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INTERSTITIAL ALLOYS OF BCC METALS

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INTERSTITIAL ALLOYS OF BCC METALS

Introductory Comments

The bcc metals form an important class of alloys with certain elements, alloys in which the solute atoms do not substitute for solvent atoms, but fill interstices in the bcc structure. Many of these alloys have striking mechanical, electrical and magnetic properties which are apparently controlled in large part by the interstitial impurities, impurities which may be present only in dilute quantity. Furthermore, since many of the important bcc metals melt at high temperatures -- in excess of 1500°C -- their use in high temperature service is extremely important. Hence knowledge of the basic properties of the alloys is desirable; this paper provides our assessment of the status of metallurgical knowledge about them.

The paper has the following main parts:

- I. A description of the geometry of the interstitial alloys.
- II. A statement of the thermodynamics of the metal-gas systems which form these interstitial alloys.
- III. Experimental studies of metal-gas systems.
- IV. Internal friction of interstitial alloys.
- V. Diffusion of interstitials.
- VI. Interstitial-interstitial interactions.
- VII. Interstitial-dislocation interactions.

I. The geometry of the interstitial alloys.

The nature of the sites into which the interstitial atoms go is determined, of course, by the general geometry of the bcc crystal itself. The unit cube has a space-filling ratio (of round spheres) of 0.68 (which is less than the corresponding ratio of 0.74 for a close-packed metal). In addition the void space is more evenly distributed about the unit cell in the bcc metals than it is in the close-packed metals. Nevertheless, the void space is concentrated chiefly into holes called interstices. Interstices in the bcc metals are commonly divided into two classes, octahedral sites and tetrahedral sites, named after the geometry of the host atoms about the sites. The location of the sites associated with one atom in the unit cube is indicated in Fig. 1. The geometry of the host atom about the two types of sites is shown in Fig. 2. Each lattice point of the crystal has associated with it 3 octahedral (O) sites and 6 tetrahedral (T) sites. The O sites have free radius r_o compared to the host radius r_h such that $r_o/r_h = 0.149$; the same ratio for the T sites is $r_T/r_h = 0.314$. Furthermore the T sites lie on the midpoint of the line connecting the centers of adjacent O sites.

Long discussion has developed concerning which of the two types of sites are occupied by interstitial atoms.^{1,2} The

radius of either class of site, r_o or r_T , is much less than the radius, r_i , of the interstitial solutes (hydrogen, nitrogen, carbon or oxygen). Hence a considerable expenditure of energy is necessary to force these atoms into the small holes. (The enthalpies of mixing of these alloys are typically much higher than those of substitutional alloys.) Since the local strain in the crystal about the interstitial is large (of order unity) and since the arrangement of atoms about neither site is an ideal octahedron or tetrahedron, calculations of the strain energy are extremely difficult. Hence the choice of site occupancy on "theoretical" grounds is inconclusive, though favoring, we believe, octahedral site occupancy. Furthermore the strain fields of both types of sites are symmetrical about the $[111]$ direction, so study of anisotropic properties, which depend on the nature of the strain field, is also inconclusive. Those measurements which have been made again seem to us to favor octahedral occupancy. Finally the relationship of the geometry of the structure of N- and C-martensite in Fe seems to favor the concept of octahedral site occupancy of N and C in Fe, though again, not conclusively.

Two features of these interstitial alloys seem worthy of note here. First, the electrical resistivity of these

interstitial alloys is large. The resistivity increment, $\Delta\rho$, accompanying the addition of these interstitials is in the range 10-30 $\mu\Omega\text{cm}$ per atom per cent.^{3,4,5} This value compares with that of about 1-2 $\mu\Omega\text{cm}$ per atom per cent of a substitutional-impurity addition in these metals. This large effect for interstitial additions makes resistivity measurements attractive in study of the interstitial alloys, however, even for them effects are difficult to measure in the low ppm range.

The second, and more important, feature of the interstitial alloys is the anisotropy of the strain field of the crystal about the interstitial. For either site, the strain field is tetragonal; i.e., of lower symmetry than the cubic symmetry of the crystal itself. Hence the interstitials behave elastically like small strain dipoles and interact with vector or tensor fields (electric, magnetic or mechanical) in a particular way. Such interactions are important in study of the properties of the alloys.

The most important of the interactions is that with mechanical strain, either internal or external. The former is thought to be important in controlling or contributing to many important mechanical properties such as yielding, ultimate strength, fracture, brittleness, etc. The second has a mani-

festation called anelasticity (or internal friction), which has proved to be an important tool in study of the alloys. This phenomenon, which occurs in all of these alloys, has been amply described many times and the reader is urged to look in one of several excellent accounts for the details of the effect.⁷ Only a few salient points will be made here:

a. The phenomenon is described by two independent material constants, τ_r , a rate constant, and Δ , a strength constant.

b. τ_r is related to the mean time required for the interstitial atoms to jump from site to site. τ_r is not a function of interstitial concentration in dilute alloys.

c. Δ describes the magnitude of the effect. It is linear with concentration in dilute alloys and is only a slowly varying function of temperature.

With this brief description of the principal features of the interstitial bcc alloys, we consider in succession some of their properties.

II. Metal-gas Equilibrium: Theory

A. General remarks

Reactions at the surface between a metal and a surrounding gas are important technological events. Many heat treatments of metals are carried out using surface reactions with a proper gas. Furthermore, metals in service often are exposed to gaseous environments which result in formation of compounds at the surface. Consequently knowledge of metal-gas reactions is of considerable importance. We limit ourselves in this discussion first to equilibrium between the metal and the gas and even more to the pressure-temperature-composition relations which describe a system when a terminal solid solution is formed between a metal and a diatomic gas.⁸ This limitation is reasonable in this discussion, since the important bcc metals do form extensive solid solutions in equilibrium with the diatomic gases H_2 , N_2 and O_2 .

The basic thermodynamics of such metal-gas systems has long been considered by many writers. Phase diagrams for such systems have been extensively discussed; emphasis has been placed on the temperature-composition (T - x) and the pressure temperature (p - T) diagrams. Three dimensional (p - T - x) plots have not often been used since they are both difficult to portray and difficult to visualize. In proper coordinates, though, these three-dimensional plots are not

difficult either to present or to grasp. We first consider the relationships which describe the essentials of the p - T - x equilibrium in a simple, well-behaved metal-gas system, then show that the geometry of the resulting p - T - x diagram need not be particularly difficult. Finally we apply it to two real metal-gas systems, the Nb-N_2 system and the Ta-N_2 system.

The treatment which follows discusses quite generally the equilibrium between the metal M and the diatomic gas G_2 which forms the solid phase MG in equilibrium with the alpha solid solution. The following assumptions for the metal-gas (M - G) system are made:

1. The gas goes into solution atomically in the interstices of the metal lattice. Henry's law holds over the complete range of solubility.
2. The solubility of the gas in the metal is low enough so that the activity of the solid solution may be considered to be that of the pure metal.
3. The partial molar heat of solution of the gas in the metal and the standard heat of formation of the phase MG are both constant with temperature.
4. The composition of the phase MG is constant.
5. The gas itself is ideal.

B. The Partial Molar Heat of Solution of the Gas in the Metal

The reaction to be considered when a molecule of a diatomic gas, G_2 , goes into solution is

Here $\underline{G}$ represents the gas in solid solution and (g) refers to the gaseous state. If the standard state for $\underline{G}$ is chosen as a solution of 1 atom per cent and if Henry's law holds, then the equilibrium constant K_G for this reaction may be written

$$K_G = \frac{a_G}{(a_{G_2})^{1/2}} = \frac{\chi}{(p_{G_2})^{1/2}} \quad (2)$$

The symbol "a" refers to the appropriate activity, χ to the atomic per cent of gas in solution and p_{G_2} to the partial pressure of G_2 in the system. Eq. 2, a statement of Sievert's law, requires that the diatomic gas is dissolved atomically and that the atoms interact negligibly with each other in the solid. The van't Hoff relation then gives the following expression involving the standard partial molar heat of solution, $\overline{\Delta H}_G^\circ$, of the gas in the metal.

$$\frac{d \ln K_G}{d 1/T} = - \frac{\overline{\Delta H}_G^\circ}{R} \quad (3)$$

$\overline{\Delta H}_G^\circ$ is the enthalpy change which occurs when one-half a mole of G_2 at one atmosphere of pressure is dissolved monatomically

at one atomic per cent in the metal. If $\overline{\Delta H}_G^\circ$ is negative, then the metal is an exothermic absorber; if it is positive, an endothermic absorber.

Further insight into the pressure dependence of composition of the dissolved gas is obtained by rewriting Eq. 2 as the partial derivative

$$\frac{\partial \ln p_{G_2}}{\partial \ln \chi}_T = 2 \quad (4)$$

Thus, at a constant temperature in the metal-rich terminal solid solution in a gas-metal system which obeys Sievert's law, a double logarithmic plot of partial pressure of the gas vs. concentration of dissolved gas is a straight line with a slope of 2. In the phase diagram of the system, this line separates the two phase region in which the vapor and the solid solution are in equilibrium from the single phase solid solution.

The temperature dependence of the pressure of gas for a given composition of the solid solution may easily be determined. Since K_G is a function of temperature alone, substitution of Eq. 2 into 3 yields

$$\frac{\partial \ln p_{G_2}}{\partial 1/T}_\chi = \frac{2\overline{\Delta H}_G^\circ}{R} \quad (5)$$

Thus a plot of $\ln p_{G_2}$ vs $1/T$ at a composition of 1 atom per cent of dissolved gas is linear with a slope which defines $\overline{\Delta H}_G^\circ$. In the composition region in which Henry's law is obeyed, all such lines have the same slope and $\overline{\Delta H}_G$ equals $\overline{\Delta H}_G^\circ$.

These observations, which have been applied separately many times, show that a judicious choice of scales for plotting p , T and χ results in a simplified way of describing one of the boundaries of the terminal solid solution. This boundary, a curved surface in a p , T , χ plot is a plane in the coordinate system $\ln p$, $1/T$, $\ln \chi$, the plane ABCD in Fig. 3. Here the top surface has been arbitrarily set at a pressure of 1 atmosphere, the bottom surface at some pressure lower than the range of interest. Similarly the left-hand side of the log composition scale does not indicate the p - T relations for the pure metal, but for a dilute alloy. The right-hand side of the $1/T$ scale represents some arbitrary temperature, the back face of the prism represents a value of $1/T = 0$.

The phase boundary ABCD intersects the near faces of the phase diagram in two lines defined by Eqs. 4 and 5. The full equation of plane ABCD is

$$X = (p_{G_2})^{\frac{1}{2}} e^{-\overline{\Delta F}_G^\circ / RT} \quad (6)$$

where ΔF_G° is the standard partial molar free energy of solution of the diatomic gas in the metal. Plane ABCD has a limit in the composition direction which corresponds to saturation of the solid solution and resulting equilibrium with a new phase MG. This equilibrium is defined at all pressures by the surface DCHI. The phase diagram is assumed to continue as a eutectic defined by the additional planes and surfaces sketched in Fig. 3.

C. Standard Heat of Formation of MG.

The partial pressure of the gas at constant temperature can be increased until the solute concentration ultimately reaches saturation; further addition of gas forms a new phase. This reaction can be written

where (s) refers to the solid state. According to the phase rule, three phases are now present; thus, only one degree of freedom remains. If this degree of freedom is temperature, then the pressure and phase compositions are fixed as long as three phases are present. If the activities of the condensed phases are unity and if the activity of the gas is equal to its partial pressure, the equilibrium constant K_f

may be written as

$$K_f = (p_{G_2})^{-1/2} \quad (8)$$

Another application of the van't Hoff relation gives

$$\frac{d \ln K_f}{d 1/T} = - \frac{\Delta H_f^\circ}{R} = -\frac{1}{2} \frac{d \ln p_{G_2}}{d 1/T} \quad (9)$$

where ΔH_f° is the standard enthalpy of formation of MG.

If ΔH_f° is constant with temperature, this equation gives the slope of a straight line at constant composition which lies in the surface separating the alpha plus MG phase region from the alpha plus vapor phase region. Each temperature defines a reaction horizontal because of the invariance of pressure and composition for a given temperature in the presence of the three phases. Two such reaction horizontals are only partially shown as DE and CF in Fig. 3. Since the reaction horizontals are straight lines parallel to the composition axis and Eq. 9 describes an intersecting straight line, a plane CDEF is defined; it intersects the first mentioned plane ABCD in line CD. This plane defines the three phase equilibrium between the alpha solid solution, MG, and the vapor. When K_f , the equilibrium constant, is substituted into $\Delta F^\circ = -RT \ln K_f$, the following expression is obtained:

$$\ln p_{G_2} = \frac{2\Delta F_f^\circ}{RT} \quad (10)$$

This is the equation for plane CDEF. In this expression,

ΔF_f° is the standard free energy of formation of MG.

Several additional features of certain surfaces and lines in Fig. 3 are immediately apparent. If the three phases defined by plane CDEF are present and the temperature is increased, the equilibrium composition of the alpha solid solution is defined by line CD. When the temperature reaches the value unique to line CF, the liquid phase can form; the pressure, temperature, and composition are given by the line of which CF is a portion.

Note that for such a phase diagram, the invariance of four phase equilibrium is given by a straight line; the univariance of three phase equilibrium is given by a surface; and the bivariance of two phase equilibrium is given by a volume. Hence, a line of four phase equilibrium such as CF will have four cylindrical surfaces leaving it. These four surfaces represent the four combinations of three phase equilibrium which are possible from the four phases in equilibrium on the straight line. One of these surfaces in addition to CDEF is, in the ideal case, also a plane. This plane is shown in part as CFGH in Fig. 3. It describes the equilibrium between the alpha solid solution, MG, and the liquid. Since these are all condensed phases, there is negligible change in composition or temperature with pressure (for pressures of less than one atmosphere), and thus the

plane is defined. The other two surfaces which leave line CF represent in one instance equilibrium between the alpha solid solution, the liquid and the vapor and in the other equilibrium between MG, the liquid, and the vapor. In general, these two surfaces are not planes; they are not discussed further.

D. Standard Heat of Solution of Mg in the Metal

Another plane in Fig. 3 has special significance in this analysis. This plane is formed by the following manipulations. Let Eq. 7 be subtracted from Eq. 1. Then

$$MG(s) = \underline{G} + M(s) \quad (11)$$

By writing the equilibrium constant for Eq. 11 as $K_s = \chi$ and again applying the van't Hoff relation, the expression

$$\frac{d \ln \chi}{d 1/T} = - \frac{\Delta H_s^\circ}{R} \quad (12)$$

is obtained. Here ΔH_s° , the standard heat of solution of MG in M, is the enthalpy change for reaction (11), that is, the solution of one mole of solid MG forms one gram atom of solid metal and one gram atom of the gas in solution at one atom per cent concentration. An examination of the phases involved in Eq. 11 shows that this is the equilibrium which is involved in the familiar solvus curve. This solvus is seen as straight line HI in Fig. 3. Since this equilibrium involves only condensed phases, as in the previous case, it does not vary significantly with pressure for pressures

of less than one atmosphere. Thus, the plane CDIH is defined. Plane CDIH separates the volume in which the alpha solid solution exists from the two phase volume occupied by the alpha solid solution and MG. The equation for plane CDIH may be obtained in a manner similar to that used in the case of the two previously mentioned planes.

It is found to be

$$\ln \chi = - \frac{\Delta F_s^\circ}{RT} \quad (13)$$

where ΔF_s° is the standard free energy of solution of MG in M.

The plane CDIH, which gives terminal solubility of the gas in the metal, is uniquely defined by the thermodynamic relations for reaction (11). Since reaction (11) was obtained from reactions (1) and (7), which, in turn, define planes ABCD and CDEF, these last two planes should uniquely determine plane CDIH. Fig. 3 shows that this is the case; the two planes ABCD and CDEF intersect at line CD. It is the projection of this line on a constant pressure plane which gives the terminal solubility.

Fig. 3 illustrates the concept that terminal solubility is determined by the competition for the gas between the solid solution and the equilibrium solid phase. When the latter has a large free energy of formation, there is only a small partial pressure of the gas to be in equilibrium

with the solid solution. If, however, the partial molar free energy of the gas in metal is large and negative, then $(\chi/p_{G_2})^{1/2}$, as given by Eq. 6, is also large, and the small partial pressure may still result in a large value for χ .

A further correlation can be made between quantities already discussed. Since reaction (11) was obtained by subtraction of reaction (7) from reaction (1), then

$$\Delta H_s^\circ = \overline{\Delta H}_G^\circ - \Delta H_f^\circ \quad (14)$$

For the phase diagram in Fig. 3 to be correct, it should be possible to obtain relation (14) from the geometry of the various intersecting planes. That this is possible may be seen as follows: Expressions (6) and (10), the equations for planes ABCD and CDEF respectively, may be combined to give an equation for line CD.

$$\ln \chi = \frac{\Delta H_f^\circ - \overline{\Delta H}_G^\circ}{RT} - \frac{\Delta S_f^\circ - \overline{\Delta S}_G^\circ}{R} \quad (15)$$

Here ΔS refers to the entropy of the appropriate reaction.

When the slope $\frac{d \ln \chi}{d 1/T}$ of line CD as obtained from Eq. 15 is set equal to the slope of line CD as obtained from Eq. 13, the desired result is obtained. The fact that Eq. 14 can be obtained analytically further verifies the phase diagram.

E. Discussion

The limited region of the p - T - χ diagram of Fig. 3 is only part of the entire phase diagram; a possible p - T - χ diagram which has been expanded to include more than just the terminal solid solution will be considered. Such a diagram appears in Fig. 4; it again depicts only a portion of the hypothetical M-G system. In this case the portion shown includes compositions slightly beyond that of the phase MG. This diagram is best visualized by considering CF, the straight line reaction horizontal at which four phases are in equilibrium. Leaving from CF are four different cylindrical surfaces which represent the combinations of three phase equilibrium which are possible in the system. For easier identification, constant composition lines appear on these four surfaces.

For the phase diagram described to be applicable to real systems the assumptions of ideality should be met. In many real systems the terminal solubility is low enough so that the assumption of Henry's law and the assumption that the alpha activity is equal to that of the pure metal both are reasonable. The assumption that the activity of the gas is equal to its partial pressure is also generally valid for the pressures involved. The remaining two assumptions

may not always be good ones for real systems. The first of these is that of constant reaction enthalpies. The reaction enthalpies, $\overline{\Delta H}_G$ and ΔH_f° , might, in fact, be expected to vary slightly with temperature since reactions involving condensed phases and gases typically have a non-zero ΔC_p . The last assumption, that of constant composition of the phase MG, is difficult to evaluate. It is a reasonable one when the second solid phase is very stable, but for many real systems it is known that the composition of this phase does vary significantly with temperature. Except for the more drastic cases of deviation from ideal behavior, (such as many of the metal-hydrogen systems), both of these assumptions should be valid over a limited temperature range. If this is so, then the p-T- χ phase diagram discussed has applicability in this range of temperature. At temperatures beyond this range the simple geometrical surfaces of the diagram become warped; the phase relations, however, are unchanged.

One sees that the graphical representation of a three dimensional diagram is not easy. There exist, however, several straight lines, planes, and simple cylindrical surfaces which do make the visualization of the diagram easier. However, use of scales of log pressure, log composition, and reciprocal absolute-temperature optimizes the number of simple surfaces. The resulting diagram should be helpful to

the understanding of metal-gas equilibrium both as it might be expected to occur ideally and as it occurs in real systems.

A cut through the phase diagram of Fig. 4 at constant pressure and a restoration of the usual linear T - χ coordinates give the more familiar representation of a phase diagram. Such a diagram is shown for the binary Nb-O system in Fig. 5. Detailed discussion of experimental determinations in the Nb-N and the Ta-N systems is given in the next section.

III. Metal-gas Equilibrium: Experiment

A. The terminal solid solution

The foregoing description of an ideal metal-gas system is found to apply with surprising success in several instances. Numerous investigations of certain of the lines and planes in Fig. 3 have been carried out for a number of metal-gas systems and numerous of the constants of Eqs. 3-13 have been determined. Some of these investigations are described in the following paragraphs.

The systems Nb-N and Ta-N have been examined most extensively. The terminal solid solution region of these alloys is large at easily attainable pressures and temperatures. The stoichiometry of the several nitrides is well known. Finally these systems are simple and reversible.

The measurements reported here were carried out using standard thermochemical techniques. N_2 gas was metered from a source into a chamber of known volume containing a specimen which could be heated to any temperature from room temperature to the melting point, Fig. 6. Measurement was made of the gas content of the specimen as a function of temperature and pressure over a wide range of these variables. All investigators have systematized their work in establishing the boundaries of the terminal solid solution, α , to keep the number of measurements small.

Determination of the degree to which the systems Nb-N⁹ and Ta-N¹⁰ obey Sievert's law are shown in Fig. 7 of this paper and in Fig. 12 of the paper of Gebhardt, Seghezzi, and Fromm. The data show that both solutions do obey Eq. 4 reasonably well, i.e. they do obey Sievert's law. Thus all lines parallel to line AD in the plane ABCD of Fig. 3 have a slope of 2, accurately for the Nb-N system and approximately for the Ta-N system.

The heats of solution of N₂ in Nb and Ta have been deduced from such data as are presented in Fig. 8. Again the lines are straight and parallel indicating that over the range of pressures and compositions studied the enthalpies of solution are constant. The equation of the plane ABCD of Fig. 3 for the Nb-N system is thus about

$$\chi_{\text{Nb,N}} = p_{\text{G}_2}^{\frac{1}{2}} \exp(-8/R) \exp(42,000/RT) \quad (16)$$

In this equation, χ is given in at%, p_{G_2} in atmospheres and ΔS and ΔH in cal/mole°K and cal/mole respectively. The Ta-N system is not quite so well behaved since χ does not vary exactly as $N_2^{\frac{1}{2}}$ for this system, although the surface ABCD is a plane. The equation which describes this plane, according to Gebhardt et al, is

$$p = \chi^{2.4} 8 \times 10^4 \exp(-43,500/RT) \quad (17)$$

where p is given in mm of Hg.

Data of Gebhardt, Fromm and Jakob,¹¹ Cost and Wert⁹ and deLamotte, Huang and Altstetter¹² for Nb-N fit Eq. 16 well (the spread of values of $x_{\text{Nb},\text{N}}$ at a given temperature is within a factor of 1.5) The negative values of $\overline{\Delta H}_G^\circ$ show that the solution of nitrogen in both Ta and Nb is an exothermic reaction. The negative value of the entropy of solution $\overline{\Delta S}_G^\circ$ (1 atomic %,T) is more difficult to rationalize. Since this entropy difference is the difference of the entropy of the gas $\frac{1}{2}S_{\text{N}_2}$ (1 atm,T) and the entropy of the dissolved gas $\bar{S}_{\text{N}}$ (1 atomic %,T), i.e., $\overline{\Delta S}_G^\circ = \bar{S}_{\text{N}} - \frac{1}{2}S_{\text{N}_2}$, at 2000°K, $\bar{S}_{\text{N}}$ is found to be about 22 cal/mole°K for the entropy of the dissolved gas in Nb (and also in Ta). Since the entropy of mixing is only about 13 cal/mole°K (for complete and random accessibility of octahedral interstitial sites) a large positive entropy contribution must be present. The origin of this entropy term is not known; a discussion of its possible origin is given in the report of deLamotte, Huang and Altstetter.¹²

B. The maximum solubility

The data of Fig. 8 show that a maximum solubility exists for each temperature, points on the steepest line in Fig. 8. This line is related to the line CD in Fig. 3 for the system Nb-N. If this maximum solubility is constant with pressure, as it is assumed to be for pressures

less than 1 atmosphere, then the standard heat of solution ΔH_S° of the nitride in the metal can be determined using Eq. 12. The maximum values of solubility at a variety of temperatures are shown from the sources indicated in the captions in Figs. 9 and 10 for Ta-N. Also shown are other data obtained by a variety of techniques for these systems. One sees quite a range of values. The slopes of the lines yield the values of ΔH_S° for Nb to be about 21 kcal per mole and for Ta to be about 5,400 kcal/mole. The nitrides with which the solid solution is in equilibrium have been determined to be Nb_2N and Ta_2N respectively. The large difference in heat of solution between Nb and Ta is so far unexplained. The reader may see from the work of Cost and Wert,⁹ however, that the heat of solution for Nb-N at low temperatures is also low, about 5 kcal/mole.

C. Equilibrium with the nitrides Nb_2N and Ta_2N

Appropriate use of the data such as that in Fig. 8 allows determination of the standard heat of formation of the nitrides ΔH_f° using Eq. 9. From such data the values of ΔH_f° for these nitrides are about -62 kcal/mole for Nb_2N and about -50 kcal/mole for Ta_2N (Gebhardt, Seghezzi and Fromm have determined for Ta_2N the actual composition to be about 24 atomic % N.)

D. Summary of the thermodynamic properties.

A tabulation of the values of the thermodynamic parameters appropriate to these systems is listed in Table I.

E. Other systems.

No other metal-gas systems have been examined with such care as have these two just cited. For a great many more, however, certain parameters of both the compounds and the single phase α solutions are known. An excellent compilation of the former is found in two books edited by Schick;¹³ no summary of the latter is known. Therefore, we summarize some of the available data on the α solid solutions.

1. The Nb-N system

This system is reasonably well established at high temperatures.^{9,11,14-18} The data in Fig. 9 show that the limit of α solubility is known to at least a factor of 2 above 1200°C. The heat of solution of Nb_2N in α , about 20 kcal/mole, is independent of composition and temperature. Furthermore the sum of this value and the heat of formation of Nb_2N , about -62 kcal/mole, is about the measured value of the heat of solution of the gas in the metal, -42 kcal/mole. (A more detailed discussion of this point is given in the book "Thermodynamics of Certain Refractory Compounds" - Schick, page I-339.)¹³

At low temperatures, the situation is unclear.^{6,9,19}

The data of Fig. 11 show that the heat of solution of the nitride decreases to about 5 kcal/mole. The reason for this change is unknown; notice should be made, however, that these low temperature measurements are of the quench aging type and are not the same as those of the Nb-N₂ equilibrium characteristic of the higher temperature. The indicated solubility of N in Nb at room temperature is about 100 ppm.

Purification of Nb by high temperature outgassing is difficult. One sees from Eq. 16 that a reduction of the atomically dissolved N to 1 ppm requires a reduction of pressure at 2200°K to about 10^{-12} atmospheres.

2. The Ta-N system

The solubility of N in Ta in equilibrium with the nitride Ta₂N is well-behaved over the entire temperature region, Fig. 10.²⁰⁻²⁴ The heat of solution is low -- some 5,400 cal over the entire temperature range; thus it is similar to the low temperature region of Nb-N. The indicated solubility at room temperature is also low -- about 100 atomic ppm. Because N in Ta seems somewhat less well-behaved than N in Nb (or at least seems less well known) we will discuss it no further.

3. The systems Ta-O and Nb-O

Data for these alloy systems have been extremely difficult to secure and these data conflict. Attempts made to determine the p-T- χ relationships for these systems have not been as fruitful as for the Nb-N and Ta-N systems. Fromm and Jehn, for example, do not find a Sievert's law pressure dependence over the entire temperature range for either Ta-O or Nb-O. Neither are they able to deduce the maximum solubility from metal-gas equilibrium measurements.

Such measurements on the solvus line as are known to us for Nb-O²⁵⁻²⁹ and Ta-O^{21,23,30,31} are plotted in Figs. 12 and 13. The data are not consistent; neither is precise knowledge available for all of the studies of the composition of the oxides with which equilibrium has been established. The best lines for both seem to be about the same:

$$\chi \approx 0.5 e^{-8000/RT}.$$

4. Systems with carbon -- α -iron

Perhaps more effort has been spent on determination of the solvus line for carbon in iron than for any other system. Prior to 1950, estimates of solubility were reasonably accurate at the eutectoid temperature, (about 0.02 wt% carbon) but were far in excess of the values we now assume to be correct at lower temperatures. In the

1950's a large number of quench-aging experiments were made using internal friction, magnetic hysteresis, and calorimetry. A summary of data from these papers is plotted in Fig. 14; they show a range of enthalpies of solution of 10 to 12 kcal/mole.³²⁻³⁸

A measurement of the solubility made during decomposition of pearlite gave much higher value of enthalpy of solution -- 20.6 kcal/mole, dashed line of Fig. 14. This discrepancy was very troublesome for many years and only recently has a satisfactory solution been proposed. Swartz has suggested that both measurements are suspect, and he has come close to resolving the difficulty -- he has reduced the discrepancy from 8 kcal/mole to less than 2. The reader is referred to his article for the details.³⁹

The principal new concept which he has brought into consideration is the elastic stressing of precipitates by the matrix in which they exist. This stress adds an additional term to the free energy of unstressed precipitates and therefore, alters the change in free energy on their dissolution. This term is small if the volume of a precipitate is not much different from the volume occupied by the same number of matrix atoms, but can be large, several kcal/mole, if these volumes are quite different -- say 10% -- as they often are. If he is right, and the evidence in the

α -iron case implies that he is, then such a term must be considered in all measurements of quench aging in metals.

5. Carbon solubility in V, Mo, Re, Ta, Nb, W

New determinations of the carbon solubility in these six refractory metals have just been determined by Gebhardt and his coworkers by an equilibration method with the appropriate carbides. These measurements were made in the range 1600°C and above. The determinations are, in general, extremely self-consistent. They are summarized by the lines in Fig. 15; the reader is urged to go to their original papers for the details of their work and comparisons with earlier investigations.^{41,42} Also sketched at the top of this figure is the C solubility in equilibrium with cementite extrapolated into this temperature range. One sees that by the standards of the refractory metals, C is extremely soluble in ferrite, were iron to be a bcc solid at 2000°C.

IV. Relaxation Behavior of Interstitials

The study of interstitial impurities in body-centered cubic metals is greatly facilitated by the existence of an anelastic relaxation process termed the Snoek effect.² The Snoek relaxation results from the stress-induced re-orientation of interstitials in sites which are made energetically non-equivalent by an elastic biasing stress. Consider interstitials located in octahedral sites, as in Fig. 1. The sites are labeled x, y, or z depending upon the crystallographic direction of the tetragonal strain field caused by an interstitial in that site. Under zero applied stress, the interstitial may occupy any of the three classes of sites with equal probability. However, suppose a stress is applied to the crystal, for example in the z direction. The z-type sites, which are expanded by the stress, then have a lower potential energy relative to x or y sites in the stressed crystal. As a result, the z sites are preferentially occupied, although the concentration differences amount to only a fraction of a per cent.

The redistribution of interstitials under stress requires mass transport and is thus time dependent. In terms of the strain response, ϵ , of the crystal to the applied stress, σ , for the Snoek effect, or any anelastic

process in general, the material obeys the constitutive equation for the standard linear solid:⁴³

$$\sigma + \tau_{\epsilon} \dot{\sigma} = M_R (\epsilon + \tau_{\sigma} \dot{\epsilon}) \quad (18)$$

Here M_R is the relaxed elastic modulus (the value of the modulus if there is no anelastic strain), τ_{ϵ} is termed the relaxation time at constant strain, and τ_{σ} is the relaxation time at constant stress.

Eq.18 may be solved to obtain the response of the crystal under boundary conditions which are easily imposed experimentally. For example, suppose $\dot{\sigma}$ is set equal to zero and a static elastic stress $\sigma(0)$ is applied to the crystal at $t = 0$ and maintained, as in a creep experiment. The strain $\epsilon(t)$ at any time t is given by

$$\epsilon(t) = \frac{\sigma(0)}{M_R} + (\epsilon(0) - \sigma(0)) \exp(-t/\tau_{\sigma}) \quad (19)$$

where $\epsilon(0)$ is the strain at $t = 0$. Similarly, if $\dot{\epsilon}$ is set equal to zero, then the stress relaxation as a function of time is given by

$$\sigma(t) = M_R \epsilon(0) - (M_R \epsilon(0) - \sigma(0)) \exp(-t/\tau_{\epsilon}). \quad (20)$$

In Fig. 16, typical stress and strain relaxation curves are given schematically. The relaxation times, τ_{σ} and τ_{ϵ} , are the times required for the respective processes to relax to $1/e$ of their total value and are necessarily, though often not significantly, different from each other. The

magnitude of the relaxation is measured by a parameter termed the relaxation strength, Δ , given by

$$\Delta = \frac{M_u - M_R}{M_R} \quad (21)$$

M_u is the unrelaxed modulus, the value of M before any relaxation occurs, and is given by

$$M_u = M_R \frac{\tau_\sigma}{\tau_\epsilon} \quad (22)$$

where $\tau_\sigma > \tau_\epsilon$. It is easily demonstrated from Fig. 16 that a definition of Δ equivalent to Eq. 22 is the ratio of the anelastic stress (or strain) to the purely elastic, i.e. time independent, stress (or strain).

If stress and strain vary sinusoidally, but out of phase by an angle Φ because of the time dependence of the solute redistribution, then

$$\tan \Phi = \Delta \frac{\omega \tau_r}{1 + \omega^2 \tau^2} \quad (23)$$

if Δ is small compared to unity. Here ω is the circular frequency and $\tau_r = (\tau_\sigma \tau_\epsilon)^{\frac{1}{2}}$, the geometric mean of τ_σ and τ_ϵ . The differences between τ_r and τ_σ or τ_ϵ are small (less than 20% in extreme cases) and will not always be distinguished from one another in the remainder of the paper. By analogy to the quality factor in resonant electrical circuits, $\tan \Phi$ is often designated by the symbol Q^{-1} and is referred to as the internal friction of the material.

All of the relaxation processes described in this paper are thermally activated; thus τ_r has an Arrhenius temperature dependence,

$$\tau_r = \tau_{ro} \exp(\Delta H_r / RT) \quad (24)$$

where the pre-exponential factor, τ_{ro} , is the product of the frequency of vibration and an activation entropy, and ΔH_r is the activation enthalpy of the process. Substitution of Eq. 24 into Eq. 23 demonstrates that at constant ω , $\tan \Phi$ goes through a symmetrical maximum as a function of $1/T$ at the condition $\omega \tau_r = 1$, Fig. 17. This condition defines the value of τ_r at the peak temperature, T_p ; Δ is given by twice the peak height.

The rate constants τ_{ro} and ΔH in Eq. 24 are obtained experimentally from stress or strain relaxation measurements of τ_σ or τ_ϵ as a function of temperature, or equivalently in a dynamic experiment from the change in peak temperature, T_p , with frequency. From the condition $\omega \tau_r = 1$ at T_p , Eq. 24 gives

$$\frac{d \ln \omega}{d(1/T_p)} = -\frac{\Delta H_r}{R} \quad (25)$$

Hence at $1/T_p = 0$, $\omega = \omega_{ro} = \tau_{ro}^{-1}$.

The above development demonstrates that knowledge of two parameters, τ_r and Δ , permits unique definition of

a relaxation process. The relaxation time gives the rate at which the process occurs. For the cases considered in this paper, the relaxation processes involve stress-induced jumping of various atom species. The relaxation time is used in two ways in subsequent sections, (1) to determine bulk diffusion coefficients by relating τ_r to the mean jump time for diffusion, τ_j , and (2) as a "velocity selector", in the sense that differences in the value of τ_r for various processes making up a total relaxation spectrum often permit separation of the spectrum into its component relaxations and aid in interpretation of results.

The relaxation strength, Δ , is a thermodynamic, rather than kinetic, parameter. It is proportional to the number of relaxation events which occur, i.e. to the concentration, C_o , of relaxing species. For any point defect relaxation in a single crystal excited longitudinally, Δ is given by⁴⁴

$$\Delta = \alpha E C_o V_o (\delta\lambda)^2 / 4k N_o (T - T_c) \quad (26)$$

where α is a geometrical constant, E is the appropriate Young's modulus, C_o is the atomic fraction of the defect, V_o is the atomic volume, $\delta\lambda$ is related to difference in local strain around the defect in different crystallographic directions, k is the Boltzmann constant, T is the absolute temperature, N_o is Avogadro's number, and T_c is the temperature

at which spontaneous ordering of the defect will occur because of defect self-interaction. If anelastic measurements are made on polycrystalline materials with the same crystallographic texture, then α and E each have some average value. Thus for measurements at a single temperature or frequency Δ can be expressed in the form

$$\Delta = \bar{a}c_0 \quad (27)$$

where $\bar{a}$ may be termed the specific relaxation strength of the defect.

The relaxation strength has already been used in the previous section on gas-metal equilibrium in that much of the lower temperature terminal solid solubility data in bcc interstitial systems (e.g. Nb-N, Ta-N) have been obtained by relaxation methods. In this application, use is made of the fact that Δ for the Snoek effect is proportional via Eq. 27 to the concentration of interstitial in solid solution.* Thus if the constant of proportionality $\bar{a}$ is known, usually by experiment, then the amount of dissolved interstitial in equilibrium with a precipitate phase can be determined as a function of equilibration temperature. The relaxation strength will also be used in later sections to describe various types of interstitial solute interaction processes which occur in the bcc metals.

*Strictly, this applies only to the concentration of unassociated (singly dispersed) interstitials in solid solution. See Section VI for details.

V. Interstitial Diffusion in BCC Metals

In general, there are two methods by which diffusion coefficients in solids are determined. Most often, the macroscopic mass flow of a particular atom species is measured. Fick's law is solved for the particular set of boundary conditions which is realized experimentally, and the diffusion coefficient is determined by a best fit of the experimental penetration data to the solution.⁴⁵ For example, from Fick's law the mean-square penetration distance $\overline{x^2}$ of a diffusing atom, determined by chemical or radioactive isotope techniques, may be related directly to the diffusion coefficient D and the diffusion time t . If atomic diffusion occurs along all three coordinate directions, but is measured along only one of them, then (for cubic crystals)

$$\overline{x^2} = 2Dt \quad (28)$$

if D is independent of concentration. For typical penetration distances of about one micron, it is clear that the experimental diffusion times become prohibitively long if diffusion coefficients of the order $10^{-16} \text{ cm}^2/\text{sec}$ and smaller are to be measured.

Lower values of the diffusion coefficients can be measured by the second of the two general methods. Specifically, D can be obtained without large penetration times of the diffusing atoms if the mean-jump-time, τ_j , the time for the atom to

move the unit distance d from one crystal site to another equivalent site, can be measured. If f_j is the jump frequency of the atom ($=\tau_j^{-1}$) and if the jumps are random and uncorrelated, then $\overline{x^2}$ is given by

$$\overline{x^2} = \frac{1}{3} f_j t d^2 \quad (29)$$

provided t is large compared to τ_j . Eqs. 28 and 29 then define D as

$$D = \frac{d^2}{6\tau_j} \quad (30)$$

Thus, measurement of τ_j gives D directly if d is known from an appropriate geometric model.

Mechanical and magnetic relaxation techniques have been used to measure diffusion coefficients of interstitials in bcc metals in the range 10^{-9} to 10^{-21} cm²/sec through use of Eq. 30. To use relaxation techniques to measure D , one must successfully relate the measured relaxation time τ_r to τ_j . Since both time constants measure unit jump times in the crystal, they are considered to be proportional to each other, i.e.

$$\tau_j = \alpha \tau_r \quad (31)$$

Here α is a constant which is generally greater than unity because the stress makes fewer jumps favorable in the stressed crystal compared to the unstressed crystal.

The expression for D in terms of τ_r , from Eqs. 30 and 31, is

$$D = d^2 / 6d\tau_r. \quad (32)$$

Now if τ_r has the temperature dependence given by Eq. 24, then

$$D = \frac{d^2}{6\alpha\tau_{ro}} \exp(-\Delta H_r / RT). \quad (33)$$

Comparing Eq. 33 with the usual description of D as a function of temperature

$$D = D_o \exp(-\Delta H / RT) \quad (34)$$

it is seen that

$$\Delta H = \Delta H_r \quad (35)$$

and

$$D_o = \frac{d^2}{6\alpha\tau_{ro}}. \quad (36)$$

For a given relaxation process, Eq. 35 should be justified either by experiment or on theoretical grounds. To determine D_o from Eq. 36 requires a detailed model from which both α and d can be defined.

α and d for diffusion of interstitials in bcc metals are easily determined. From Fig. 1, $d = a_o/2$ for octahedral sites (e.g. $(1/2, 0, 0)$) and $a_o/2\sqrt{2}$ for tetrahedral sites (e.g. $1/2, 1/4, 0$), where a_o is the lattice parameter. Wert^{46,47} has shown that $\alpha = 3/2$ for occupancy of either octahedral or tetrahedral sites. α is calculated in the following manner.

In bcc crystals, three classes of octahedral or tetrahedral sites, --x, y, and z-- can be distinguished. At zero stress, the total number of interstitials, N , is equally distributed among the three classes, i.e.

$$N_{xo} = N_{yo} = N_{zo} = N/3.$$

When a stress is applied, for example in the z direction, the interstitials are redistributed with time so that

$$N_x(t) = N_{xo} + \Delta N_{xo}$$

$$N_y(t) = N_{yo} + \Delta N_{yo}$$

$$N_z(t) = N_{zo} + \Delta N_{zo}$$

where

$$-\Delta N_{zo} = \Delta N_{xo} + \Delta N_{yo}.$$

If the stress is removed, the interstitials relax toward their original distribution. From Eq. 19 it is expected that

$$\Delta N_x = \Delta N_{xo} \exp(-t/\tau_o)$$

$$\Delta N_y = \Delta N_{yo} \exp(-t/\tau_o)$$

$$\Delta N_z = \Delta N_{zo} \exp(-t/\tau_o). \quad (37)$$

The interstitials in each type of site must also obey the flux equations

$$\frac{d(\Delta N_i)}{dt} = -\frac{\Delta N_i}{\tau_j} + \sum_{k \neq i} \frac{\Delta N_k}{2\tau_j}. \quad (38)$$

Substitution of Eq. 37 into Eq. 38 gives

$$\tau_j = (3/2)\tau_\sigma. \quad (39)$$

The previous calculation of α can be generalized to account for preferred sites being nearest neighbor sites. If the stress divides all crystal sites, equivalent under zero stress, into two energy groups, then the following general expression for the constant α may be derived:⁴⁷

$$\alpha = \frac{N(n-n')}{(N-N')n} \quad (40)$$

where N is number of types of sites which the atoms can occupy with equal probability under no stress, N' is the number of the N sites which become preferred under stress over the other $(N-N')$ sites, n is the number of the N sites into which the atoms can make a single jump with equal probability from other N sites at zero stress, and n' is the number of the N' preferred sites reached in a single jump from any of the preferred sites.

If the applied stress divides the crystal sites into more than two energy groups, if all sites are not equivalent in energy at zero stress, or if the non-equivalent sites are present in unequal numbers, then an expression for α more general than Eq. 40 is required. For interstitial solutes in the bcc metals, Eq. 40 applies directly. If the octahedral sites are occupied then

$$D = (a_o^2/36\tau_{ro})\exp(-\Delta H_r/RT) \quad (41)$$

If tetrahedral sites rather than octahedral sites are occupied, the calculated diffusion coefficients are smaller by a factor of two. The general acceptance of octahedral sites as the occupied ones has followed from a number of arguments. Originally, the selection of octahedral sites was suggested by the tetragonality of martensite in iron.⁴⁸ Later, Zener⁴³ argued that the octahedral sites, though smaller in size than the tetrahedral sites, were the sites of lower strain energy because of the relative elastic softness along $\langle 001 \rangle$ directions in iron. Finally, the anisotropy of the Snoek relaxation⁴⁹⁻⁵¹ strength, the agreement between experimental relaxation strengths and calculated values based on the tetragonality of martensite, and the usual agreement between anelastic and mass flow diffusion coefficients cited later have also been used as additional evidence of octahedral occupancy.

For each of the above arguments, counter-arguments which question their validity at least in part can be made.⁵²⁻⁵⁴ As a result, there has been renewed interest in recent years in the site occupancy of interstitials in bcc metals. Major interest has focused on explanations of a high temperature inflection in the diffusion coefficient of carbon in iron^{38,55-59} and on structure determinations of interstitial of

pre-precipitates in the Group VA metals (See Section VI), in terms of availability of tetrahedral sites. The problem is not fully resolved at present.

Interstitial diffusion in the bcc metals has been measured by both of the methods described above. In general, in systems for which the interstitial solid solution is stable with respect to precipitation at the measuring temperature in relaxation experiments, the determination of D by measuring τ_r is most often used because of the simplicity of the technique. In cases where both mass flow techniques and relaxation techniques have been used, agreement between the two methods is usually good. As an example, the temperature dependence of the diffusion coefficient of nitrogen in iron, taken from a tabulation by Lord and Beshers,⁵¹ is given in Fig. 18. Here, the excellent agreement of the data with Eq. 41 over sixteen decades in the diffusion coefficient obtained by many investigators using either type of technique is striking evidence that the techniques are compatible. It is important to point out that in some instances apparent discrepancies between the two types of measurements occur. A small but definite difference in slope occurs in $\ln D$ versus $1/T$ for Fe-C in the temperature range over which the "transition" from relaxation to mass flow measurements occurs⁵¹ is one example.

In Table 2, a summary of diffusion data for the interstitials O, N, C, and H in Fe, V, Nb, Ta, Cr, Mo, and W is given. The data given in brackets have been obtained by mass flow techniques alone. Unbracketed data are either internal friction data alone or combined data. In cases where notable discrepancies exist between results obtained by mass flow and relaxation techniques, two sets of diffusion coefficients are given, encompassing both types of measurements. The validity of all the data is obviously not the same, and it is difficult in many instances to assess it at present, except perhaps for the statements given below.

Relaxation Methods. The data for O, N, and C diffusion in the Group VA elements V, Nb, and Ta⁶⁰ and for C and N in Fe⁵¹ are very reliable. Relaxation techniques have not been applied as successfully to the Group VI metals Cr, Mo, and W. While several interstitial-induced peaks have been observed^{61,62} in these metals, appropriate identification of the specific interstitial involved has often not been made. Only for N^{63,64,65} and perhaps C⁶⁶ in Cr have definite assignments been made. Of the data available on Cr-N, the results of Klein⁶⁵ appear to be the most accurate and theoretically reasonable⁶⁷ and are the data given in Table 2. Measurement

of diffusion of H in the bcc metals by relaxation techniques has only in recent years received reasonable attention. The activation energy in Table 2 for H in Fe is accurate to approximately ± 0.5 kcal/mole, D_0 to an order of magnitude.^{68,69} Measurements by a single investigator over a wide frequency range is needed for this important system. Data for H in Nb and Ta⁷⁰ appear to be more accurate, though in less agreement with mass-flow data than data for Fe-H. Relaxation peaks ascribed to interstitial boron diffusion in Fe have often been reported,^{71,72} but in temperature ranges (at similar frequencies) which are too widely different to permit assessment of the relative reliability.

Mass-Flow Methods. Only the Fe-C and Fe-N systems have been studied intensively enough by both internal friction and mass-flow methods to permit critical comparison of the techniques. In these cases, there is excellent agreement in Fe-N (Fig. 18), while for Fe-C there is a small, but definite deviation.⁵¹ For Fe-H,^{71,72} Cr-N,^{73,74,75} Cr-C,⁶⁶ and possibly Mo-C,^{76,77} the agreement of the two techniques is good, based however on limited data. For all these systems, the mass-flow data may be classed as at least reasonably reliable. For all other systems, the agreement of limited data is either poor (Nb-H,⁷⁹ Ta-H,⁸⁰

Ta-C⁸¹ or no data exist for comparison. (Cr-O, Mo-H, Mo-N, Mo-O, W-C, W-N, and W-O).⁷⁷⁻⁸¹ All of the bracketed mass-flow data for O, N, and C in Cr, Mo, and W, taken from a tabulation by Stringer and Rosenfield,⁷⁷ appear to be reasonable.

VI. Multiple Relaxation Effects

The Snoek effect is one of many examples of a relaxation process which occurs in annealed crystals for which the prominent defect is a collection of isolated impurity atoms of a single type, usually intentionally added. In such situations, the impurity atom causes a relaxation peak which is close to ideal in shape according to Eq. 23 and is well characterized by a unique relaxation time and specific relaxation strength. This is generally true only in crystals which contain the single type of impurity in dilute concentrations, so that virtually all of the impurity atoms are singly dispersed in solid solution. If they are not singly dispersed or if the crystal has other impurity types, then the major impurity may have a spectrum of relaxation times (hence diffusion rates) and specific relaxation strengths. The breadth of the spectrum will depend upon the kinds of impurity clusters which exist in the solution in addition to the singly dispersed atoms. Each cluster configuration in the crystal might have its own unique relaxation time, τ_{ri} , and relaxation strength, Δ_i .

Two types of impurity clusters in bcc metals are discussed in this section: (1) interstitial clusters of small size, e.g. one to four atoms, in "concentrated" binary

solid solutions (>0.1 at.%), and (2) substitutional impurity-interstitial association in ternary solutions. Both types of clustering phenomena show rich relaxation spectra which can be analyzed in detail to disclose the physical nature of the solute interaction processes in the non-ideal solid solutions.

Having a crystal in which solute atoms are non-randomly dispersed in such a way as to give a spectrum of relaxation processes poses the analytical problem of how to separate an experimental relaxation curve into its component relaxations. The complication of multiple relaxation may be accounted for directly in Eq. 18 by addition of extra terms in the time derivatives of stress and strain to account for some number N active processes instead of just one. Thus the solutions, Eqs. 19, 20, and 23 become

$$\epsilon(t) = \sigma(o)/M_R + \sum_{i=1}^N A_i \exp(-t/\tau_{\sigma i}) \quad (42)$$

$$\sigma(t) = M_R \epsilon(o) - \sum_{i=1}^N B_i \exp(-t/\tau_{\epsilon i}) \quad (43)$$

$$Q^{-1} = \sum_{i=1}^N \Delta_i \frac{\omega \tau_{ri}}{1 + \omega^2 \tau_{ri}^2} \quad (44)$$

where A_i and B_i are proportional to the relaxation strength Δ_i of the i -th process, and $\tau_{\sigma i}$, $\tau_{\epsilon i}$, and τ_{ri} are the appro-

appropriate relaxation times. The specific method of analysis to determine all Δ_i or A_i or B_i and τ_{oi} , τ_{ei} , or τ_{ri} depends upon the type of physical model which can realistically be applied to the relaxing crystal. Some of these methods are described in this and the next section.

A. Relaxation of Interstitial Clusters

In many situations N in Eqs. 42-44 is probably a reasonably small number, say less than ten and as few as two. Analysis of a relaxation spectrum into components is often extremely difficult, particularly if the value of N must also be determined. The usual procedure is to apply a form of optimization theory, i.e. to find the smallest number of processes, N , each with relaxation parameters Δ_i and τ_{ri} , which consistently describes all experimental curves to within the known experimental accuracy. The analysis is subject to whatever constraints are considered physically reasonable boundary conditions. For example, some of the Δ_i 's or τ_{ri} 's may be known or the magnitudes of the Δ_i 's or τ_{ri} 's may be related in some particular way according to an assumed model.

In one situation the separation can be accomplished unambiguously. This is the case where the τ_{ri} 's of the component relaxations in a complex spectrum are sufficiently

different from one another (a factor of three or four or more). Even in this case, of course, use of the condition $\tau_{r(i+1)} \gg \tau_{ri}$ must be justified by application of a self-consistent physical model.

As an example, consider the case of concentrated interstitial solid solutions (> 0.1 at.% interstitial) for which the interstitials are likely to be present not only as singly dispersed atoms, but also as small clusters. Pairs, triplets, quadruplets, and larger clusters of interstitials may individually contribute to the total interstitial-related relaxation spectrum. As the total interstitial concentration is increased, more clusters would be expected relative to singly dispersed atoms. In this situation, use of the condition $\tau_{r(i+1)} \gg \tau_{ri}$ appears to be justified. The tumbling motion of an interstitial pair with a characteristic relaxation time τ_{r2} at a given temperature would be expected to be more difficult than motion of the singly dispersed atoms with a rate constant τ_{ri} . Thus $\tau_{r2} \gg \tau_{ri}$. Similarly $\tau_{r3} \gg \tau_{r2}$, $\tau_{r4} \gg \tau_{r3}$, etc.

Indirect evidence for these suppositions is readily available. For example, systematic changes in the apparent rate parameters of the Snoek relaxation with increasing interstitial concentration are often noted in the range above

approximately 0.5 at.%.⁸²⁻⁸⁴ Figs. 19 and 20 demonstrate this behavior for the Nb-O system. The apparent peak temperature in Fig. 19 increases from 151°C to 160°C with increasing oxygen concentration in the range 0.4 to 1.1 at.%. These results imply an increase in the activation energy for the Snoek spectrum⁸⁵ over this (or a larger) composition range; indeed, the temperature dependence of the average relaxation time confirms this change, Fig. 20. The Nb-O system will be used to illustrate analysis of these complex internal friction data and to demonstrate the large amount of important information which can be obtained from such experiments.

Decomposition of stress or strain relaxation curves for a spectrum in which $\tau_{rn} \gg \tau_{r(N-1)} \gg \tau_{r(N-2)}$ etc. has often been accomplished successfully by the "subtraction of tails" method.⁸⁶⁻⁹¹ The analysis is described in the following paragraphs for strain relaxation measurements, although the analysis is general, and in fact has been in use for years to analyze for radioactive decay half-lives and concentrations.^{92,93}

The raw data in such an experiment are a plot of anelastic strain or some quantity proportional to it as a function of elapsed time. The time dependence of the strain

relaxation is given by Eq. 42 for N relaxations occurring simultaneously but at different rates. At $t = 0$ and $t = \infty$, Eq. 42 becomes

$$\epsilon(0) = \sigma(0)/M_R + \sum_{i=1}^N A_i \quad (45)$$

and

$$\epsilon(\infty) = \sigma(0)/M_R, \quad (46)$$

respectively. Thus

$$\frac{\epsilon(t) - \epsilon(\infty)}{\epsilon(0) - \epsilon(\infty)} = \sum_{i=1}^N A'_i \exp(-t/\tau_{\sigma i}) \quad (47)$$

where A'_i is the fraction of the total relaxation contributed by the i -th process.

Suppose $\tau_{\sigma N}$ is the longest relaxation time in the spectrum. Then if $\tau_{\sigma N} \gtrsim (3 \text{ or } 4) \tau_{\sigma(N-1)} \gtrsim (3 \text{ or } 4) \tau_{\sigma(N-2)}$ etc., then at time $t \gg \tau_{\sigma(N-1)}$, the contribution of only the N -th process should be dominant. Thus

$$\frac{\epsilon(t) - \epsilon(\infty)}{\epsilon(0) - \epsilon(\infty)} \equiv \epsilon_N = A'_N \exp(-t/\tau_{\sigma N}) + \sum_{i=1}^{N-1} A'_i \exp(-t/\tau_{\sigma i}) \quad (48)$$

from which

$$\ln \epsilon_N \approx \ln A'_N - t/\tau_{\sigma N} \quad (49)$$

for data in the time range $t \gg \tau_{\sigma(N-1)}$. If $\ln \epsilon_N$ is plotted as a function of t , then A'_N and $\tau_{\sigma N}$ can be determined unambiguously.

The natural logarithm of A'_N is the intercept at $t = 0$ of the plot according to Eq. 49, while $\tau_{\sigma N}$ is the reciprocal of the slope of the plot. If the total relaxation strength is designated Δ_t , then Δ_N is simply $A'_N \Delta_t$.

Once A'_N and $\tau_{\sigma N}$ are known, the same parameters for faster processes occurring dominantly in other time intervals can be obtained. For the $(N-1)$ -th process, at times $t \gg \tau_{\sigma(N-2)}$ but much less than $\tau_{\sigma N}$ the working equation is

$$\epsilon_N - A'_N \exp(-t/\tau_{\sigma N}) \equiv \epsilon_{N-1} = A'_{N-1} \exp(-t/\tau_{\sigma(N-1)}) + \sum_{i=1}^{N-2} A'_i \exp(-t/\tau_{\sigma i}) \quad (50)$$

or

$$\ln \epsilon_{N-1} \approx \ln A'_{N-1} - t/\tau_{\sigma(N-1)}. \quad (51)$$

Here ϵ_{N-1} is known from the previous determination of A'_N and $\tau_{\sigma N}$. Reiteration of this procedure eventually gives the parameters for all relaxation processes contributing to the total curve as long as the relaxation times are well separated.

A sample analysis of elastic after-effect data ("d" in Fig. 16) for a Nb-1.1 at.% O alloy is given in Fig. 21 (a-d). This is the same alloy for which the internal friction curve ($-\square-$) is given in Fig. 19. Four relaxations are

disclosed by successive subtraction of exponential tails. Fig. 22 shows the total experimental curve and the four component processes to point out the time range of importance of each.

Analysis of a complex internal friction curve consisting of the same component processes proceeds in much the same manner as described above for the after-effect data. The analysis relies on either the high or low temperature side of a component peak at the high or low temperature edge of the total spectrum being the dominant contribution to the total spectrum at those temperatures. Consider the analysis of the internal friction curve ($-\square-$) of the Nb-1.1 at.% O alloy in Fig. 19. These data, less background, are plotted as a function of $1/T$ in Fig. 23 ($-\odot-$). The only information known initially for this spectrum are Δ and τ_r for a small residual nitrogen Snoek peak (Peak N) on the high temperature side and τ_{ri} and an approximate value of Δ_1 for the oxygen Snoek peak (Peak 1 and Process 1 in Figs. 21 and 22) on the low temperature side. Analysis of the remainder of the spectrum by successive subtraction of peaks discloses that at least three additional peaks, corresponding to Processes 2, 3, and 4 in Figs. 21 and 22, are necessary to describe accurately the total spectrum. The nitrogen Snoek relaxation is not observed in after-effect curves

because its relaxation time is extremely long at the lower temperatures compared to the oxygen processes.⁶⁰

From the temperature dependence of the relaxation times, τ_{ri} , the kinetics of the four processes described above can be determined. The after-effect and low frequency internal friction data just described gives values of τ_{ri} over six orders of magnitude as a function of temperature. Each relaxation time has an Arrhenius temperature dependence

$$\tau_{ri} = \tau_{roi} \exp(\Delta H_{ri}/RT). \quad (52)$$

These dependences are given in Fig. 24; the rate constants τ_{roi} and ΔH_{ri} are given as part of Table 3. The diffusion coefficients D_i for each process can be determined from the τ_{ri} if the relaxing defects are identified and their geometries are defined. The D_i are given by

$$D_i = d_i^2 / \alpha_i \tau_{ri} \quad (53)$$

where d_i is the distance over which the center of gravity of the cluster moves in a unit jump of the whole cluster.

From the concentration and temperature dependences of the relaxation strengths of each process, considerable thermodynamic information is available: (1) The four processes disclosed in Figs. 21 to 23 can be identified as relaxations caused by movement of interstitial singles, the Snoek relaxation, (No. 1), pairs (No. 2), triplets (No. 3),

and possibly quadruplets (No. 4). (2) The binding enthalpy, ΔH_N^O , and other thermodynamic parameters of each cluster can be evaluated.^{85-90, 94}

The identifications follow from application of the law of mass action to the solid state reactions of the type

For these reactions the concentration of the cluster of size N, C_N , and the concentration of single interstitials C_1 are related by

$$C_N = Z_N 3^{-N} C_1^N \exp\left(-\frac{\Delta S_N^O}{R}\right) \exp\left(\frac{\Delta H_N^O}{RT}\right) \quad (55)$$

Z_N is the number of independent ways the cluster of size N can be arranged in the bcc crystal, 3^N is the number of ways of arranging N singly dispersed atoms, and ΔS_N^O is the binding entropy of the cluster of size N. Hence if the relaxation strengths Δ_N and Δ_1 are proportional to the respective concentrations through Eqs. 26 and 27, i.e.

$$\Delta_N = Na_N C_N \quad (56)$$

where $Na_N = \bar{a}$ in Eq. 27, then in general for data obtained at a constant temperature

$$\Delta_N \approx \Delta_1^N \quad (57)$$

if the above equilibria occur. Relationships such as these have been confirmed for the four processes disclosed in Figs. 21 to 23.⁸⁹

The binding enthalpies ΔH_N^O are determined from the temperature dependence of the relaxation strengths. Assume $T \gg T_c$ in Eq. 26.⁹⁵ Then

$$\Delta_N \approx \frac{Na_N'}{T} C_N \quad (58)$$

where $a_N' = Ta_N$ in Eq. 56. Hence Eq. 55 becomes

$$\ln \frac{\Delta_N}{T^{N-1} \Delta_1^N} = \frac{\Delta H_N^O}{R} \left(\frac{1}{T} \right) + \{ \ln (Na_N / T^{N-1} a_1^N) + \ln Z_N - N \ln 3 - \Delta S_N^O / R \} \quad (59)$$

where the term in brackets is assumed to be temperature independent. A plot of $\ln \frac{\Delta_N}{T^{N-1} \Delta_1^N}$ versus $\frac{1}{T}$ gives $\frac{\Delta H_N^O}{R}$

as the slope. Evaluation of the parameters in the intercept permits other thermodynamic functions of each cluster to be determined. The binding free energy of each cluster, ΔG_N^O , and the binding entropy, ΔS_N^O , are given by

$$\Delta G_N^O = -RT \ln \{ (Na_N / a_1^N) (\Delta_1^N / \Delta_N) Z_N 3^{-N} \} \quad (60)$$

and

$$\Delta S_N^O = T^{-1} (\Delta H_N^O - \Delta G_N^O) \quad (61)$$

or

$$\Delta S_N^O = R \left[\ln \frac{Na_N}{T^{N-1} a_1^N} + \ln Z_N - I_N \right] \quad (62)$$

where I_N is the $1/T = 0$ intercept of the plot of Eq. 59.

Values for these functions for Nb-O and other systems investi-

gated to date are included in Table 4. It is clear from Eqs. 60 and 62 that the constants a_N and their temperature dependences must be determined to completely determine the thermodynamic parameters. The a_N 's are also necessary to determine the actual concentrations of each cluster.

The constants a_N are determined from the concentration dependence of the relaxation strengths Δ_N .^{89,94} The mass balance for all interstitial atoms is combined with Eq. 56 and solved for the a_N from any of the following sets of simultaneous equations:

$$C_t = \sum_{i=1}^N iC_i = \sum_{i=1}^N (\Delta_i/a_i) \quad (63a)$$

or since the total relaxation strength is

$$\Delta_t = \sum_{i=1}^N \Delta_i, \quad (64)$$

then

$$C_t/\Delta_t = \sum_{i=1}^N \frac{\Delta_i}{\Delta_t} \left(\frac{1}{a_i} - \frac{1}{a_1} \right) + \frac{1}{a_1} \quad (63b)$$

or some similar form, where a_1 is replaced by one of the a_i .

Here C_t is the total interstitial concentration. Notice that

if $N = 2$, the working equation can be reduced to

$$C_t/\Delta_t = \frac{\Delta_2}{\Delta_t} \left(\frac{1}{a_2} - \frac{1}{a_1} \right) + \frac{1}{a_1}. \quad (63c)$$

Thus a plot of C_t/Δ_t versus Δ_2/Δ_t gives a_1 and a_2 directly.⁹⁴ Values of these constants are given for the Ta-O and Nb-O systems in Table 5. Notice that all of the constants for both systems are "large", inferring that the defects have large shape factors $(\delta\lambda)_N$, as is well known for the Snoek effect.⁹⁵ Notice also $a_N > a_{N-1}$, i.e. atoms in larger clusters have greater damping capacities than in smaller clusters (or as single atoms).

At present, the data described above have been obtained only in polycrystalline materials. Thus, the actual values for the parameters $(\delta\lambda)_N$ cannot be determined from Eq. 26 unless average values of the quantities α , E , and Γ are determined or estimated. Data on the anisotropy of the relaxation strength will also give important clues toward determination of the geometry of the clusters. Experiments on single crystals would obviously represent a valuable contribution to the present state of knowledge of clustering of interstitials.

In Tables 3 and 4, the kinetic and thermodynamic parameters are given for several interstitial clusters in systems which have been studied so far. Notice that for all binary systems $\Delta H_{rN}^0 > \Delta H_{r(N-1)}^0$, indicative of slower movement (larger τ_r 's) of larger clusters at a given temperature. Notice also

that $\Delta H_{rN} \lesssim \Delta H_{rl} + \Delta H_N^O$, so that it is unlikely that the clusters dissociate completely during reorientation.

Tables 3 and 4 also include information on the association of unlike interstitials, for which the interaction processes and the analyses of relaxation data are alike in detail. Data at present are limited to the Ta-O-N and Nb-O-N systems.^{83,90} Fig. 25 demonstrates qualitatively these processes in niobium. The moderately highly damping for Curve A in the temperature range 200°C to 250°C due primarily to O-N pairs is a result of the non-negligible residual nitrogen content in this alloy.

Clearly accurate data are necessary to allow analyses of the type described above. For example in stress or strain relaxation studies, moderately accurate curve decomposition even by computer techniques⁹³ requires sensitivity of about one part in 10^3 . Thus, in strain relaxation measurements if a total elastic strain is 10^{-4} and Δ_t is 0.1, (both typically large values), then strains of 10^{-8} should be measurable to obtain τ_{ri} 's and Δ_i 's accurately. Furthermore, at strain levels this small, temperature control to better than $\pm 0.01^\circ\text{C}$ is required if background strains caused by thermal expansion are to be eliminated. In internal friction experiments, temperature changes during individual measure-

ments and temperature gradients along the length of the specimen should be $\lesssim 0.1^\circ\text{C}$ to avoid spurious peak broadening.

The results of this section show that the regions of solid solution may be not ideal, and that the planes ABCD and CDIH are not really planes. Nevertheless the departure from ideality is so slight that chemical measurements of the type described in section III are not sensitive enough to detect differences. For example, consider a system consisting of singles and pairs of an interstitial I in equilibrium with a compound Me-I. If the heat of solution of singles is 8,000 cal/mole and the binding enthalpy be 2000 cal/mole (this is about the case for O-singles and O-O pairs in equilibrium with TaO), the effect on the solvus line can easily be calculated. The calculation is sketched in Fig. 26, where the ratio C_p/C_s is adjusted to be about $10^{\frac{1}{254}}$ at 725°C . (This is the value obtained inserting reasonable values of constants into Eq. 55.) One sees that the overall concentration of oxygen in the α solution is almost completely made up of singles at all temperatures and the solvus line is almost identically that for singles. Only in the case where one would quench material of high interstitial content (say $X = .01$ or more) to low temperatures (say 200°C or below) would one have a large number of pairs.

B. Relaxation of Substitutional-Interstitial Clusters

If a bcc crystal contains substitutional as well as interstitial impurities in dilute solution, then additional relaxation processes are often observed in the vicinity of the Snoek peak. These processes are attributed to the pairwise (or higher order) association of the interstitial (i) and the substitutional impurities (s) in the solid solution. The total damping spectrum is considered in the simplest situation to consist of two processes: (1) the true Snoek relaxation, involving the stress-induced reorientation of unassociated interstitials, and (2) the s-i relaxation, occurring invariably at a somewhat higher temperature (at the same frequency) and involving the local reorientation of an interstitial among sites with a substitutional atom as a nearest neighbor. Fig. 27 gives an internal friction curve for an Fe-Mn-N alloy (a classic system for these studies) from the extensive work of Dijkstra and Sladek.⁹⁶ Also shown is the approximate decomposition of the total curve into the two components described above. Fig. 28 portrays one way by which the reorientation of the interstitials in both types of sites might occur. The data in Fig. 28 indicate that the mean-time-of-stay of the nitrogen atom near a manganese atom is greater than when it is near only iron atoms. Thus $D_{SP} > D_{s-i}$

at the same temperature. If the nearest neighbor sites are those occupied by the interstitial atom, the simplified model of Fig. 28, a two-jump s-i process, would account for the longer time-of-stay near an Mn atom. Only a small positive binding enthalpy, ΔH_{si}^0 , for the s-i interaction is required for the nearest neighbor s-i pair to remain associated under stress.

These types of association processes are amenable to the same analysis applied to interstitial clusters previously. The s-i pairs are in equilibrium with unassociated interstitial and substitutional atoms by a reaction

for which

$$C_p = (Z_p/3) C_s C_i \exp\left(-\frac{\Delta S_{si}^0}{R}\right) \exp\left(\frac{\Delta H_{si}^0}{RT}\right) \quad (65)$$

Here C_p , C_s , and C_i are the atom fractions (ratio of the number of defects to the number of occupiable sites) of s-i pairs, unpaired substitutionals, and unpaired interstitials, respectively. ΔS_{si}^0 is the binding enthalpy of the s-i pair. Z_p is the number of independent positions the interstitial can assume about the substitutional atom in a s-i pair.

$Z_p = 6$ for the configuration given in Fig. 28. Eq. 65

holds only for dilute ternary solutions. For these solutions, C_s is closely approximated by the total substitutional content.

The binding enthalpy of s-i pairs is apparently never negative, and judging from the height of the Mn-N peak in Fig. 27, it is probably larger than typical values of ΔH_2^0 for interstitial pairs given in Table 4. Consider from Fig. 27 that although the octahedral interstitial sites near Mn atoms in the 0.5% Mn alloy are only about 1% of the total number of sites as many of one-half of them may be occupied by interstitials near room temperature. For the Fe-0.5% Mn-0.02% N alloy in Fig. 27, it is possible to determine from Eq. 65 that ΔH_{si}^0 (strictly speaking, ΔG_{si}^0) is approximately 3000 cal/mole, if it is assumed that the specific relaxation strengths of nitrogen in both types of sites are equal.^{47,97,101} Hence, C_p is likely to be significantly greater than the expected concentration of s-i pairs from random statistics, i.e. $(Z_p/3) C_s C_i$.

The Mn-N peak occurs at about 10°C above the N Snoek peak for internal friction measurements at about 1 cps. By comparison in Fe-V-N alloys, a V-N peak occurs at approximately 60°C above the Snoek peak, inferring a relatively higher activation enthalpy and binding enthalpy for the V-N relaxation. In agreement with these qualitative observations, Perry, Malone, and Boon⁹⁸ have determined from one-point calculations on data of Fast and Meijering⁹⁹ a binding enthalpy of approximately 6.2 kcal/mole for the V-N pair.

An extreme case of high binding of S-i pairs occurs in Nb-Zr-O alloys. Bunn, Cummings, and Leavenworth¹⁰⁰ observe in Nb-1% Zr only a "Zr-O" peak of the two-peak spectrum unless the atomic ratio of O to Zr is 2 to 1 or greater.

Unfortunately, while many ternary systems exhibiting s-i-type interaction peaks have been investigated, there are no data on any one system complete enough for analysis of s-i pair formation in the manner demonstrated previously for interstitial clustering in binary systems. Systematic studies of an s-i relaxation as a function of concentration and especially of temperature seem desirable.

From the temperature dependence of the relaxation strengths, all of the thermodynamic parameters which characterize the s-i reaction, the specific relaxation strength, and the actual concentration of interstitials participating in the s-i relaxation can be determined in principle. Particularly valuable information could be obtained by including torsional after-effect results with the now well established internal friction measurements at low frequencies (0.3 to 2.5 cps) by torsion pendulum techniques. Analysis of the after-effect data in components by the subtraction of tails method, if possible, or other methods could add greatly to the understanding of these processes.

Several investigators have studied concentration dependences of s-i relaxation strengths, generally only in the 1 cps temperature range. There is clearly a linear dependence of Δ_p on interstitial and substitutional concentration in dilute alloys, confirming the relationships expected from Eq. 65. However, these studies have also disclosed that in detail the s-i interaction is much more complicated than indicated thus far.¹⁰¹⁻¹⁰⁴ For example, the small bump on the low temperature side of the damping curve in Fig. 27 is a real effect. It develops into a full-sized peak as the Mn content is increased. Changes in the concentration of substitutionals over wide ranges, as in the work by Nacker and Kulman¹⁰³ and Ritchie and Rawlings,¹⁰⁴ clearly demonstrate how complicated the damping spectra may be. Both of these investigations disclose that at least seven independent relaxation peaks may be required to accurately describe the total curves, although there is not a clear peak-to-peak correspondence in the two analyses. See Fig. 29 for some of these data. Ritchie and Rawlings observe their seven peaks over a narrower temperature range, even though they apparently used materials of higher nitrogen content. In Table 6, the analyses of several investigators of their work on Fe-(Me)-N alloys are given. Clearly, a great deal more work is required for better understanding of these processes.

Table 6 also includes a compilation of many of the systems in which s-i relaxations have been observed. Decomposition of the interstitial spectrum into only the Snoek peak and a higher temperature s-i peak is considered, and the approximate temperature of the s-i peak at 1 cps is given. As an approximate rule for determining the activation enthalpy for the s-i peak, figure for each degree difference in temperature between the SP and the s-i peak, about a 62 cal/mole addition to the activation enthalpy of the SP.⁸⁵

Two final points should be mentioned. (1) The s-i interaction peaks are a general feature of ternary alloys, not only for bcc crystals but for all crystal types.^{44,105} (2) Nevertheless, not all substitutional elements cause s-i relaxation with nitrogen or carbon;^{104,106} in fact, few substitutional elements in Fe cause s-i relaxations with carbon. Here, it would seem, exists an excellent opportunity for correlation of s-i relaxation behavior with classical thermodynamic data on the same systems. Clearly, deviations from thermodynamic ideality and the extent of s-i pair formation should correlate. Of course, it is important to have both types of measurement at comparable temperatures, if possible. Since the concentration of s-i

pairs obeys the mass action law, their numbers from Eq. 68 relative to unassociated interstitial become small at high temperatures, where thermodynamic data are usually obtained.

C. Other Evidence for Interstitial Clustering

Evidence which demonstrates the importance of interstitial association processes in solid solution also comes from analytical methods other than relaxation techniques. Some of these methods are considered briefly in this subsection.

Theoretical Predictions. Many years ago Zener^{43,108,109} first considered the importance of interstitial clustering in bcc metals with regard to the formation of martensite in iron-nitrogen and iron-carbon alloys. Zener reasoned that the interaction between interstitials should be attractive because of elastic strain energy relaxation about an interstitial pair. He predicted that the interaction would result in a spontaneous martensitic-like ordering of the solute at some low critical temperature (T_c in Eq. 26) and would account for the tetragonality of martensite if interstitial pairing in one favored orientation occurred. Zener calculated a binding enthalpy of approximately 2 kcal/mole for the elastic interaction of an interstitial pair. Thus, the cluster formation observed in anelastic experiments might

be regarded as the earliest stages of the complex ordering processes which eventually result in the formation of martensites, coherent pre-precipitates, etc.

In more recent years, Fisher¹¹⁰ and Johnson¹¹¹⁻¹¹³ have made more detailed calculations of the binding between interstitials. Both investigators obtain similar results from moderately different approaches, although interaction of interstitial strain fields is calculated in both instances. The results of these calculations for interstitial pair formation are illustrated in Fig. 30. Apparently, as many as three types of interstitial pairs might be stable. The binding enthalpies calculated for Fe-C by Fisher (F) and Johnson (J) are given under the sketch for each configuration. The values are in good agreement with experimental results given in Table 4. One might wonder, however, why the relaxation of each pair configuration, if stable, is not observed experimentally. Aside from problems of experimental accuracy or validity of calculations, a number of possible explanations exist. These include: (1) The relaxation times of the various pair configurations may not be different enough to distinguish the individual processes, particularly by peak subtraction methods or subtraction of exponential tails. (2) The dipole shape factors $(\delta\lambda)_i$

may be small for one or more of the relaxations, so that they are not observed. This is probably especially true for configuration number 3 in Fig. 30.

Johnson has recently¹¹³ extended his calculations to include carbon clusters in iron of as large as twelve atoms. For clusters of five atoms and larger, he predicts an incremental binding enthalpy (the increase in binding enthalpy per atom added to the cluster) of approximately 7 kcal/mole (0.3 ev). The larger clusters tend to form platelets along either {100} or {110} planes from elementary pair interactions number 1 or 2 in Fig. 30, depending presumably upon the kinetics of nucleation. The total binding enthalpies calculated for two, three, and four atom clusters are included in Table 5 for comparison with experimental results. The higher calculated values may result from short-ranged, though non-negligible, carbon-carbon electronic repulsion not considered in the calculation.

Another theoretical approach to the study of interstitial clustering and related problems is a more purely thermodynamic one, involving analysis of the compositional dependence of the thermodynamic activity of the interstitial in solid solution. In general, the free energy of the solution is formulated as a function of temperature and composition with the non-ideality of the solution expressed by an appro-

priate thermodynamic model. Invariably, the binding enthalpy of the interstitials in solution (or some equivalent parameter) is incorporated in a quantitative manner into the activity coefficient and determines the extent of the deviation of the solution from ideality. The binding enthalpy can then usually be determined as the value which gives the best fit of the model to the experimental data of activity as a function of concentration.

Several investigators¹¹⁴⁻¹¹⁸ have employed this approach to study the thermodynamics of interstitial solid solutions, most often the γ -Fe+C system. As an example pertinent to the theme of this paper, consider an application to ferrite solutions. Recently, Aaronson, Domian, and Pound¹¹⁷ have examined the predictions of interstitial clustering by the thermodynamic models of Darken and Smith¹¹⁴ and Lacher and Fowler and Guggenheim.^{119,120} These models give for the relationship between the activity of carbon, a_α , and mole fraction of carbon in ferrite, x_α , the following:

$$\ln a_\alpha = \ln \frac{x_\alpha}{3 - (12 - 8 \exp[-\omega_\alpha/RT])x_\alpha} + \frac{C+DT}{RT} \quad (66)$$

and

$$\begin{aligned}
 \ln a_{\alpha \text{ LFG}} = & 3 \ln \frac{3-4X_{\alpha}}{X_{\alpha}} + \frac{w_{\alpha}}{RT} \\
 & + 4 \ln \frac{\{[9-6X_{\alpha}(2J_{\alpha}+3)+(9+16J_{\alpha})X_{\alpha}^2]^{\frac{1}{2}}-3+5X_{\alpha}\}}{\{[9-6X_{\alpha}(2J_{\alpha}+3)+(9+16J_{\alpha})X_{\alpha}^2]^{\frac{1}{2}}+3-5X_{\alpha}\}} \\
 & + \frac{C+DT}{RT}
 \end{aligned} \tag{67}$$

Here C and D are standard state constants and J_{α} is given by

$$J_{\alpha} = 1 - \exp(-w_{\alpha}/RT) \tag{68}$$

w_{α} , the interaction energy between adjacent carbon atoms in ferrite, is the negative of the binding enthalpy ΔH_2^0 as defined in this paper. Notice that the two equations reduce to approximately the same expressions if $w_{\alpha} = 0$. From the data of Smith¹²¹ at 750°C and 800°C, Aaronson et al. deduce values of ΔH_2^0 in the range of about 7.5 and 9.6 kcal/mole, respectively. The standard deviations for these values are large however, approximately one-half of the value of ΔH_2^0 at 800°C. It appears that the thermodynamic models are too demanding for the accuracy of the available thermodynamic data. As a result, these calculations can be considered to be only qualitatively in agreement with the predictions of the relaxation experiments.

Interestingly, analysis of thermodynamic data by equations similar to Eqs. 66 and 67 predicts a negative

binding energy $\Delta H_2^0 = -0.8$ to -1.7 kcal/mole for carbon pair formation in austenite.¹¹⁷ Thus, interstitial pairs in fcc metals may be present in less than random numbers according to Eq. 55. Confirmation of this behavior from relaxation measurements has not been made, although only a very small ($\ll 10^{-3}$) carbon pair peak in nickel is observed,^{91,122} even with about 2 at.% C in solution. The absence of a Snoek relaxation in close-packed metals prohibits measurement of the binding enthalpy by the methods employed for bcc metals.

The s-i interaction process in ternary alloys can in principle be analyzed by the same formal thermodynamic approach,¹²³ although only beginning attempts have been made. In these cases, correlation of relaxation behavior with thermodynamic data could perhaps permit prediction of alloying elements which cause s-i relaxations. In iron, for example, the role of austenite or ferrite stabilizers and strong or weak carbide or nitride formers might be better assessed analytically. Unfortunately, there is insufficient experimental information on the thermodynamics and the relaxation behavior of ternary alloys to approach these problems very directly. The intent here is to point out the different types of information which might be correlated and in which ways this might be done.

Electron Microscopy. Resolution in the electron microscope is not sufficient to permit direct observation of clusters of the size described thus far. There is however considerable evidence that the interstitials order into larger, observable domains or pre-precipitates,¹²⁴⁻¹²⁹ particularly in the Group VA metals V, Nb, and Ta. An example of the domain structure which is observed in Nb-O alloy if all of the oxygen is not maintained in solution is shown in Fig. 31, taken from work by van Landuyt.

These domains in Nb-O alloys appear to have the composition Nb_2O ,¹³⁰ and if octahedral sites are occupied they would likely nucleate from pairs of orientation no. 2 in Fig. 30. It should be noted that there are only subtle differences between the Nb_2O superlattice deduced by van Landuyt et al.¹³⁰ and the structure of the cluster of nine carbon atoms in iron determined from the computer calculations of Johnson et al.¹¹¹ However, from electron diffraction patterns alone the interstitial superstructure could as easily result from tetrahedral site occupancy.

The domains are observed to migrate under the irradiation of the electron beam of the microscope.^{125,130} While, of course, the essentially two-dimensional character of the film is important here, the movement of the large domains lends support to the idea that interstitial clusters as

"large" as three or four atoms would have reasonable mobility to contribute to an anelastic spectrum.

Thus, the pair-wise and higher order interaction of interstitials deduced from damping experiments and large scale interstitial ordering observed by electron microscopy are complementary. Indeed, it appears that the ordering is a result of the pair-wise attractive interaction, although the observed ordered domains are too large to contribute to the damping. Once ordered, the interstitials cease to contribute to the Snoek peak spectrum, and the damping is decreased.¹³¹

Field Ion Microscopy. The most ideal method to study interstitial clustering effects would be to directly count the numbers of each type of cluster in the crystal. The closest approach to such experiments now available involves use of the field-ion microscope,¹³² which is capable of resolving individual atoms at the surface of a metal specimen in the shape of a finely tipped pin. The method suffers the obvious disadvantage of having to obtain information from a surface which is curved drastically enough to perhaps thermodynamically affect the interstitial equilibria there. Nevertheless, the initial efforts in this direction deserve description and comment.

Nakamura and Muller¹³³ have studied the oxidation of tantalum in the field-ion microscope. Of particular interest here are their experiments on quenched and aged specimens. Tantalum tips with about 0.8 - 1.1 at.% oxygen were quenched from 1100°K and aged at temperatures in the range 360°K to 900°K. Afterwards, oxygen atoms were counted several atom layers deep by stripping off layers by field evaporation. Significant differences in the numbers of paired and unpaired interstitials were noted in aged and unaged specimens; similarly the lower the aging temperature, the higher the relative concentration of pairs. The results given in Table 7 are consistent in trend with the predictions of the clustering thermodynamics described earlier and are in basic agreement with results expected from internal friction measurements,^{88,89,94} also included in Table 7. The temperature dependence of the field-ion microscopy data gives a binding enthalpy $\Delta H_2^O \approx 1.5$ kcal/mole when analyzed in terms of Eq. 55. See Fig. 32. This result is in good agreement with other values given in Table 4. There is no indication in the paper by Nakamura and Muller that clusters larger than pairs were observed in spite of the high concentration of oxygen. However, recently Machlin¹³⁴ has observed in a field-ion micrograph what appears to be a cluster of four oxygen atoms in tungsten. It is clear that

use of this technique has not been exploited to anywhere near its potential in this area.

Other Techniques. The power of two additional techniques, nuclear magnetic resonance and the Mössbauer effect, to discern the nature of solute interaction processes in alloys should be mentioned. The absorption amplitudes of various nuclei in measurements by both techniques are known to be extremely sensitive to solute distributions through dependence of the spectra on the nature of the local charge or spin configurations.^{135,136} The recent work of Gielen and Kaplow¹³⁷ is indicative of the potential of these techniques. In both martensite and austenite of Fe-N and Fe-C alloys, they determine distinct Mössbauer spectra for iron atoms with single C or N atoms in nearest and next-nearest neighbor sites from differences in the hyper-fine interactions between the nuclei and their electronic surroundings. The approach should naturally extend to determination of cluster sites.

Another type of physical measurement applicable to the study of interstitial clustering is the determination of superconducting properties. For example, these properties are very sensitive to the amount and distribution of interstitial oxygen and nitrogen in niobium.^{138,139} However, data which infer interstitial clustering are only qualitative at present.

VII. Interstitial-Dislocation Interaction

Interstitial impurities in the bcc metals are capable of interactions with more complex defects than other interstitials, substitutional atoms, or point defects in general. Interaction with dislocations, grain boundaries, precipitates, and other extended defects can in fact often overshadow the solute association effects described above. Indeed, it is well recognized that strong interstitial-dislocation interactions are responsible for the rapid solid solution hardening, the yield point phenomenon, Portevin-LeChatelier serrations, and other important mechanical behavior features of bcc metals. In this section interstitial-dislocation interaction is discussed as an example of one of the important interactions which interstitials undergo with extended defects. Descriptions of the interaction process and methods of measuring the interstitial-dislocation interaction energy (enthalpy) are given briefly. Then one of the methods of measurement, which employs the relaxation techniques described earlier, is applied to the important and often studied Fe-H system as an example of the experimental study interstitial-dislocation interactions.

A. Basis for the Interaction

The interaction of a solute atom and a dislocation can arise from several sources. Those sources which have been

treated theoretically include:¹⁴⁰⁻¹⁴³ (1) the elastic misfit interaction, which results from the distortion caused by the solute atom (assumed to be a rigid sphere) when it is inserted into a lattice site for which it is either undersized or oversized, (2) the elastic modulus interaction, which occurs because of the differences in compressibility of the solute and solvent atoms, (3) the electronic interaction, the electrostatic interaction resulting from the redistribution of conduction electrons from regions of compression to tension in the strain field of the dislocation and the valency difference between solute and solvent atoms, and (4) the chemical interaction, which arises from the difference in the effective chemical solubility of solute atoms in the crystal matrix and stacking faults.

Of these various interactions, the elastic misfit interaction is quite reasonably thought to be the major contribution to the binding enthalpy, ΔH_{il}^0 , for the interaction between a dislocation and the interstitials O, N, and C in Fe and the Group VA and VI-A refractory metals. The large tetragonal strain caused by the interstitial and either the predominantly shear strain field of a screw dislocation or the large dilatation about an edge dislocation can be relaxed by association of the two defects. The elastic misfit binding enthalpy is simply the excess elastic work done to place the interstitial in the crystal

containing the dislocation over the work done to place the interstitial in the perfect crystal.¹⁴⁴ Hence

$$\Delta H_{ii}^o = -v^{(i)} \sum_{i,j=1}^3 \sigma_{ij}^{(-)} \epsilon_{ij}^{(i)} \quad (69)$$

where $v^{(i)}$ is the volume of the unit cell occupied by the interstitial, $\sigma_{ij}^{(\downarrow)}$ is the stress field of the dislocation, and $\epsilon_{ij}^{(i)}$ is the distortion of the unit cell caused by the introduction of one interstitial atom. If linear isotropic elasticity theory is used to determine $\sigma_{ij}^{(\downarrow)}$ and $\epsilon_{ij}^{(i)}$, then

$$\Delta H_{i-}^o (\text{screw}) = -\frac{Gb_s \sqrt{2} a_o^3}{3\pi r} (\epsilon_{11} - \epsilon_{22}) \cos \theta \quad (70)$$

and

$$\Delta H_{i-}^o (\text{edge}) = -\frac{Gb_e a_o^3}{2\pi(1-\nu)r} [f(\epsilon_{ij}^{(i)}, \theta)] \quad (71)$$

Here G is the shear modulus, b_s and b_e are the Burger's vectors, a_o is the lattice parameter, ν is Poisson's ratio, r is the radial distance between the dislocation line and the interstitial, and θ is the angle between the vector $\underline{r}$ and the slip plane of the dislocation. The parameter f is an involved function of $\epsilon_{ij}^{(i)}$ and θ .

With both screw and edge dislocations, $\Delta H_{i\downarrow}^o$ is calculated to be of the order 0.7 ev for carbon in iron and is in reasonable agreement with values determined experimentally by methods discussed below. Hence it would appear that contributions due to the modulus, electronic, and chemical interactions are generally of secondary importance for interstitials

causing these large distortions.

B. Methods of Measurement

The binding enthalpy, $\Delta H_{i\downarrow}^{\circ}$ is a thermodynamic quantity, and can thus in principal be determined experimentally by any technique which is sensitive to the concentration of interstitials at dislocations. Partitioning of interstitials between dislocation sites and sites in the solid solution may be analyzed as before for solute-solute interactions in terms of a mass action process

where i and $\downarrow$ are occupied and unoccupied interstitial sites respectively in the metal crystal (Me), and $i\downarrow$ and $\downarrow$ are occupied and unoccupied sites respectively along the dislocation for interstitials. The binding enthalpy and entropy are related to the total numbers of these sites (for dilute solutions only) by

$$\frac{n_{i\downarrow}}{n_{\downarrow} - n_{i\downarrow}} = \frac{n_i}{n_{\downarrow} - n_i} \exp\left(-\frac{\Delta S_{i\downarrow}^{\circ}}{k}\right) \left(\exp\frac{\Delta H_{i\downarrow}^{\circ}}{RT}\right). \quad (72)$$

The reaction is written above, as always throughout the paper, so that $\Delta H_{i\downarrow}^{\circ}$ is positive if energy is expended when the defect complex (here it is $i\downarrow$) is dissociated. Eq. 72 of course can be derived alternatively from a statistical mechanical determination of the interstitial atom distribution function.^{143,145}

Application of Eq. 72 requires explicit knowledge of the temperature dependence of the interstitial concentration both at dislocations and in solution for the measurement of ΔH_{il}° and ΔS_{il}° .

Fiore and Bauer¹⁴³ have recently reviewed several methods of measuring the thermodynamic parameters which characterize the solute-dislocation atom interaction. These methods derive values of ΔH_{il}° (more often ΔG_{il}°) from measurements of (1) the temperature dependence of the disappearance of the sharp yield point,¹⁴⁷ (2) the temperature dependence of the Petch grain size parameter k_y ,¹⁴⁸ (3) the time and temperature dependence of strain-aging,¹⁰⁵ (4) the compositional dependence of the activation energy for creep,¹⁴⁹ (5) the temperature dependence of Granato-Lücke amplitude-dependent damping¹⁵⁰ in dilute alloys,^{151,152} and (6) solid solution hardening parameters of theories of solute strengthening.^{140,153} In principal, the high-resolution direct observation techniques, such as transmission electron microscopy, field-ion microscopy, and divergent-beam x-ray diffraction, should give the most direct information on the distribution of solute atoms near both edge and screw dislocations. However, in practice these techniques have as yet given only qualitative information.¹⁵⁴⁻¹⁵⁶

All of the methods given above determine in some way the concentration of solute atoms at dislocations and relate this to the appropriate thermodynamic parameters by a particular model. One technique not mentioned above which is sensitive to the solute atoms both in solution and at dislocation sites involves use of the anelasticity of the solid solution. For interstitials in bcc metals, the Snoek peak serves well as a measure of the interstitials in solution, while the Koster' or "cold-work" peak,¹⁵⁷⁻¹⁶⁶ which involves in some way an interstitial-dislocation relaxation at higher temperatures, can serve as a measure of the interstitials at dislocations. Thus, if the dislocation density contributing to the cold-work peak is known, ΔH_{il}^O and ΔS_{il}^O can be determined from the temperature dependent redistribution of solute atoms through use of Eq. 72. In the following subsection of this paper, an application of this method to the very important, yet difficult-to-study system Fe-H is presented as an example of the use of this method.

C. Interstitial-Dislocation Interaction in Fe-H

The concept of the hydrogen-dislocation interaction in iron has been a focal point of considerable attention with respect to several hydrogen-related problems in iron-based materials.^{167,168} The existence of a low temperature ($\sim 130^\circ\text{K}$) yield-point in hydrogen-charged iron,^{169,170} low strain-rate

hydrogen embrittlement,¹⁷¹ and anomalous diffusion and solubility behavior of hydrogen below approximately 200°C¹⁷² have been attributed at times to hydrogen-trapping by dislocations. In as many or more instances^{167,173} arguments have been advanced that hydrogen-dislocation interaction is inconsequential in these cases, largely because the small size of the hydrogen atom would dictate relatively small strain energies according to Eq. 70 and 71. Clearly, quantitative data on the extent of the binding are needed to help resolve this problem.

Several difficulties inherent to the study of hydrogen in iron prevent straightforward investigation of the hydrogen-dislocation interaction. (1) The solubility of hydrogen is very low in the vicinity of room temperature, and as a result the major portion of the total hydrogen concentrations usually investigated, say of the order 10 ppm by weight, precipitates as molecular hydrogen at internal interfaces.¹⁶⁸ (2) In addition to the small and uncertain amount of hydrogen with which to work, the effect of interstitial hydrogen on physical and perhaps mechanical properties is apparently much less per atom than other interstitials, carbon and nitrogen. Since even trace amounts of C or N can amount to more H added to solution intentionally, one has the continual problem of these interstitials masking the effects of hydrogen. (3) There are

many experimental and interpretive problems associated with the relatively high mobility of hydrogen, the plastic deformation generally caused by hydrogenation (particularly cathodically), and the complex partitioning of hydrogen among many types of available sites.

The anelastic Snoek and cold-work peaks are well-suited for studies of hydrogen-dislocation interaction because of their selective sensitivity only to treatments which alter hydrogen in solution and at dislocations, respectively. The existence of both Snoek peak_(SP) and cold-work peak_(CWP) in Fe-H is now reasonably well-documented.^{68,174-181} Examples of these peaks are given in Fig. 33. Prestrain is used to develop the CWP to heights which are convenient to work with in subsequent experiments.

Two methods which involve the behavior of these peaks can be used to examine the hydrogen partitioning. One method involves use of hydrogen strain-aging (at room temperature) to redistribute hydrogen between the solid solution and dislocations. In terms of Eq. 72, equal and opposite changes in n_i and n_{il} are afforded by a change in n_l , provided of course that this is the most dominant equilibrium involving the interstitial. Experimental evidence of such repartitioning is shown in Fig. 34, where a decrease in the SP and a corresponding increase in the CWP are observed after room temperature

strain-aging. The second method involves partial removal and subsequent redistribution of hydrogen from solution and dislocations without alteration of dislocation substructure by outgassing at temperatures just above room temperature. In this case n_i and n_{il} readjust to new values after a change in $n_i + n_{il}$ according to the magnitudes of ΔH_{il}^0 , ΔS_{il}^0 , n_i , and T . Fig. 35 shows an example of this type of repartitioning.

The binding enthalpy is determined in both methods from Eq. 72 for which the various parameters n_i , n_{il} , and n_l must be determined. n_i and n_{il} are determined from the relaxation strengths of the SP and the CWP respectively. From Eq. 27,

$$\Delta_i = \bar{a}_i c_i \quad (73)$$

and

$$\alpha \Delta_{il} = \bar{a}_{il} c_{il} \quad (74)$$

Here α is a parameter which accounts for the CWP being much broader than the ideal width predicted by Eq. 23. The constant $\bar{a}_i$ for many interstitial systems has been determined experimentally⁶⁰ or can be estimated;⁴⁴ $\bar{a}_{il}$ can be determined from interstitial repartitioning by strain aging.^{68,166}

From experiments of the type demonstrated in Fig. 34,^{68,157,160,165,166}

the incremental changes in the strength of the CWP, $\delta \Delta_{il}$ and the corresponding changes in the SP, $\delta \Delta_i$, are linearly related.

Thus from Eq. 73 and 74,

$$\delta\Delta_{i1}/\delta\Delta_i = \frac{1}{2} \frac{\bar{a}_{i1}}{\bar{a}_i} \quad (75)$$

If the slope of the plot of $\delta\Delta_{i1}$ vs $\delta\Delta_i$ is known (usually a number of the order 10), then $\bar{a}_{i1}$ can be determined if α is calculated from an appropriate peak width analysis. Generally, the description of the CWP in terms of a "log-normal" distribution of relaxation times¹⁸² is adequate to determine α .⁶⁸ The number of dislocation sites available for occupation is difficult to determine with certainty. An upper limit may be obtained from a knowledge of the experimentally determined total dislocation density, Λ . If it is assumed that there is one dislocation site per unit length of dislocation cut by atom planes normal to the dislocation line, then for edge dislocations

$$n_1(\text{edge}) = \frac{3}{\sqrt{2}b_e} \Lambda_e \quad (76a)$$

and for screw dislocations

$$n_1(\text{screw}) = \frac{3}{b_s} \Lambda_s. \quad (76b)$$

A lower limit of n_1 can be obtained from the interstitial concentration at which the relaxation strength of the CWP saturates⁶⁸,^{157,160,165,166,184} for a given amount of cold-work. From Eq. 75,

$$n_1 = n_l \frac{\Delta_{i1}}{\bar{a}_{i1}} = \frac{n_l}{\alpha \bar{a}_i} \left(\frac{\delta\Delta_{i1}}{\delta\Delta_i} \right)^{-1} \Delta_{i1}(\text{sat.}) \quad (77)$$

This method assumes that Δ_{i1} is smaller than the saturation relaxation strength, $\Delta_{i1}(\text{sat.})$. With all of this information available, determination of ΔG_{i1}^0 follows from a series of one-

point calculations using Eq. 72. ΔH_{i1}^0 and ΔS_{i1}^0 can be separated by determining the temperature dependent changes of n_i and n_{i1} ,^{158,166} in the manner described for interstitial clusters previously.

If the total interstitial concentration C_t is larger than that required to saturate the CWP by strain-aging then an approach used by Petarra and Beshers¹⁶⁶ can be followed. For a given internal friction spectrum, n_i is obtained as before, but n_{i1} is determined as the difference $n_{i1} = C_t - n_i$, assuming a simple partitioning of interstitials only between interstitial sites and dislocations. n_i is obtained from Eq. 77 or from

$$n_i = n_{i1} + \frac{1}{a_i} \left(\frac{n_i}{n_0} \right) (\Delta_i - \Delta'_i) \quad (78)$$

where Δ'_i is the strength of the SP after a quench from the temperature of the CWP. n_0 is the number of interstitial sites per solvent atom (=3). The determination of the thermodynamic functions is done in the same manner described above.

Repartitioning data such as portrayed in Fig. 35 are used in a manner similar to the use of the strain aging method. A relationship between the corresponding incremental changes in the CWP, $\delta\Delta_{i1}^*$ and the SP, $\delta\Delta_i^*$, is determined and is related to the thermodynamic functions of the interstitial-dislocation interaction. For Fe-H, a linear relationship is observed experimentally;⁶⁹ specifically, $\delta\Delta_{i1}^*/\delta\Delta_i^*$ is observed to be approximately 23 (see Fig. 35). From Eqs. 72-75 $\delta\Delta_{i1}^*/\delta\Delta_i^*$ is

given by

$$\frac{\delta \Delta_{i1}^*}{\delta \Delta_i^*} = \frac{\delta \Delta_{i1}}{\delta \Delta_i} \left(\frac{n_1 - n_{i1}}{n_l - n_i} \right) \exp\left(\frac{\Delta G_{i1}^0}{kT}\right) \quad (79)$$

Thus, ΔG_{i1}^0 , ΔS_{i1}^0 , and ΔH_{i1}^0 can again be determined from the temperature dependence of n_i and n_{i1} .

For data on the Fe-H system as given in Figs. 33-35, the binding free energy calculated by these methods appears to approximately 6400 cal/mole.⁶⁹ Because of the small values of n_1 and n_{i1} in this system and the high mobility of hydrogen (demanding measurements at low temperatures), separation of ΔH_{i1}^0 and ΔS_{i1}^0 has not been made. Thus direct comparison with the predictions of Eqs. 70 and 71 is not possible, although unless ΔS_{i1}^0 is unusually large, ΔH_{i1}^0 (experimental) is likely to be significantly larger than ΔH_{i1}^0 (elastic misfit). The reasons for the discrepancy are not resolved at the present time.

Application of the strain aging technique to the Fe-N system has been more successful,^{158,166,185} and the thermodynamic parameters are found to be in better agreement with the theoretical predictions from elastic misfit calculations. ΔH_{i1}^0 is found to be approximately 11,000 cal/mole (0.5 ev) and ΔS_{i1}^0 of the order 6 cal/mole deg. The outgassing method of

Fig. 35 cannot be used, because temperatures which are high enough to cause permanent changes in the dislocation substructure are required for the outgassing. The closest approach to this method is the chemical equilibration method used by Wriedt and Darken¹⁸⁶ to study nitrogen absorption in deformed and partially recovered (300°C to 500°C) steel. These results are interpreted to show that $\Delta H_{i\downarrow}^{\circ} = 2560$ cal/mole for screw dislocations, and $\Delta H_{i\downarrow}^{\circ} = 20,530$ cal/mole for edge dislocations (or possibly microcrack surfaces).

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Table 1

Molar Thermodynamic Parameters of
Nb-N and Ta-N Systems

<u>Parameter</u>	<u>Nb</u>	<u>Ta</u>	<u>Definition</u>
$\overline{\Delta H}_G^\circ$	-42,000 K cal	-43,500 K cal	Heat of solution of $\frac{1}{2}$ mole gas in α
$\overline{\Delta S}_G^\circ$	-8 K cal/ $^\circ$ K	-8 K cal/ $^\circ$ K	Entropy of solution of $\frac{1}{2}$ mole gas in α
ΔH_S°	21,000 K cal	5,4 K cal	Heat of solution of Me_2N in α
ΔH_F°	-62,000 K cal	-50,000 K cal	Heat of formation of Me_2N

TABLE 2
INTERSTITIAL DIFFUSION IN BCC METALS

Metal	Interstitial			
	Hydrogen	Carbon	Nitrogen	Oxygen
Vanadium	-----	$D_o = 0.0045$ $\Delta H = 27,290$	$D_o = 0.0092$ $\Delta H = 34,060$	$D_o = 0.0130$ $\Delta H = 29,010$
Niobium	$D_o = 0.0072$ $\Delta H = 4150$ $\left(D_o = 0.0215 \right)$ $\left(\Delta H = 370 \right)$	$D_o = 0.0040$ $\Delta H = 33,020$	$D_o = 0.0086$ $\Delta H = 34,920$	$D_o = 0.0212$ $\Delta H = 26,910$
Tantalum	$D_o = 0.000019$ $\Delta H = 2,760$	$D_o = 0.0061$ $\Delta H = 38,510$ $\left(D_o = 0.00278 \right)$ $\left(\Delta H = 24,600 \right)$	$D_o = 0.0056$ $\Delta H = 37,840$	$D_o = 0.0044$ $\Delta H = 25,450$
Iron	$D_o = 0.008$ $\Delta H = 2,000$ $\left(D_o = 0.0013 \right)$ $\left(\Delta H = 2970 \right)$	$D_o = 0.00394$ $\Delta H = 19,160$ $\left(D_o \approx 0.1 \right)$ $\left(\Delta H \approx 23,000 \right)$	$D_o = 0.00488$ $\Delta H = 18,350$	-----
Chromium	-----	$D_o = 0.00874$ $\Delta H = 26,500$	$D_o = 0.016$ $\Delta H = 27,500$	$\left(D_o = ? \right)$ $\left(\Delta H \approx 37,000 \right)$
Molybdenum	$\left(D_o = 0.01 \right)$ $\left(\Delta H = 14,000 \right)$	$D_o = ?$ $\Delta H \approx 31,000$ $\left(D_o = ? \right)$ $\left(\Delta H \approx 34,000 \right)$	$\left(D_o = ? \right)$ $\left(\Delta H \approx 44,000 \right)$	$\left(D_o = ? \right)$ $\left(\Delta H \approx 48,000 \right)$
Tungsten	-----	$\left(D_o = 0.00922 \right)$ $\left(\Delta H = 40,400 \right)$	$\left(D_o = ? \right)$ $\left(\Delta H \approx 51,000 \right)$	$\left(D_o = ? \right)$ $\left(\Delta H \approx 62,000 \right)$

TABLE 3
SUMMARY OF KINETIC RATE PARAMETERS
OF INTERSTITIAL CLUSTERS IN BCC METALS

SYSTEM	Cluster of ___ atoms			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Ta-O τ_{ro}	7.0×10^{-15}	1.8×10^{-15}	----	----
ΔH_r	25,500	27,700	----	----
Ta-N τ_{ro}	8.0×10^{-15}	4×10^{-14}	----	----
ΔH_r	37,800	40,000	----	----
Nb-O τ_{ro}	1.7×10^{-15}	1.2×10^{-15}	7.3×10^{-15}	3.3×10^{-15}
ΔH_r	26,800	28,600	29,300	29,800
Fe-N τ_{ro}	2×10^{-14}	3×10^{-14}	1.0×10^{-15}	----
ΔH_r	17,500	19,000	21,000	----
Fe-C τ_{ro}				----
ΔH_r				----
Ta-O-N τ_{ro}	7.0×10^{-15}	1.0×10^{-14}	----	----
ΔH_r	25,500	27,800	----	----
Nb-O-N τ_{ro}	1.8×10^{-15}	2.6×10^{-14}	----	----
ΔH_r	26,200	28,300	----	----

TABLE 4

SUMMARY OF THERMODYNAMIC DATA FOR
INTERSTITIAL CLUSTERS IN BCC METALS

SYSTEM	CLUSTER OF ATOMS	ΔH_N°	ΔS_N°	ΔG_N°
Ta-O	2	2,000	- - -	2,500 (349°K)
Ta-N	2	~ 2,000	- - -	- - -
Nb-O	2	1,600	-3.4	2,700 (352°K)
	3	4,100	- - -	6,200 (352°K)
	4	6,200	- - -	10,600 (352°K)
Fe-N	2	1,500	- - -	- - -
	3	5,000	- - -	- - -
Fe-C	2	1,800 (2700)*	- - -	- - -
	3	6,000 (8500)	- - -	- - -
	4	--- (8500)		
Ta-O-N	2	~ 2,000	- - -	- - -
Nb-O-N	2	2,500	- - -	- - -

* Data in parentheses are calculated values by Johnson et.al.⁽¹¹¹⁾

TABLE 5

SPECIFIC RELAXATION STRENGTHS OF
OXYGEN ATOMS IN CLUSTERS IN Nb AND Ta

	<u>T (^oK)</u>	<u>a₁</u>	<u>a₂</u>	<u>a₃</u>	<u>a₄</u>
Ta-0	349	25.4	39.8	----	----
Nb-0	352	12.5	15.0	18.5	20.5

TABLE 6

Compilation of Data on s-l Relaxation Peaks
in Ternary bcc Alloys

A. Detailed decomposition of data on Fe-(Mn)-N alloys into component relaxations.

Peak Temperature Relaxation Strength, Identification

Ref.	Alloying Elements	Freq.	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	Data
96	0.5%Mn, 0.02%N	~1cps	22°C 8.9×10^{-3} (Fe, Fe-N)	32.5°C 8.9×10^{-3} (Fe, Mn-N)	--	--	--	--	--	T_p $\Delta/2$ Identif.
101	0.33%Mn, 0.02%N	~1cps	7°C 3.3×10^{-3} (Mn, Mn-N)	24°C 5.5×10^{-3} Fe, Fe-N)	35°C 10×10^{-3} (Fe, Mn-N)	--	--	--	--	T_p $\Delta/2$ Identif.
	0.65%Mn, 0.02%N	~1cps	4.0×10^{-3}	5.0×10^{-3}	10.3×10^{-3}	--	--	--	--	$\Delta/2$
103	0.27%Mn, 0.05%N	0.5cps	-0.5°C 1.0×10^{-2} (Mn, Mn-N)	18.5°C 5.6×10^{-2} Fe, Fe-N)	29°C 2.7×10^{-2}	46.5°C 1.8×10^{-2} (--- Fe, Mn-N ---)	64°C 0.6×10^{-2} (--- Mn, Mn-N ---)	84°C 4.0×10^{-2}	108°C 0.2×10^{-2}	T_p $\Delta/2$ Identif.
	0.75%Mn, 0.05%N	0.5cps	2.0×10^{-2}	2.5×10^{-2}	4.4×10^{-2}	1.6×10^{-2}	0.5×10^{-2}	0.7×10^{-2}	0.8×10^{-2}	$\Delta/2$
104	0.2%Mn, ~0.03%N	1.25cps	-6.5°C 0.15×10^{-3} (--- Mn, Mn-N ---)	3°C 0.15×10^{-3}	11.5°C 0.75×10^{-3}	25.5°C 14.8×10^{-3} (Fe, Fe-N)	31.5°C 2.05×10^{-3} (Fe, Mn-N)	42°C 1.85×10^{-3} (Fe, Fe-C)	64°C ~ 0 ?	T_p $\Delta/2$ Identif.
	0.9%Mn, ~0.03%N	1.5cps	-5°C 0.57×10^{-3}	7°C 1.46×10^{-3}	13.5°C 4.00×10^{-3}	28°C 2.97×10^{-3}	34.5°C 4.05×10^{-3}	44°C 3.53×10^{-3}	66°C 0.17×10^{-3}	T_p $\Delta/2$
107	1.83%Al, 0.005%C 0.004%N	1cps	24°C 1.6×10^{-3} (Fe, Al-C)	40°C 4.8×10^{-3} (Fe, Fe-C)	67°C 5.0×10^{-3} ?	87°C 2.8×10^{-3} ?	--	--	--	T_p $\Delta/2$ Identif.

TABLE 6 - Continued

B. Peak Temperature of s-i Relaxations at ω cps

<u>Base Metal</u>	<u>Alloying Element</u>	<u>Interstitial</u>		
		<u>O</u>	<u>N</u>	<u>C</u>
Fe	[SP]	-	24°C	40°C
	Mn	-	32	-
	Cr	-	41	-
	Mo	-	75	-
	V	-	87	-
	Al	-	-	67
	P	-	-	~ 60
Nb	[SP]	140°C	290	270
	Zr	200	350	-
	Al	-	-	-
Cr	[SP]	-	155	~ 150
	Re	-	190	-

TABLE 7

Concentration of Interstitials in Clusters in Nb-O and Ta-O
Alloys by Internal Friction and Field-ion Microscopy

<u>System</u>	<u>Method</u>	<u>Total Oxygen Concentration</u>	<u>Atoms in</u>	<u>Percentage of Atoms</u>
Nb-O	I.F.	1.1 at.%	Singles	49 (352°K)
			Pairs	34
			Triplets	12
			Quadruplets	5
Ta-O	I.F.	0.5 at.%	Singles	74 (349°K)
			Pairs	26
			Triplets	not det.
			Quadruplets	not det.
Ta-O	F-I.M.	~ 1.0 at.%	Singles	75 (360°K)
			Pairs	25
			Triplets	not det.
			Quadruplets	not det.

Figure Captions

- Fig. 1. Interstices in bcc crystal associated with a lattice atom.
- Fig. 2. Geometry of atoms about the two types of sites.
- Fig. 3. Metal-gas phase diagram in $\log X$, $\log p$, $1/T$ coordinates.
- Fig. 4. Metal-gas phase diagram of a eutectic system.
- Fig. 5. The Nb-O system at 1 atmosphere.
- Fig. 6. Sketch of apparatus for determination of metal-gas equilibrium.
- Fig. 7. Log p -log X plots in the Nb-N system at constant temperature. The data are taken from the work of Cost and Wert.⁹
- Fig. 8. Log p - $1/T$ plots in the Nb-N system at constant composition. The data are taken from the work of Cost and Wert,⁹ the dashed lines from the work of deLamotte, Huang and Altstetter.¹²
- Fig. 9. The α -solubility line for the Nb-N system at high temperatures.
- Fig. 10. The α -solubility line for the Ta-N system.
- Fig. 11. The α -solubility line for the Nb-N system at both high and low temperatures.
- Fig. 12. The α -solubility line for the Nb-O system.
- Fig. 13. The α -solubility line for the Ta-O system.
- Fig. 14. Some of the data available in the literature for the solvus line of α -Fe.
- Fig. 15. Solubility of C in several of the refractory metals in equilibrium with carbides. The line for α -Fe is that of Swartz extrapolated into this region.
- Fig. 16. Stress and strain relaxation curves for a series of boundary conditions. (a) $\dot{\epsilon} = 0$, $\epsilon = \epsilon(0)$; (b) $\dot{\epsilon} = \epsilon = 0$; (c) $\dot{\sigma} = 0$, $\sigma = \sigma(0)$; (d) $\dot{\sigma} = \sigma = 0$.
- Fig. 17. A plot of $\tan \Phi$ vs $1/T$ for an ideal anelastic process obeying Equations 23 and 24.
- Fig. 18. The diffusion coefficient of nitrogen in alpha-iron by mass flow and relaxation techniques. (After Lord and Beshers⁵¹)

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- Fig. 20. Apparent activation energies of the oxygen Snoek relaxation in niobium for a dilute alloy and a very concentrated one. (After Powers and Doyle²⁰)
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- Fig. 22. Component and total after-effect curves from Fig. 21 showing the time range of importance of each process.
- Fig. 23. Analysis of the internal friction spectrum of a Nb-1.1 at.% O alloy into component peaks.
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- Fig. 25. Internal friction of Nb-O alloys, showing the effect of N contamination on the damping spectrum.
- Fig. 26. Concentration of pairs and singles in a solid solution where $\Delta H_{\text{Binding}}$ is small compared to $\Delta H_{\text{Solution}}$.
- Fig. 27. Internal friction of an Fe-0.5 wt. % Mn-0.02 wt. % N alloy. (After Dijkstra and Sladek⁹⁶)
- Fig. 28. A model for interstitial reorientation under stress in the pure crystal (left) and in the vicinity of a substitutional atom (right).
- Fig. 29. The concentration dependence of the damping spectrum of Fe-Mn-N alloys. (After Nacken and Kulman⁶¹) $f = 0.5$ cps. The dotted line is a trace of a curve for an Fe-2.0% Mn- ~0.03% N alloy by Ritchie and Rawlings¹⁰⁴ at ~1.5 cps for comparison.
- Fig. 30. Three interstitial pair configurations which are stable according to elastic strain energy calculations. F = Fisher calculation,¹¹⁰ J = Johnson calculation.¹¹¹

Fig. 31. Interstitial domain structure in niobium-oxygen alloys.
(Courtesy of J. van Landuyt)

Fig. 32. Determination of the binding enthalpy, ΔH_2^0 , for oxygen pairs in tantalum from field-ion microscopy data.

Fig. 33. Internal friction of hydrogen-charged Ferrovac E iron.
 $f = 80$ kc/s.

Fig. 34. Repartitioning of hydrogen between the Snoek peak and the cold-work peak by room temperature strain aging.

Fig. 35. Repartitioning of hydrogen between the Snoek peak and the cold-work peak by partial hydrogen outgassing at 60°C .

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$$\Delta H_2^0 (F) = 0.02 \text{ ev}$$

$$\Delta H_2^0 (J) = 0.11 \text{ ev}$$

$$\Delta H_2^0 (F) = 0.07 \text{ ev}$$

$$\Delta H_2^0 (J) = 0.13 \text{ ev}$$

$$\Delta H_2^0 (F) = 0.11 \text{ ev}$$

$$\Delta H_2^0 (J) = 0.08 \text{ ev}$$