

Theory of Strain Interaction of Solute Atoms*

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A general method is developed for evaluating the strain-energy interaction of solute atoms in body-centered and in face-centered cubic lattices. The method has many features in common with that used in the evaluation of the interaction of electric or magnetic dipoles, a surface distribution of forces replacing a surface distribution of electric charge or of magnetic poles. Particular emphasis is given to the interaction of interstitial solute atoms in b.c.c. lattices, where the possibility exists of a self-induced preferential distribution of solute atoms in one of the three types of tetragonal interstitial positions.

I. INTRODUCTION

THE present study was undertaken for the purpose of understanding the strain interaction of interstitial solute atoms in body-centered cubic (b.c.c.) metals. Many of the problems encountered were found to be common to substitutional as well as to interstitial solutions, and not to be confined to b.c.c. lattices. In this paper primary emphasis is therefore placed upon the general theory.

The particular interest of interstitial solutions in b.c.c. lattices lies in the tetragonal symmetry of the interstitial positions in these lattices. As was first demonstrated by Snoek¹ in his anelastic studies of alpha-iron containing carbon and nitrogen, studies which have been recently extended by Kê² to tantalum, the positions occupied by interstitial solute atoms in b.c.c. lattices are of the type $(0, \frac{1}{2}, \frac{1}{2})$, or $(\frac{1}{2}, 0, \frac{1}{2})$ or $(\frac{1}{2}, \frac{1}{2}, 0)$. These three positions have tetragonal symmetry with their tetragonal axes along the x , y , or z principal axes, respectively. They will be designated as the x , y and z type positions. In the absence of an externally applied stress, and of strain interaction, the interstitial atoms will be distributed at random among the three types of positions. When a tensile stress is applied along, say, the z axis, the equilibrium distribution of solute atoms will be one in which more atoms are in the z type position than in the other two. The continual striving of the solute atoms to maintain

the equilibrium distribution during cyclic vibration gives rise to the anelastic effects observed, and interpreted in this manner, by Snoek. On the other hand, even in the absence of an externally applied stress the existence of a strain-energy interaction between the solute atoms gives rise to the possibility of a self-induced preferential distribution. The author³ has previously suggested, without, however, a detailed analysis, that it is just such a self-induced preferential distribution which gives rise to the tetragonality of martensite, alpha-iron supersaturated with atomically dispersed carbon. Such a self-induced preferential distribution would, of course, have a critical temperature above which, in the absence of applied stresses, the distribution would be random. Nevertheless, the effect of the ordering tendency should be detectable above the critical temperature in the magnitude of the preferred distribution induced by an externally applied stress, just as coupling in ferromagnetic materials influences the magnetic susceptibility above the Curie temperature. Such an effect has been sought by Kê,² with negative results. The magnitude of this effect above the critical temperature will, of course, depend upon the magnitude of the strain-energy coupling between the solute atoms. The calculation of this coupling is one of the objectives of this paper.

When solid solutions are quenched considerably below their solubility limits it has frequently been observed,⁴ through x-ray diffraction studies, that the solute atoms segregate along certain crystallographic planes prior to

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¹ J. Snoek, *Physics* **6**, 591 (1939); **8**, 711 (1941); **9**, 862 (1942); and *Chemisch Weekblad*, **39**, 454 (1942).

² T. S. Kê, *Phys. Rev.* **74**, **9**, 16 (1948).

³ C. Zener, *Trans. A.I.M.E.* **167**, 550 (1946).

⁴ C. S. Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1943) p. 470.

precipitation of the stable phase. The driving force for such segregation may of course reside in the difference between the bonds linking like and unlike atoms, the strain energy playing only a minor role in determining the shape of the segregate region. On the other hand it is possible that in some cases the driving force for segregation arises entirely from strain-energy interaction. A second purpose of this paper is to examine this possibility.

II. GENERAL THEORY

One can enumerate many ways in which solute atoms may interact, as for example by electrostatic forces if they carry a net charge. In this paper we are considering only that interaction which arises from a coupling of their strain energies.

The essential features of strain interaction can best be obtained by an analysis of an auxiliary problem. Suppose two atoms of a lattice, designated by subscripts 1 and 2, are acted upon by external forces F_1 and F_2 . These forces are then linear functions of the components of the resulting displacements along the direction of the applied forces. Thus if h_1 and h_2 are these displacement components, then

$$\begin{aligned} F_1 &= a_{11}h_1 + a_{12}h_2, \\ F_2 &= a_{21}h_1 + a_{22}h_2. \end{aligned} \quad (1)$$

The strain energy of the lattice is a quadratic function of h_1 and h_2 , and hence may be written as

$$E = \frac{1}{2}(F_1h_1 + F_2h_2). \quad (2)$$

In view of Eq. (1), this strain energy may also be written in the form

$$\begin{aligned} E &= \frac{1}{2}(F_{11}h_1 + F_{22}h_2) \\ &\quad + \frac{1}{2}(F_{21}h_1 + F_{12}h_2), \end{aligned} \quad (3)$$

where the force coefficients are defined as

$$F_{ij} = a_{ij}h_i. \quad (4)$$

The first term in Eq. (3) would alone give the strain energy if the two atoms were so far apart that the coupling term a_{12} were negligible. This first term is not, however, itself independent of the coupling. Thus, if we regard a_{12} as a first-order small quantity, F_2 will give rise to a first-order small change in h_1 , and hence to a first-order small change in the first term of Eq. (3). If, however, the force F_1 has a potential $V_1(h_1)$,

the value of h_1 in the absence of interaction is such as to minimize the sum

$$\frac{1}{2}F_{11}h_1 + V_1(h_1).$$

The first order changes in this sum, due to the coupling between the two atoms, vanishes. If we therefore neglect second-order small quantities, the change in the total energy introduced by the coupling between the two atoms is given by the second term in Eq. (3), namely by

$$E_{\text{Int}} = \frac{1}{2}(F_{21}h_1 + F_{12}h_2). \quad (5)$$

The force coefficient F_{21} may be interpreted as the external force which must act upon atom 1 in order to maintain its displacement component h_1 zero in the presence of the force F_2 acting upon atom 2. This force coefficient may also be interpreted as the negative of the force $f_{2,1}$ with which the rest of the lattice acts upon atom 1 when the two displacement components have the values $(0, h_2)$ respectively. The strain energy interaction may thus be written in terms of these lattice forces as

$$E_{\text{Int}} = -\frac{1}{2}(f_{2,1}h_1 + f_{1,2}h_2). \quad (6)$$

It is to be particularly noted that the sign of the interaction energy is negative if the lattice coupling forces $f_{i,j}$ are in the same direction as the displacements h_j . At first sight this conclusion seems erroneous, since under these conditions strain energy is increased by the coupling. This apparent contradiction is removed when we recall that the total energy includes the potential of the applied forces, and that in the case under consideration the lowering of these potentials more than compensates for the rise in strain energy.

One further simplification will be introduced before passing to our original problem of solute atoms. We have already considered the coupling a_{12} as a small-order correction, and have neglected second-order small changes in the quantities $\frac{1}{2}F_{11}h_1 + V(h_1)$ and $\frac{1}{2}F_{22}h_2 + V(h_2)$. In order to take into account these second-order small changes we would have to know more precisely the form of the potentials $V_1(h_1)$ and $V_2(h_2)$. We are therefore not justified in retaining second-order small quantities in the right side of Eq. (6). Since the lattice forces $f_{2,1}$ and $f_{1,2}$ are already first-order small quantities, the displacement components h_1 and h_2 will be regarded as having

those values which minimize $\frac{1}{2}F_{11}h_1 + V_1(h_1)$ and $\frac{1}{2}F_{22}h_2 + V_2(h_2)$, respectively, i.e., h_i will be regarded as the solution of the elastic problem in which only the force potential $V_i(h_i)$ is different from zero.

The characteristic feature of the forces exerted by a solute atom upon a lattice is that the resultant of all the forces is precisely zero. In b.c.c. and f.c.c. lattices these forces occur in pairs, the two forces of each pair being equal in magnitude but opposite in direction, their line of action passing through the solute atom position, and acting on two atoms symmetrically placed on either side of the solute atom. Thus a substitutional solute atom in a b.c.c. lattice is associated with four pairs of forces, each pair acting along one of the four cube diagonals. An interstitial solute atom is associated with three pairs of forces. If it is occupying a z type position, one pair acts along the z principal axis, the other two along the $[\bar{1}10]$ and $[\bar{1}\bar{1}0]$ axes. The pairs of forces will be called force dipoles. We shall denote each corresponding pair of solvent atoms by the subscript σ ; the relative radial displacement of each atom of the pair with respect to the other, referred to their equilibrium displacement, we shall denote by $h_{j\sigma}$, j denoting the associated solute atom. Each system of force dipoles will then have a potential which is a function of the corresponding displacements $h_{j\sigma}$. The interaction energy may then be generalized from the form of Eq. (6) to

$$E_{\text{Int}} = -\frac{1}{2} \sum_{\sigma} \{f_{2,1\sigma}h_1 + f_{1,2\sigma}h_2\}. \quad (7)$$

In our former equation for the interaction energy the force coefficient $f_{2,1}$ was the force exerted by the lattice upon lattice atom 1. In the present equation the coefficient $f_{2,1\sigma}$ is the radial force dipole exerted by the lattice upon the pair σ of solvent atoms associated with solute atom 1 while the relative separation of all pairs of lattice atoms surrounding solute atom 1 are held fixed when solute atom 2 is introduced.

III. LONG RANGE FORCES

In estimating the strain energy interaction of solute atoms, we shall adopt the conventional procedure used in estimating the interaction of magnetic or electric dipoles. Thus, in estimating the strain energy interaction of a particular

solute atom 1 with all other solute atoms, we imagine this solute atom enclosed by a small sphere, and that all the other solute atoms are outside this sphere. In the first approximation we consider that the positions of the solute atoms outside the sphere are completely independent of the presence of the single solute atom within the sphere. The interaction computed in this manner will be called the long-range interaction. In the second approximation we take partially into account the effect of the presence of the single solute atom inside the sphere upon the positions of the solute atoms outside the sphere. The change in the interaction energy introduced in this approximation will be called the short-range interaction.

From Eq. (7) we note that the effect of solute atom 2 upon the strain energy of solute atom 1 may be expressed in terms of that stress pattern at the site of solute atom 1 which is induced by the presence of solute atom 2. In the evaluation of the long-range interaction it is therefore sufficient to compute the stress within the sphere arising from the presence of all the solute atoms outside the sphere. In the evaluation of this stress we continue to follow the conventional method used with magnetic and electric dipoles. For interstitial solutions, in place of considering a discrete number of sets of dipole forces, one set for each solute atom, we shall consider that a set of dipole forces is associated with each potential interstitial position, the magnitude of the forces in each set being equal to the actual magnitude for a solute atom times the atomic concentration of solute atoms referred to the number of potential lattice sites. A very similar procedure may be adopted in the case of substitutional solute atoms in a b.c.c. or f.c.c. lattice. Here the dipole forces specifically associated with each solute atom are defined as the difference between the actual dipole forces exerted by the solute atoms and the dipole forces which would be exerted if the solute atom were replaced by a solvent atom. The net force acting upon each lattice atom is thus precisely zero provided this lattice atom is not near a surface, either the exterior or the interior surface. The problem of long-range interaction has thus been reduced to finding the stress produced by a system of surface forces.

In the case of a substitutional solution in a b.c.c. or a f.c.c. lattice the net force acting on any element of surface is directed normal to the surface, and is in the direction away from the uniform distribution of force dipoles provided the solute atoms are larger than the solvent atoms. For our present purpose we are not interested in the magnitude of the surface density of this force, but only in the fact that this surface density is uniform and is independent of crystallographic orientation, being the same on the interior surface as on the exterior surface. The forces acting on the exterior surface will give rise to a hydrostatic tensile stress throughout the specimen, including the interior of the sphere. The magnitude of this hydrostatic tensile stress will simply be the bulk modulus K , times the observed dilation of the lattice, Θ . On the other hand, the forces acting upon the interior spherical surface will give rise to a compressive stress which tends to counteract the stress produced by the forces acting on the external surface. However, the inner surface forces must not only compress the inner sphere, they must also compress the whole of the surrounding lattice, i.e., the surrounding lattice must be deformed so as to maintain contact with the compressed sphere. Now the elastic modulus for the compression of a sphere is K , while the elastic modulus for the compression of a spherical cavity⁵ is $(4/3)\mu$, where μ is the rigidity modulus. That fraction of the surface force which is available for compressing the sphere is therefore the ratio $K/(K+4\mu/3)$. The net hydrostatic stress σ within the sphere is therefore given by

$$\sigma = \alpha K \Theta, \quad (8)$$

with

$$\alpha = \frac{(4/3)\mu}{K + (4/3)\mu}. \quad (9)$$

Upon taking as an example the typical case of a Poisson ratio of $1/3$, we find that α itself has a typical value of $1/3$. It is of interest to note that the present treatment gives the correct value of zero strain interaction in the limiting case of a fluid, for in a fluid the rigidity modulus μ , and hence α , is precisely zero.

Our next step is to evaluate the effect of the

⁵ A. E. H. Love, *Mathematical Theory of Elasticity* (Cambridge University Press, Cambridge, 4th ed., 1934) p. 187.

hydrostatic stress σ upon the strain energy of our solute atom. Towards this end we consider a unit volume to which we apply a hydrostatic tensile stress σ . The number of solute atoms will be denoted by n , the total energy of the system by E . If we now denote by U the energy required to introduce a new solute atom under conditions of constant stress, exclusive of the work done by the applied forces, then

$$dE - \sigma dv = U dn. \quad (10)$$

This equation may be written in the form of a perfect differential, namely as

$$d(E - \sigma v) = -v d\sigma + U dn, \quad (11)$$

from which we deduce

$$(\partial U / \partial \sigma)_n = -(\partial v / \partial n)_\sigma. \quad (12)$$

In our actual problem the stress σ is produced by the forces of the solute atoms within the lattice itself. These forces have of course a potential, and the dilation of the lattice is just such as to minimize the sum of these potentials and of the strain energy. In evaluating the change in energy associated with the introduction of a solute atom into our spherical region, we must therefore neglect the change in strain energy σdv , as this is compensated by the change in the potentials of the solute atoms. We may therefore apply Eq. (12) for the variation of the energy of a solute atom due to the long-range interaction of the other solute atoms. We may thus write for the long-range strain interaction

$$E_{\text{Int}} = -(\partial \Theta / \partial n)_\sigma \cdot \sigma, \quad (13)$$

where n is the number of solute atoms per unit volume. Upon combining Eqs. (8) and (13) we thereby obtain for the long-range interaction energy

$$E_{\text{Int}} = -\alpha K (\partial \Theta / \partial n) \cdot \Theta. \quad (14)$$

Since, at least for small concentrations, Θ is a linear function of n , this equation may be rewritten as

$$E_{\text{Int}} = -\alpha n K (\partial \Theta / \partial n)^2. \quad (15)$$

It is to be noted that E_{Int} in this equation is the increment in energy, due to the other solute atoms, when one additional solute atom is introduced. Since this is proportional to n , the interaction energy per solute atom is just half as great as given in Eq. (15).

We shall now consider the interaction of interstitial solute atoms in a b.c.c. lattice, where the stress pattern surrounding each solute atom has tetragonal symmetry. So far we have emphasized the similarities in the interaction of solute atoms and of magnetic and electric dipoles. A consideration of interstitial solute atoms in a b.c.c. lattice provides us with the opportunity of pointing out some striking dissimilarities in the two types of interaction. Suppose, for example, that we have a single crystal in which only the z type positions are occupied, and further that the solute atoms in these positions are associated with only a single force dipole, acting parallel to the z axis. The long-range influence of all the other solute atoms upon one particular solute atom may then be represented as the effect of two sets of surface forces, one acting on the external surface, and one acting over the surface of a sphere surrounding the given solute atom. The external surface force will give rise to a pure tensile stress Z_z whose magnitude is independent of the shape of the specimen. The magnitude of Z_z is identical in the case of a thin slab normal to the z axis as in the case of a long rod along the z axis. The shape invariance of the effect of the surface forces is of course in marked contrast to the corresponding cases with magnetic or electric dipoles. The physical interpretation of this difference lies in the fact that the stress field produced by the mechanical forces is confined to the specimen itself, while the magnetic and electric fields produced by a surface distribution of poles are not so confined.

In the case of actual interstitial solute atoms in b.c.c. lattices, we cannot consider each solute atom as equivalent to a single force dipole. If such were the case, then when all the solute atoms were in the same type of position, e.g., the z type, the observed contraction along the x and y axes would be related to the extension along the z axis by the appropriate Poisson ratio. Thus in the case of carbon dissolved in iron this ratio would be 0.37. Its observed⁶ value in martensite is 0.15, indicating that at least in this system the solute atoms exert radial forces upon the neighboring four atoms lying in a plane normal to the z axis.

⁶ S. Epstein, *The Alloys of Iron and Carbon*, I. (McGraw-Hill Book Company, Inc., New York, 1936) p. 212.

The stress in the interior of our sphere due to a preferred distribution of sets of dipole forces not having cubic symmetry is difficult to evaluate. The author has not been able to evaluate the constant α in the relation corresponding to Eq. (8). It is anticipated, however, that only a slight error will be made by assuming this constant to have the same value as in the case of a hydrostatic tensile stress. We shall therefore set

$$\begin{pmatrix} X_x \\ Y_y \\ Z_z \end{pmatrix} = \alpha \begin{vmatrix} c_{11} & c_{12} & c_{12} \\ c_{12} & c_{11} & c_{12} \\ c_{12} & c_{12} & c_{11} \end{vmatrix} \begin{pmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \end{pmatrix} \quad (8a)$$

as the relation between the stress in the interior of the sphere due to long-range interaction and the over-all strain produced by the solute atoms. The interaction energy associated with this stress may be found by an analysis identical to that used in the case of a hydrostatic tensile stress. We find that the effect of the stress upon the energy required to introduce a solute atom into a given type of interstitial position is

$$E_{\text{Int}} = - \sum_i \delta \epsilon_i \sigma_i, \quad (13a)$$

where $\delta \epsilon_i$ is the i th principal strain attending the introduction of one solute atom per unit volume into the given type of interstitial position, and σ_i is the i th principal stress.

Equations (8a) and (13a) will now be used to evaluate the influence of long range strain interaction upon the relaxation associated with a stress-induced preferential distribution of interstitial solute atoms in one of the three types of interstitial positions. We suppose a tensile stress σ is applied along one principal axis, hereafter called the preferred axis. We shall denote by N_p and N_n the number of solute atoms per unit volume, in the preferred and non-preferred type of interstitial positions, respectively, and by $\delta \epsilon_p$, $\delta \epsilon_n$ the increments in principal strains along the preferred and along one of the non-preferred principal axes, respectively, introduced by one atom per unit volume into a p position. Upon denoting the preferred axes by the subscript 1, the principal strain components associated with the solute atoms become

$$\begin{aligned} (\epsilon_1, \epsilon_2, \epsilon_3) = & \{ N_p \delta \epsilon_p + N_n \delta \epsilon_n, \\ & \frac{1}{2} N_n \delta \epsilon_p + (N_p + \frac{1}{2} N_n) \delta \epsilon_n, \\ & \frac{1}{2} N_n \delta \epsilon_p + (N_p + \frac{1}{2} N_n) \delta \epsilon_n \}, \end{aligned} \quad (16)$$

and the change in long-range strain energy inter-

action associated with the transfer of one solute atom from an n to a p interstitial position becomes, according to Eq. (13a)

$$\delta U = -(\delta\epsilon_p - \delta\epsilon_n)(\sigma_p - \sigma_n). \quad (17)$$

When we now utilize Eqs. (8a) and (16) to compute σ_p and σ_n , we find

$$\delta U = -\alpha(N_p - \frac{1}{2}N_n)(c_{11} - c_{12})(\delta\epsilon_p - \delta\epsilon_n)^2. \quad (18)$$

We now utilize this explicit expression for the change in long-range strain interaction energy to compute the equilibrium value of $N_p - \frac{1}{2}N_n$, as was first carried out by Polder⁷ for an arbitrary δU , and compute the relaxation strength

$$\Delta_E \equiv (E_U - E_R)/E_R, \quad (19)$$

where E_U is the elastic modulus E_{100} as measured under conditions in which N_p remains constant, and E_R is the same modulus measured under conditions in which N_p has its equilibrium value. We find

$$\Delta_E = T_0/(T - \gamma T_0), \quad (20)$$

where

$$T_0 = (2/9)nE_{100}(\delta\epsilon_p - \delta\epsilon_n)^2, \quad (21)$$

in agreement with Polder, and where the constant γ has the explicit form

$$\gamma = (3/2)[(c_{11} + c_{12})/(c_{11} + 2c_{12})]\alpha. \quad (22)$$

In the author's³ original derivation of Eq. (20) the constant γ was undetermined, and was assumed to be of the order of magnitude of unity. The recent measurements of Kê² upon the relaxation strength associated with interstitial solute atoms in a b.c.c. lattice showed definite disagreement with Eq. (20) when γ was taken as unity. Upon taking our previously estimated value of α , namely 1/3, and upon observing that C_{12} is always less than C_{11} , we find that γ varies between 1/3 and 1/2, being 0.38 for iron. The data of Kê are not sufficiently extensive to distinguish between the above lower theoretical limit of 1/3 and his assumed value of zero.

The change in the constant γ from unity to 0.38 for the case of iron has important theoretical consequences. As was shown by Polder,⁷ the data on the variation of the lattice parameters of martensite with carbon concentration may be used in conjunction with Eq. (21) to obtain an explicit expression for T_0 for iron con-

taining carbon, namely

$$T_0 = 1190X_c \quad (23)$$

where X_c is the weight percent concentration of carbon. Now the critical temperature for ordering by long-range interaction is very close to γT_0 , namely⁸

$$T_c = 1.05\gamma T. \quad (24)$$

One should therefore anticipate that for iron the critical temperature would be given by

$$T_c = 470X_c. \quad (25)$$

According to this equation, the carbon concentration would have to be above 0.64 wt. percent for the critical temperature to lie above room temperature. The self-ordered structure of martensite has been observed at carbon concentrations as low as 0.4 wt. percent. We are therefore led to believe that the long-range strain interaction between the carbon atoms is not sufficient alone to cause the observed self-induced ordering. One possibility is that the strain-interaction between close pairs of carbon atoms is of such a sign and magnitude as to aid the long-range strain interactions in establishing an ordered distribution. This possibility is investigated in the following section.

IV. SHORT RANGE STRAIN INTERACTION AND SEGREGATION

Interesting qualitative conclusions may be reached merely by considering the general form of the strain interaction as developed in Section II. We there saw that the strain energy interaction of two solute atoms 1 and 2 is negative if the force resulting from solute atom 2 upon the nearest neighbors of solute atom 1 is in the same direction as that exerted by solute atom 1 itself. In applying this rule it would appear unprofitable to consider cases where the solute atoms are themselves nearest neighbors, since in such cases the interaction will usually be dominated by types of interaction other than strain.

The first example to be considered will be substitutional solutions in b.c.c. lattices. If two solute atoms are neighbors along a principal axis, as in a of Fig. 1, having four common lattice atoms as nearest neighbors, the strain inter-

⁷ D. Polder, Philips Research Reports, 1, 5 (1945).

⁸ C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, Illinois, 1948) p. 125.

action will be negative. Thus in this case the cosine of the angle between the vectors from each solute atom to a common nearest neighbor is positive, namely $3^{-1/2}$. On the other hand, if the two solute atoms are situated as in *b* of Fig. 1, having two neighbors in common, the corresponding cosine is negative, namely $-3^{-1/2}$, and hence the two solute atoms repel one another. A still less favorable situation is illustrated in *c* of Fig. 1, where the two solute atoms tend to displace a common nearest neighbor in opposite directions. We conclude that the strain energy interaction of substitutional solute atoms in b.c.c. lattices is highly dependent upon relative crystallographic orientation, a common $\langle 100 \rangle$ axis being preferred, while a common $\langle 110 \rangle$ or $\langle 111 \rangle$ axis tends to be avoided. By examining in a similar manner the interaction between solute atoms spaced further along a $\langle 100 \rangle$ axis than one lattice constant, we conclude that they likewise have a negative interaction strain energy. A linear array of solute atoms along a $\langle 100 \rangle$ axis thus has a lower strain energy than if the solute atoms were in pairs, which paired system in turn has a lower strain energy than if the solute atoms were atomically dispersed. We next inquire as to whether a planar array, formed by placing linear arrays side by side, would have a still lower strain interaction. At first sight it would appear that the energy would not be lowered since, when two linear arrays are placed next to each other so as to have a common face, the attraction of each solute atom by its nearest neighbor in the other linear array is exactly counteracted by the repulsion of the two next nearest neighbors. However, in a plane array of solute atoms in a plane containing two crystallographic axes, the strain will be confined essentially to the unit cubes containing the solute atoms, the strain outside these unit cubes decreasing exponentially as we go away from the plane of solute atoms. Such a planar array must therefore have a lower strain energy than an assembly of isolated linear arrays.

If we exclude from our discussion the case of nearest neighbor solute atoms, as discussed above, the case of substitutional solution in f.c.c. lattices appears less interesting. It seems that no strong strain-energy attraction between two substitutional solute atoms can be obtained

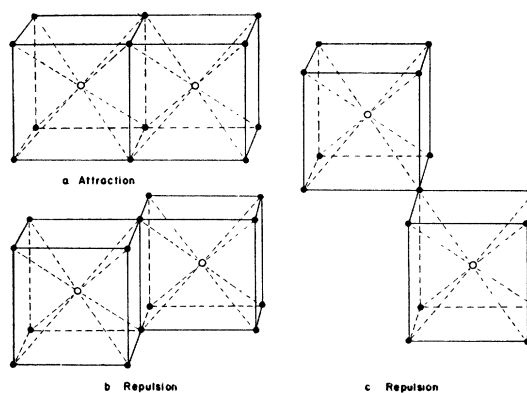


FIG. 1. Examples of strain interaction.
○ Solute atom; ● solvent atom.

for any positions. Thus if two solute atoms are one lattice constant apart along a $\langle 100 \rangle$ axis, the common nearest lattice neighbors are displaced by the two solute atoms in directions normal to one another. If the two solute atoms are on opposite corners of the face of a unit cell, the displacements of their common lattice nearest neighbor due to the two solute atoms are in opposite directions, and hence the solute atoms repel one another. A similar situation of no strong strain energy attraction exists in the case of interstitial solutions in f.c.c. lattices. In order that substitutional solute atoms may form a stable planar array in a f.c.c. lattice, it appears as if they must themselves be nearest neighbors, and hence interactions other than strain energy must be operative.

Since considerable data are available regarding the interstitial solution of carbon in the b.c.c. lattice of alpha-iron, this case will be treated in considerable detail. The energy of the iron lattice will be considered as expressible in terms of central force bond energies, i.e., bond energies which are a function only of the distance between the two atoms under consideration. As is well known,⁹ such a representation of the lattice energy cannot be exact, since it would require that the Cauchy relations between the elastic coefficients be satisfied. For a cubic metal these relations reduce to the single equation

$$c_{12} = c_{44}. \quad (26)$$

In most cubic metals this relation is far from being even approximately satisfied, c_{12} being

⁹ A. E. H. Love, reference 5, pp. 616-627.

greater than c_{44} by a factor as great as 3. However, in the case of iron, this relation is approximately satisfied, c_{12} being only 22 percent greater than c_{44} .

Once we have decided to use central force bonds, and hence require that the lattice satisfy Eq. (26), only two elastic coefficients, or independent linear combinations thereof, are available for specifying the force constants of the bonds. We shall therefore consider only two types of bonds, those between nearest neighbors, and those between next nearest neighbors. These will be designated as the α and β type bonds, respectively. In the unstrained lattice the α bonds are along the $\langle 111 \rangle$ axes, the β bonds along the $\langle 100 \rangle$ axes. The two shear coefficients c_{44} and $(c_{11} - c_{12})/2$ will be chosen to determine the force constants of the α and β bonds, corresponding to the fact that the local distortions surrounding solute atoms are primarily shear distortions. We denote by A and B the force constants of the α and β bonds, respectively, i.e.,

$$\begin{aligned} A &= d^2 U_\alpha / dr^2 \\ B &= d^2 U_\beta / dr^2, \end{aligned}$$

where U_α and U_β are the corresponding bond energies, and where the second derivatives are to be taken at the value of r corresponding to an unstrained lattice, namely

$$r = \begin{cases} (\sqrt{3}/2)a, & \alpha \text{ bond} \\ a, & \beta \text{ bond}, \end{cases}$$

where a is the lattice constant. One then finds that

$$\begin{aligned} a^2 A &= (3a^3/2)c_{44}, \\ a^2 B &= a^3(c_{11} - c_{12})/2. \end{aligned} \quad (27)$$

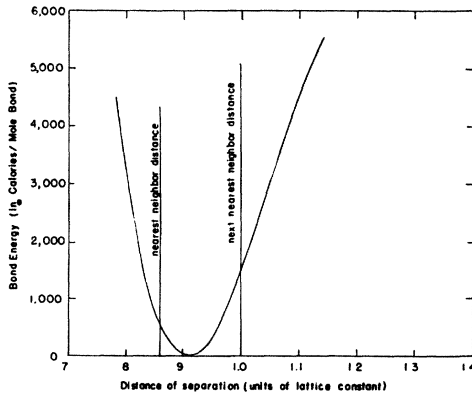


FIG. 2. Bond energy of iron atoms in b.c.c. lattice, computed from elastic constants.

Upon taking the known values of the two shear coefficients¹⁰ for iron,

$$\begin{aligned} c_{44} &= 1.16 \times 10^{12} \text{ dynes/cm}^2, \\ (c_{11} - c_{12})/2 &= 0.48 \times 10^{12}, \end{aligned} \quad (28)$$

we find

$$a^2 A = \begin{cases} 4.1 \times 10^{-11} \text{ ergs} \\ 595,000 \text{ cal/mole bond}, \end{cases} \quad (29)$$

and

$$B = 0.276A. \quad (30)$$

One could interpret the force constants A and B as being the second derivatives of a single bond energy $V(r)$ taken at the distance of separation corresponding to nearest and next nearest neighbors. An estimate of $V(r)$ has been obtained by expanding in a Taylor series about $r = a$ up to the cubic term, and determining the three coefficients by the condition of stability with respect to a cubical expansion and by the condition that the second derivation at $(\sqrt{3}/2)a$ and at a reduce to A and B , respectively. An estimate of V obtained in this manner is reproduced in Fig. 2.

We are now in a position to compute the distortion surrounding an interstitial carbon atom. Suppose a carbon atom is at a z type position, as in Fig. 3. It then acts downwards upon iron atom 1, upwards on atom 2, and horizontally upon atoms 3-6. In the preceding section we saw how the over-all distortion may be computed in terms of these forces. In the present case the computation will be reversed, since the over-all distortion is known from the data upon the variation of the lattice parameters of martensite with carbon content. Upon letting C be the atomic concentration of carbon, the over-all tetragonal strain in martensite induced by the addition of carbon is given by⁶

$$\begin{aligned} e_{zz} &= 0.90C, \\ e_{xx} = e_{yy} &= -0.14C. \end{aligned} \quad (31)$$

As discussed in the last section, the carbon atoms may be thought of as giving rise to these strains by means of a distribution of surface forces. The dependence upon carbon concentration of the stress system arising from this surface distribution of forces is

$$\begin{aligned} Z_z &= c_{11}e_{zz} + 2c_{12}e_{xx}, \\ X_x &= c_{11}e_{xx} + c_{12}(e_{xx} + e_{zz}). \end{aligned} \quad (32)$$

¹⁰ E. Goens and E. Schmid, Naturwiss. 19, 520 (1931).

The vertical force F_V acting upwards on atom 2 and downwards upon atom 1, and the horizontal force F_H acting upon each of atoms 3–6, are given by

$$\begin{aligned} CF_V &= (a^2/2)Z_z, \\ CF_H &= (a^2/2^3)X_x. \end{aligned} \quad (33)$$

We now solve for these two forces from Eqs. (31)–(33), and express the results in terms of A through Eq. (27), obtaining

$$\begin{aligned} F_V &= 0.50aA, \\ F_H &= 0.30aA. \end{aligned} \quad (34)$$

An approximate description of the distortion of the lattice in the vicinity of the carbon atom is now obtained by allowing all the atoms shown in Fig. 3 to attain those positions which minimize the strain energy, all other atoms of the lattice being held constant. We find that atoms 1 and 2 are displaced along the vertical axis by the amount

$$\delta_{100} = 0.13a;$$

atoms 3–6 are displaced in the horizontal plane radially away from the carbon atom by the amount

$$\delta_{100} = 0.052a;$$

and finally, atoms 7–14 are displaced along the corresponding $\langle 111 \rangle$ axes by the amount

$$\delta_{111} = 0.022a.$$

With these distortions, and the general theory developed in Section II, some conclusions may be drawn regarding short-range strain energy interaction of carbon atoms in iron. We shall, somewhat arbitrarily, take the radius of the sphere surrounding a carbon atom as equal to one lattice constant, a . Interstitial positions lying on or outside of this sphere will then be regarded as potential sites for other carbon atoms. We shall consider the given carbon atom as being in a z type position, as in Fig. 3. Of the six nearest potential z type positions, the two on the same z axis have a strong positive interaction, the four lying on the same x - y plane have fairly strong negative strain interaction, namely -2000 calories/mole. If p is the probability of any given potential interstitial position being occupied in the absence of interaction, the above

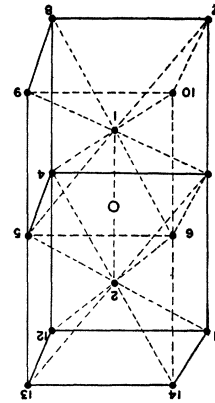


FIG. 3. Vicinity of carbon atom in iron lattice.
○ Carbon; ● iron.

mentioned interaction reduces the probability of occupancy of two of the neighboring z type positions from p to essentially 0, at the same time increasing the probability of occupancy of four of the neighboring z type positions from p to $28p$, the factor 28 being the value of $\exp(2000/RT)$ at room temperature. The short-range interaction thus greatly increases the average number of carbon atoms in a neighboring z type position. On the other hand, the nearest potential x and y type positions correspond to a positive interaction, and hence to a reduction in the probability of occupancy. We therefore conclude that in the case of carbon in iron, the short-range interaction aids the long-range interaction in giving rise to a self-induced preferential distribution.

While the conclusions regarding long-range interaction have been expressed in terms applicable to any solute atoms in any b.c.c. or f.c.c. lattice, the above conclusions regarding the short-range interaction of carbon atoms in iron cannot be extended to the general case of interstitial solute atoms in b.c.c. lattices. Each case will have to be examined separately. Thus we anticipate carbon will introduce considerably less distortion in the b.c.c. lattice of tantalum, which has a larger lattice constant than iron. If the strains are half that in iron, the interaction energy will be reduced by approximately a factor of four, resulting in an increase in the probability of occupancy of a neighboring interstitial position of like type by a factor of only 2.3, rather than of 28 as in the case of iron.