, normally occupied in the perfect crystal, from which an atom is missing. Often the term vacancy is used to denote a so-called Schottky defect, which is the imperfection formed when an atom is removed from a normal lattice site and replaced in an average position on the surface of the crystal. An average position is a position such that the energy gained when an atom joins the crystal at this point is exactly equal to the heat of sublimation. When the crystal is an alloy or solid solution there will be many different types of Schottky defect, corresponding to the different possible environments of the vacant lattice site.

An interstitial is an atom occupying a definite position in the lattice which is not normally occupied in the perfect crystal. The interstitial may be either a normal atom of the crystal or a foreign atom. An interstitial is a defect formed by removing an atom from an average position on the surface and placing it in an interstitial site; a Frenkel defect, on the other hand, is formed by removing an atom from a normal lattice site to form a vacancy and placing it in an interstitial position remote from the vacancy. Vacancies and interstitials can move through the crystal. A vacancy moves through having a neighboring atom jump into the empty site. The motion of an interstitial can be more complicated. In interstitial solid solutions, for example, the interstitial solute

¹ The figures appearing in parentheses pertain to the references appended to this paper.

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atom jumps directly from one interstitial position to a neighboring one. On the other hand, in self-diffusion by an "interstitialcy" (2) mecha-

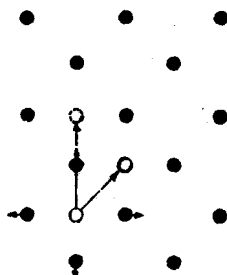


Fig. 1—Diffusion of an Interstitial Atom (arrow to right) and Diffusion by the "Interstitialcy" Mechanism (vertical arrow).

nism, an atom in an interstitial position replaces an atom in a normal position and pushes it into an adjacent interstitial site. Both situations are illustrated for a face-centered cubic structure in Fig. 1. It is seen that interstitial solute diffusion requires much closer crowding of atoms than the interstitialcy self-diffusion mechanism, and thus it is that interstitial solute diffusion can only occur with very small solute atoms.

This simple classification of imperfections is complicated by the possibility of various associations of imperfections. For example, vacancies can associate in pairs or in complexes containing several vacancies. Vacancies and interstitials, on the other hand, usually cannot associate with each other because they will mutually annihilate. Vacancies or interstitials can become associated with edge dislocations, or with the edge parts of complex dislocations. When they do so they form jogs in the dislocation line; jogs due to vacancies and interstitials project in opposite directions, and can migrate along the dislocation line until they meet and annihilate one another. Vacancies can also form "atmospheres" around dislocations, especially at high temperature. Vacancies may also associate preferentially with substitutional impurity atoms, especially if these differ appreciably in size from the surrounding lattice. Such associated vacancies may enhance the diffusion rate of certain impurities.

Since grain boundaries and mosaic boundaries are thought to be composed of dislocations, vacancies and interstitials can also associate with such boundaries, and also form atmospheres near them at high temperature.

2. FORMAL THERMODYNAMIC THEORY OF ATOMIC IMPERFECTIONS

Let f_v be the energy necessary to form a single isolated vacancy in a pure metal, and N_v be the number of such vacancies present, while N

is the total number of atoms in the system. A careful analysis shows that f_v is actually the increase in Gibbs free energy of the crystal as a whole when a Schottky defect is formed at a particular lattice site and a particular surface site.

The total number of lattice sites available to vacancies is $N + N_v$. The free energy of the system, taking into account the various possible positions of the vacancies, is then given by:

$$\begin{aligned} F &= N_v f_v - kT \ln \frac{(N + N_v)!}{N! N_v!} \\ &= N_v f_v - kT \left(N_v \ln \frac{N}{N_v} + N_v \right) \end{aligned} \quad \text{Equation 2.1}$$

using Stirling's approximation for the factorials. In order to find the most probable number of vacancies we minimize Equation 2.1 with respect to N_v , keeping N constant. The result is:

$$\frac{N_v}{N} = e^{-f_v/kT} \quad \text{Equation 2.2}$$

A similar analysis applies to interstitials. The combination of an interstitial and a vacancy, located at different lattice sites is a Frenkel defect, and its free energy of formation may be denoted by f_i , and the number of such defects by N_i . In this case the free energy of the system is given by:

$$F = N_i - kT \left[N_i \ln \frac{qN}{N_i} + N_i \ln \frac{N}{N_i} + 2N_i \right] \quad \text{Equation 2.3}$$

where q is the number of interstitial sites per normal lattice site. Of the two terms in the entropy the first arises from the different possible locations of the interstitial and the second from the different possible locations of the vacancy in the lattice. Minimizing with respect to N_i , we have:

$$\begin{aligned} \frac{N_i}{N} &= q^{1/2} e^{-\frac{f_i}{2kT}} \\ &= q^{1/2} e^{-\frac{f_i + f_v}{2kT}} \end{aligned} \quad \text{Equation 2.4}$$

where f_i is the free energy of formation of an interstitial alone.

A more interesting case is that which obtains when vacancies and interstitials can occur independently. We now denote by f_i the free energy necessary to form an interstitial by taking an atom from the surface and putting it at an interstitial position in the interior, while f_v has the same meaning as previously. The result is, that since N_i and N_v are independent we have the independent relations:

$$\frac{N_i}{N} = q e^{-\frac{f_i}{kT}} \quad \text{Equation 2.5}$$

$$\frac{N_v}{N} = e^{-\frac{f_v}{kT}}$$

A similar analysis may be applied to simple complexes of atomic defects. In each case the relation for the number of such complexes is:

$$\frac{N_n}{N} = p_n e^{-\frac{f_n}{kT}} \quad \text{Equation 2.6}$$

where N_n is the number of complexes of size n , f_n the corresponding free energy, and p_n the number of distinguishable orientations which the complex can assume. For example, for a pair $p = z/2$, where z is the co-ordination number.

Also of interest is the relative number of complexes under the condition that the total number of vacancies is fixed, but not necessarily at the equilibrium value. This is the condition that might obtain, for example, in a crystal quenched from a high temperature. Without going through the detailed derivation it may be noted that the fractional number of n 'th order complexes is given by:

$$\frac{N_n}{N} = p_n \left\{ \frac{N_v}{N} \exp\left(\frac{f_1 - f_n/n}{kT}\right) \right\}^n \quad \text{Equation 2.7}$$

where the free energy in the exponential is the binding energy per unit imperfection of the n 'th order complex. Equation 2.7 is valid only if the quantity in brackets is small compared with unity. This equation shows that, as we should expect, the number of complexes decreases very rapidly with the order. Even binary associations of defects usually are of little importance unless a high degree of supersaturation exists. For the case of a binary complex Equation 2.7 may be put in the form:

$$\frac{N_2}{N_1} = \frac{z}{2} \frac{N_v}{N} \exp\left(\frac{2f_1 - f_2}{kT}\right) \quad \text{Equation 2.8}$$

where N_2/N_1 is the ratio of pairs to single vacancies. If we adopt the crude model that the energy of a vacancy complex is approximately proportional to its surface area, and we represent each vacancy by a cube, then we find:

$$2f_1 - f_2 = \frac{1}{2}f_1$$

Now, the temperature at which motion of vacancies is appreciable (taken as about 10^4 jumps per sec.) is determined roughly by the condition:

$$e^{\frac{f_1}{kT}} = 10^4 \quad \text{Equation 2.10}$$

From this it follows that a face-centered cubic crystal can have appreciable binary complexes compared with single vacancies at room temperature if the concentration of vacancies is of the order of 10^{-4} , which is of the order that exists just below the melting point in common metals.

It has sometimes been suggested (22) that pairs of vacancies may make important contributions to diffusion because they are much more mobile than single vacancies. (27) The above discussion would indicate that this can be true only under conditions of considerable supersaturation, although it is possible that the binding energy of a pair may be substantially larger than given by the crude estimate above.

The above general theory of complexes applies almost unchanged to aggregates of interstitials, and is especially applicable when the interstitials constitute a second species of atom, for in this case the number is fixed by composition. There is some indication of the existence of binary associations in interstitial solid solutions.

3. ESTIMATES OF FORMATION ENERGY IN TERMS OF MACROSCOPIC CONCEPTS

Even though there is no rigorous justification for using such macroscopic concepts as surface energy and elastic constants on an atomic scale, it is still instructive to attempt to apply such concepts to the calculation of the free energy of formation of vacancies and interstitials. The more rigorous quantum mechanical calculations which can be made involve such drastic approximations that there is some question as to whether they are any more reliable than the cruder estimates. In any event, where the two methods agree, one may have additional confidence in both results.

The simplest approximation would be to regard the atoms of the metal as bound by pairwise interactions between nearest neighbors. In this case the cohesive energy, or heat of sublimation, is represented by:

$$E_{coh} = \frac{1}{2} z w$$

where z is the number of nearest neighbors, and w the pair interaction energy. Then a vacancy is formed by breaking z bonds and restoring, on the average, $z/2$ bonds when the missing atom is returned to the surface. Thus, in this picture, the energy of formation of a vacancy should be equal to the sublimation energy. That this is an overestimate for metals is clear from the fact that the same concept results in an overestimate of the free surface energy of a metal.

For example, the pair interaction would imply a vacancy formation energy of about 3.6 ev. in copper, whereas the actual value is probably less than 1.2 ev. (2). Similarly the bond picture would suggest that the surface energy per atom of a close packed surface in Cu would be about one half the heat of sublimation, and would be an even larger fraction for other surfaces, whereas actually the surface energy is less than one third the heat of sublimation. If the energy of a vacancy were reduced in the same ratio, its formation energy would be about 2.4 ev. In fact, this reduction of the surface energy is a result of the nature of the metallic bond. In terms of bond language, a large part of metallic binding arises from "resonance" among the various possible bonding direc-

tions, and the result is that when a few bonds are broken some of the bonding strength is transferred to the remaining bonds. In terms of the energy band picture, the electrons in a metal are highly mobile and will adjust their distribution to shield out any disturbance in the lattice in such a way as to reduce its energy. Qualitatively this effect should be the same whether the defect is a free surface or a vacancy, although empirically the correction factor appears to be somewhat larger for a vacancy.

A more precise treatment would be the following. The formation of a vacancy is considered as equivalent to creating new surface equal to the area of one unit cell, or approximately the spherical surface corresponding to the atomic volume. In order to preserve the volume energy the missing atom must be regarded as spread uniformly over the outer surface, and it is easily shown that the resultant increase in external surface area becomes negligible as the volume gets large. Thus the energy becomes:

$$f_v = 4\pi r_s^2 \gamma \quad \text{Equation 3.2}$$

where γ is the specific surface free energy. However, the surface tension of the hole will tend to contract its size by distorting the rest of the crystal elastically. Let us suppose that this elastic distortion results in a displacement ϵr_s of the surface of the hole. Then, using ordinary elasticity theory, which involves the assumption that ϵ is $\ll 1$, we find for the total elastic energy associated with the contraction of the hole:

$$f_{el} = 8\pi G r_s^3 \epsilon^2 \quad \text{Equation 3.3}$$

where G is the rigidity modulus of the surrounding crystal. G may be taken as the reciprocal mean of the two principal cubic shearing elastic constants $\frac{1}{2}(C_{11} - C_{12})$ and C_{44} . The precise relationship used is derived in Appendix A, and is given by:

$$\frac{1}{G} = \frac{0.6}{C_{44}} + \frac{0.4}{\frac{1}{2}(C_{11} - C_{12})} \quad \text{Equation 3.3'}$$

Taking into account also the reduction in surface energy due to the contraction of the hole we have for the total energy:

$$\begin{aligned} f_v &= a\epsilon + b\epsilon^2 \\ a &= 8\pi r_s^2 \gamma \\ b &= 8\pi G r_s^3 + 4\pi r_s^2 \gamma \end{aligned} \quad \text{Equation 3.4}$$

The minimum energy occurs for $\epsilon = -a/2b$, and its value is given by:

$$f_v = 4\pi r_s^2 \gamma \left\{ \frac{1}{1 + \frac{1}{2} \frac{\gamma}{G r_s}} \right\} \quad \text{Equation 3.5}$$

In choosing the value of γ in Equation (3.5) we take as the surface area of a close-packed face not the plane surface area but rather an

effective area for the atoms exposed on such a surface. The plane area associated with each surface atom is:

$$\frac{\sqrt{3}a_0^2}{4}$$

where a_0 is the cube edge. Each surface atom has one quarter of its neighbors missing so that in effect we may take its surface area as one quarter that of an atomic polyhedron or

$$\frac{3a_0^2}{4\sqrt{2}}$$

The effective area is thus $\sqrt{\frac{3}{2}} = 1.225$ times the plane area. As an example for copper this gives

$$\gamma_{\text{eff}} = \frac{1430}{1.225} = 1165 \text{ ergs/cm}^2$$

whence

$$4\pi r_s^2 \gamma_{\text{eff}} \approx 2.02 \text{ ev.}$$

For Cu

$$r_s = 1.414 \times 10^{-8}, G = 3.94 \times 10^{21} \text{ and}$$

$$\frac{\gamma}{2Gr_s} = 0.1045$$

and thus

$$f_v = 1.83 \text{ ev. for copper.}$$

Analogous calculations may be made for the assumption that the measured surface energy is that of a 100 face and a 110 face respectively. In this way we find:

$$f_v = 1.59 \text{ ev. for 100 assumption}$$

$$f_v = 1.80 \text{ ev. for 110 assumption}$$

If we consider that the surface energy, measured at high temperature, represents an average of many possible orientations, we may estimate a lower limit for f_v at about 1.45 ev.

Results of similar calculations for other elements are shown in Table I. Actual measurements of surface energy are available only for copper, silver, and gold. In the other cases the surface energy was taken as one sixth the heat of sublimation, per surface atom. Values of G were computed from Equation 3.3' and are also shown in Table I, as are the ratios γ/Gr_s . It is probable that the method of calculation gives an upper limit for f_v because, as discussed in the example of copper, the measured free surface energy is probably an average for several crystallographic orientations rather than for a close-packed face as assumed in the computations.

The only more rigorous calculation available is that for copper by Huntington (3), who gives:

$$E_v = 1.8 \text{ ev.}$$

It is shown in Appendix B that Huntington's calculation should be modified and the true predicted value of E_v should lie between 1.0 and

Table I
Calculation of formation energy of vacancy from surface energy and elastic contraction.

Element	γ (plane)	a_0	$G^{(0)}$	$\frac{\gamma}{Gr_s}$	f_v^\dagger (uncorrected)	$f_v^{\dagger\dagger}$ (corrected)
Cu	1430 ergs/cm ²	3.615 Å	3.94×10^{11} dynes/cm ²	0.210	2.02 ev.	1.83 ev.
Ag	1180	4.086	2.78	0.218	2.12	1.91
Au	1550	4.078	2.44	0.326	2.78	2.38
Al	(900)	4.049	2.60	0.179	1.59	1.46
Pb	(520)	4.950	.642	0.342	1.37 ^b	1.17
Ni	(1830)	3.524	7.17	0.151	2.44	2.27
Na †††	220	4.291	0.152	0.582	0.715	0.554
α -Fe	(1880)	2.866	7.4	0.153	2.73	2.54
W	(3460)	3.165	15.1	0.124	6.10	5.73

† Computed assuming that γ (plane) is for close-packed face, not corrected for contraction.

†† Corrected for contraction.

††† Body-centered cubic results computed assuming that surface energy γ is that for a close-packed face, (110).

1.2 ev.(8). These results are not strictly comparable, since Huntington's calculation give the energy of formation for absolute zero, whereas the calculation outlined above gives something more nearly equal to a free energy at room temperature. The two should not differ by more than about 0.05 ev. It appears that the surface energy calculation overestimates the formation energy of a vacancy as compared with experimental values.

We may also compute the energy of formation of an interstitial by similar arguments. An upper limit to this should be given by a calculation of the strain energy in the lattice produced by the interstitial. For interstitials of the same species, the strain energies involved are so large, that the problem cannot be considered even approximately in terms of linear elasticity theory. However, if we assume that the nonlinearities in the stress strain relationship are of similar functional form for different materials of the same crystal structures we arrive, by a dimensional argument, at an expression for the strain energy of the form:

$$f_{s1} = 8\pi Gr_s^2 f(r_1/r_0) \quad \text{Equation 3.6}$$

We may evaluate the function $f(r_1/r_0)$ roughly as follows. The total force acting across a spherical surface of radius r is given approximately by:

$$F_r = 16\pi Gr^2 \ln(r/r_0)$$

where r_0 is the initial radius with the crystal in equilibrium. The work done in expanding the cavity from r_0 to r_1 is then given by:

$$\int_{r_0}^{r_1} F_r dr = 8\pi Gr_s^2 \left[\frac{2}{3} \ln(r_1/r_0) - \frac{2}{9} (1 - r_0^3/r_1^3) \right] \quad \text{Equation 3.7}$$

In the case of an interstitial r_0 may be taken as the radius of the interstitial site while r_1 is the radius of a normal site. G is now given by Equation (A.6) and is 5.4×10^{11} dynes/cm² for copper. For an interstitial site in the face-centered cubic structure we have

$$\begin{aligned} \text{Hence} \quad & r_1/r_0 = 2.414 \\ & f(r_1/r_0) = 0.381 \\ \text{and} \quad & f_1 = 9.2 \text{ ev.} \end{aligned}$$

A quantum mechanical calculation (2) yields a value of 9.5 ev. It may be more appropriate to use the value of G given by Equation A.5 for a (100) direction, since the neighbors of an interstitial lie entirely in such directions. The interstitial formation energy is, then, reduced to 4 ev., which agrees better with a recent revised quantum mechanical calculation by Huntington (26).

For the body-centered structure the largest interstitial position has the property:

$$\begin{aligned} r_1/r_0 &= 3.44 \\ f(r_1/r_0) &= 0.608 \end{aligned}$$

where the cage is formed by 3 atoms located in (210) directions from the interstitial. The appropriate shear modulus is the same as for the FCC structure. However, there are fewer neighbors than in the FCC case, so that the effective value of f may be substantially smaller, and macroscopic considerations even less applicable.

The foregoing discussion makes it plausible that interstitials do not play an important part in diffusion in FCC metals. The same conclusion seems valid for BCC metals, although Paneth (28) has discussed a more rigorous atomic calculation which indicates the possibility of a modified interstitialcy mechanism of diffusion in sodium. Such a mechanism would, however, have a negative volume of activation, since the crystal would tend to be more dense in the activated state. A volume of activation may be deduced from the pressure coefficient of the activation energy for self-diffusion according to the thermodynamic relation:

$$(\partial H / \partial p)_T = -V$$

The results of Nachtrieb et al. (13) yield a positive activation volume which varies from 0.5 the molar volume at atmospheric pressure to about 0.4 the molar volume at 8000 atmospheres. This is strongly suggestive of a vacancy mechanism. The presence of a Kirkendall effect in beta brass, another BCC structure, does not rule out the possibility of an interstitialcy mechanism in this substance.

The energy necessary to move a vacancy through the saddle-point configuration may also be estimated from elasticity theory. In the FCC structure let us assume with Buffington and Cohen (10) that the atom jumps from $(1/2, 0, 1/2)$ to $(0, 0, 1)$ and that the saddle configuration occurs for the atom at $1/2(1-x), 0, 1/2(1+x)$, where x is a fraction to be determined by maximizing the energy. The nearest atoms are at positions $1/2, 1/2, 1; 0, 1/2, 1/2; 0, -1/2, 1/2; 1/2, -1/2, 1$. The distance between the saddle-point atom and any of these neighbors in

the normal lattice is represented by the vector $1/2 x, 1/2, 1/2(1-x)$. The magnitude of this vector is a minimum when $x=1/2$ and has the value $(\sqrt{3}/2\sqrt{2})$. Of this interatomic spacing the distance $(1/2\sqrt{2})$ may be considered as occupied by the neighboring atom, so that we must assign a distance $(\sqrt{3}-1)/2\sqrt{2}$ to the atom at the saddle-point. Furthermore all the atoms are displaced in 211 directions, so that we should use the shear modulus appropriate to that direction from (A.5). We thus have for Cu:

$$r_1/r_0 = 1/(\sqrt{3}-1) = 1.366$$

$$f(r_1/r_0) = 0.0725$$

$$\text{Equation 3.7}^1$$

$$\text{saddle point energy} = 2 \text{ ev.}$$

This is probably a large overestimate since the cage for the saddle-point position is defined only by 4 atoms. The result of this calculation for all

Table II
Calculation of activation energy of self-diffusion for cubic
metals using macroscopic concepts.

Element	G	Saddle-Point Energy	Total Activation Energy	Experimental Activation Energy	Theory Experiment
Cu	6.2×10^{11} dynes/cm ²	2.01 ev.	3.84 ev.	2.07 ev.	1.85
Ag	3.72	1.74	3.65	2.00	1.82
Au	3.53	1.64	4.02	2.22	1.81
Al	2.73	1.25	2.71	1.43	1.89
Pb	1.17	0.98	2.15	1.17	1.83
Ni	10.01	3.04	5.31		
Na	0.593	.12	0.68	0.46	1.47
α -Fe	11.6	.72	3.26	2.60	1.25
W	15.14	1.25	6.98	6.10	1.12

the FCC metals is shown in Table II. This table also gives for reference the value of G from Equation A.5, the total activation energy for self-diffusion from combining with Table I, and the experimental values of this quantity.

For the case of the BCC structure we find:

$$r_1/r_0 = 1.13$$

$$f(r_1/r_0) = 0.0140$$

and the result is that the saddle-point energy is much lower than in the FCC case. Values of the saddle-point energy and of the total activation energy for some BCC metals are also shown in Table II.

The principal conclusion from Table II is that the macroscopic theory substantially overestimates the activation energy for self-diffusion. For FCC metals the elastic energy at the saddle-point seems to vary between 40 and 50% of the total energy. The theory is probably much more accurate in the prediction of the relative magnitude of different contributions to the energy, and no reliance should be placed on absolute magnitudes. The low value for the saddle-point energy in

BCC metals, however, appears to be an inescapable conclusion from the geometry. For the FCC metals the ratio of theoretical to experimental values of activation energy seems to be surprisingly constant, but this is not true in the BCC case.

Nachtrieb and co-workers (13) have pointed out a remarkable empirical correlation between the latent heat of fusion and the activation energy for self-diffusion. It is simply that

$$H = 16.5 L_m$$

where H is the activation energy and L_m is the latent heat per mole or per atom. Comparison between calculated and experimental values is indicated in Table III. The discrepancy for Pb and Al may be significant, since a corresponding discrepancy does not appear in Table II.

Table III
Correlation between self-diffusion activation energy and latent heat of melting.
Activation energies are given in ev. per atom.

Element	$16.5 L_m$	Experimental
Cu	2.21 ev.	2.07 ev.
Ag	1.95	2.00
Au	2.18	2.22
Al	1.82	1.43
Pb	0.89	1.17
Ni	2.85	
Na	0.46	0.46
α -Fe	2.59	2.60
W	8.00	6.10
Co	2.64	2.69

The same authors have also shown that the change with pressure of the activation energy in Na can be closely correlated with the change in melting properties. No theoretical justification for these relations has been found.

The above calculations refer to the free energy of formation of a vacancy and to the free energy associated with the saddle-point configuration. At finite temperatures the free energy consists of two parts, and may be written as:

$$f_v = h_v - Ts_v \quad \text{Equation 3.8}$$

Hence the equilibrium concentration of vacancies is given by:

$$c_v = \exp(s_v/k) \exp(h_v/kT) \quad \text{Equation 3.9}$$

In general we should expect s_v to be positive for vacancies, since the neighbors will be less constrained and can tend to oscillate towards the vacant site at somewhat less than their normal frequency in the crystal. If ν_D is the normal crystal frequency, usually taken as the Debye frequency, and ν_v is the frequency of a neighbor in the direction of the vacancy, then it follows that:

$$S_v = z k \ln(\nu_D/\nu_v)$$

where z is the number of neighbors. A crude but plausible assumption is that ν varies as the square root of the total bond energy. Since each neighbor has one missing bond, this gives the relation:

$$\exp(s_v/k) = \left(\frac{\nu_D}{\nu_v}\right)^{\frac{z}{2}} \quad \text{Equation 3.11}$$

$$\exp(s_v/k) = \left(\frac{z}{z-1}\right)^{\frac{z}{2}}$$

This factor is about 1.7 for both face-centered and body-centered cubic structures. Another approach to this problem is to use Equation (3.5), bearing in mind the temperature coefficient of the elastic constant. Assuming the surface energy contribution to be negligible, we have:

$$\frac{df_v}{dT} = f_v \frac{\gamma/2 Gr_s}{1 + \gamma/2 Gr_s} \frac{1}{G} \frac{dG}{dT} \quad \text{Equation 3.12}$$

We may obtain the necessary data from Table I and from Ref. 6. For example, for copper we obtain:

$$-\frac{df_v}{dT} = 2.5 \times 10^{-6}$$

$$\frac{s_v}{k} = 0.28 \quad \text{Equation 3.13}$$

$$\exp(s_v/k) = 1.33$$

where we have taken the observed value of f_v (cf. section 5). If we take the calculated value, the corresponding factor is raised to 2. Hence, we may say that within the crude limits set, the two methods of computing the entropy agree.

In the case of interstitials, it is evident that the entropy of formation should be negative, since the vibration frequencies of the neighboring atoms will certainly be increased.

It might be thought that an additional contribution to the entropy of formation would arise from a volume coefficient of the energy of formation combined with the effect of thermal expansion. There is reason to believe, however, that this effect may be small for metals. If the energy of formation were strictly proportional to the cohesive energy, the latter has a zero volume coefficient at the equilibrium lattice spacing by the definition of equilibrium. Thus we might expect df_v/dV to be very small.

Entropy of activation is also associated with the saddle-point as emphasized by Zener (6). In the FCC metals reference to Equations 3.7 and 3.7' shows that:

$$s_{s.p.} = H_{s.p.} (1/G dG/dT + 1/V dV/dT)$$

$$= 2.1 \times 10^{-4} H_{s.p.} = 2.27 \times 10^{-4} \text{ ev./}^\circ\text{C.}$$

$$\text{or } s_{s.p.}/k = 2.63 \text{ for Cu}$$