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On the Theory of Diffusion in Metals

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Zener has generalized the interchange mechanism of metallic diffusion by considering interchange processes in which more than two atoms may change places at once. The position of these calculations relative to those of Huntington and Seitz on the mechanism of diffusion is discussed. It is emphasized that the calculations still favor the vacancy mechanism, although the purely theoretical support is not as overwhelming as it seemed to be previously. The experimental situation is reviewed. It is pointed out that the existing experiments on the Kirkendall effect, which is concerned with the motion of fiducial markers during diffusion, and the diffusion of minor additions in substitutional alloys strongly support either a vacancy or interstitial mechanism and exclude a direct interchange mechanism as the major contributing process. Taken as a whole the theoretical and experimental evidence supports the vacancy mechanism as previously. Bardeen's derivation of Darken's relations between the chemical diffusion coefficient and the diffusion coefficients of individual atoms is examined somewhat more generally in the Appendix.

1. Introduction

In a recent paper Zener (1950) has reopened the question of the mechanism by which diffusion occurs in the common substitutional alloys. Following the procedure employed by Huntington and the writer (Huntington & Seitz, 1942; Huntington, 1942), he has focussed attention upon self-diffusion in copper, since this seems to provide a reasonably typical example of a case in which the influence of the *d* shells is not negligible and in which there is reasonable hope of employing well-developed approximations of atomic theory.

Huntington and the writer had carried out calculations for three competing mechanisms:

(1) Direct interchange of *pairs* of neighboring atoms.

(2) Interstitial diffusion. Attention was focussed on the case which seemed to have lowest activation energy, namely that in which the interstitial atom moves into a normal lattice site and pushes the atom which occupies this normal site into a neighboring interstitial position.

(3) Vacancy diffusion.

At the time at which these calculations were made, the best measured values of the activation energy were those of Steigman, Shockley & Nix (1939) and of Rollin (1939), which gave values of 57 kg.cal. or 2·5 eV. More careful measurements of Maier & Nelson (1942) on single crystals support a substantially lower value of about 48 kg.cal. or 2·1 eV. Rudimentary calculations showed that the third mechanism possesses greatest likelihood of yielding the correct magnitude for the activation energy for self-diffusion. As a result attention was focussed on it in more refined calculations. These calculations showed that there was relatively little difficulty in obtaining calculated values of the activation energy that are close to the observed value with the use of the vacancy mechanism. These calculations indicated that the energy required to form a vacancy in copper is about 1·8 eV. and the activation energy for motion is about 1·0 eV., giving a total activation energy for diffusion by means of vacancies of about 2·8 eV. The more rudimentary calculations for the other two mechanisms yielded values of about 17·2 eV. for the activation energies for direct interchange of pairs (mechanism (1)) and a value of about 10·0 eV. for the interstitial mechanism (mechanism (2)). Since it seemed highly unlikely that careful refinement of the calculations of mechanisms (1) and (2) would radically alter the relative values of the activation energies for the three mechanisms, Huntington & Seitz concluded that: 'The results of these computations...seem to show beyond a reasonable doubt that the vacancy mechanism of diffusion is greatly preferred over the other two considered here for copper.' Huntington was careful to point out that this conclusion could not be extrapolated to cases such as the alkali metals in which the inner shells are much smaller.

In a private communication Zener subsequently criticized the rudimentary calculation of mechanism (1), and a more careful examination (Huntington & Seitz, 1949) showed that the true value is probably more nearly in the range of 10·3 eV. It is probably also true that the activation energy for interstitial diffusion could be reduced somewhat from the value of 10·0 eV. quoted above by more refined calculation. However, it seems very doubtful that any serious exertion in this direction would place mechanisms (1) or (2) in close competition with the vacancy mechanism.

Finally, Zener has sought for an essentially new mechanism for diffusion to place in competition with the vacancy mechanism. He does not offer a serious concrete criticism of the calculations for the vacancy mechanism described above but offers the new mechanism as an alternative for consideration. The new mechanism proposed by Zener is a more sophisticated form of the direct interchange mechanism in which a number of atoms change places at once instead of merely two, as in mechanism (1) described above. He finds that the influence of the closed-shell repulsive terms is greatly mitigated and arrives at an activation energy of about 90 kg.cal., or 4·0 eV. He is inclined to ascribe the large difference between the calculated and observed values to the fact that proper account is not taken of the deformation of inner shells as the copper atoms move from the normal to the activated state, an effect associated with a decrease in co-ordination number and observed in a number of compounds.

There seems to be no doubt that Zener's analysis of the exchange mechanism represents a distinct generalization of this process and a great improvement of the calculations of Huntington & Seitz for this type of mechanism. His results suggest that in any case in which the exchange mechanism occurs, as may be true for the alkali metals, the process may involve more than two atoms. On the other hand, if the various calculations are taken at their face value, his contribution cannot be said to rule out the vacancy mechanism. In fact, if one had unlimited confidence in the approximations employed in the calculations, it could be said that they strongly favor the vacancy mechanism in copper, since Zener's best value of the activation energy is almost twice as large as the observed one, whereas the value obtained by Huntington for the vacancy mechanism is much closer.

The writer cannot regard Zener's comments on the distortion of inner shells as being particularly favorable to his mechanism in comparison with the vacancy mechanism. Either this lack of rigidity should be taken into account in a uniform way in all calculations, in which case it will probably favor the vacancy mechanism as well, or it should be ignored systematically. If the second path is chosen, we accept the existing calculations with the consequences described above; if the first path is chosen, it would not be satisfactory to alter the parameters in the Born–Mayer repulsive potential in going to the activated state and accept the decrease in activation energy which results from the decrease in the repulsive term. In addition to the points mentioned by Zener, the apparent decrease in ion radius which takes place when an ion is moved from a given site to one in which it has a lower co-ordination number arises from the fact that the inner shell electrons lose some of the benefit of the attractive field of neighboring ions in moving to the new position and hence cluster closer to their own nucleus so that they screen the coulomb field of this nucleus better. One cannot include the gain resulting from this screening without taking account of the compensating loss in binding energy which the electrons suffer because the field of the neighboring ions is less favorable.

One other factor which favors acceptance of the present calculations at their face value in lieu of far more painstaking analysis is the circumstance that the parameters used in the Born–Mayer repulsive terms are either semi-empirical or are closely the same as semi-empirical values. Hence at least part of the effect which causes the inner shells to deform is already included.

2. Empirical evidence against the vacancy mechanism

One of the frequently repeated arguments that is given against the vacancy mechanism in metals is the fact that effects associated with frozen-in vacancies have not been observed. For example, the diffusion coefficient when plotted as a function of temperature does not exhibit the type of knee commonly observed in salts. Actually, the evidence which continues to accumulate for salts* indicates that most of the vacancies which are normally frozen-in in salts are associated with impurity ions having a valence higher than that of the normal anion or cation of the bulk material. These vacancies are present because they establish electrostatic equilibrium. On the other hand, there are effects such as the polarization phenomena observed by Breckenridge (1948, 1949) which probably are associated with vacancies that have been trapped as a result of rapid cooling.

If the vacancy mechanism is correct, it should be possible to trap vacancies in metals. However, simple estimates show that these probably have not been present in sufficient quantities to influence experiments which have been carried out to date. We shall consider the influence such vacancies would have on the measured density of a pure metal and upon a particular type of internal friction observed by Zener (1947) and Kê (1948) in alpha brass, which has been interpreted by them in terms of the reorientation of atoms in the unit cell of this substitutional alloy.

Consider a specimen of a metal such as copper which is a good thermal conductor. If wires of the order of 1 mm. in diameter are cooled, it should be possible to effect cooling from a high temperature to a low temperature in the order of 10^{-2} sec. If specimens of the order of 1 cm. are employed, the cooling time should be of the order of 1 sec. Conversely, it is possible, with the use of careful thermostating, to cool through the same range of temperature in a period of time of the order of a day or more, that is, over a time that is at least 10^5 times as long.

Now the vacancies in a specimen of metal are probably generated and absorbed at edge dislocations where an extra plane of atoms provides an excellent source or sink (Nabarro, 1948, p. 38). It is probably possible to obtain well-annealed specimens in which the density of dislocation lines is as low as 10^8 per cm.^{2}, so that a given vacancy would have to diffuse about 10^7 atom distances along its trajectory to be absorbed. The time required for this is, in order of magnitude,

$$\tau = 10^7 \exp(\epsilon'/kT)/\nu_0, \tag{1}$$

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* For example, as yet unpublished work of H. Etzel and R. J. Maurer.

where ϵ' is the activation energy for migration of the vacancy, which we shall take to be 1 eV., and ν_0 is of the order of 10^{13} sec.$^{-1}$. Using these values, we may place (1) in the form

$$\tau = 10^{-6}\,10^{5000/T}\,\text{sec.} \qquad (2)$$

This lies in the vicinity of 10^{-1} sec. when T is near 1000° K., so that the density of vacancies that would be trapped in the metal during a rapid cooling would correspond to the equilibrium density near this temperature. If the energy ϵ_v required to form a vacancy is about the same as, or somewhat larger than ϵ', as the calculations of Huntington indicate to be the case, the density of vacant sites that would be frozen in would be of the order of 10^{17} per cm.^{3} or less, which is probably beyond detection by combined density and X-ray measurements, as attempted by Straumanis (1949) and others (Stockdale, 1940; Lipson, Petch & Stockdale, 1941).

During slow cooling, for example, at a rate of the order of 10^5 times smaller than in quenching, the temperature at which vacancies are frozen would be the temperature at which the coefficient $\exp(\epsilon'/kT)$ in (1) is 10^5 times smaller than in the case of rapid cooling. It follows that the density of vacancies should be at least 10^5 times smaller than in the case of rapid cooling if ϵ_v and ϵ' are nearly equal. In fact, if these energies are about equal, we should generally expect the density of trapped vacancies to be proportional to the cooling rate in the range of temperature where the freezing-in of vacancies occurs.

Zener (1947) and Kê (1948) have studied a type of internal friction in single crystals of 70–30 brass that presumably originates in the desire of the atoms of zinc and brass to alter their local order in the presence of a stress field. The peak in internal friction should occur at the frequency with which the diffusion mechanism permits atoms to interchange. The lowest temperature at which the effect is observed in the standard internal-friction measurements is determined by the lowest frequency at which it is convenient to vibrate the specimen, namely, about 1 cyc./sec. A simple calculation shows that the corresponding temperature is such that

$$\exp[-(\epsilon_v+\epsilon')/kT] = 10^{-13}. \qquad (3)$$

This, unfortunately, is very close to the temperature at which freezing-in occurs in rapid quenching in specimens of normal size, so that the conventional internal-friction measurements cannot be carried into the range where the vacancies are no longer at equilibrium.

D. Lazarus (private communication) has suggested that it may prove possible to detect the type of reorientation which is presumed to be responsible for the internal friction described above in static creep tests which are carried out at a much slower rate than is necessary in the measurement of internal friction.

3. Empirical evidence against Zener's interchange mechanism

There are several excellent sources of experimental evidence which make it seem highly unlikely that Zener's mechanism of diffusion is the correct one in the ordinary substitutional systems.

(1) *The Kirkendall experiment*

Smigelskas & Kirkendall (1947) have found that fiducial markers at the boundary between copper and 70–30 brass move in the direction of the brass when diffusion occurs. This experiment has been repeated by Da Silva and Mehl* for several alloy systems under more carefully controlled conditions. Although a complete report of the quantitative aspects of their work is not yet available, they have also found that the markers move. This motion appears to be intimately coupled with the diffusion mechanism, so that an explanation should be sought most naturally in terms of the diffusion mechanism. To quote a letter on this topic from Prof. R. F. Mehl (3 January 1950):

'(1) We have repeated this experiment some thirty times, in five metallic systems and at various temperatures. We are able to attain a very satisfactory degree of precision in all measurements, greater than that which Kirkendall attained.

'(2) We were able to demonstrate that the Matano boundary does coincide with the initial boundary in all cases, when correction is made for change of lattice parameter. This, to be sure, is, as you say, merely the law of conservation of mass, with the sole qualification that it demonstrates also that changing percentages of vacancies in the couples are not great enough to affect the experiment, as might be expected.

'(3) The fiducial markers move in all systems studied and at all temperatures by an amount which varies markedly from system to system.

'(4) For a time we entertained the thought that vapor pressure might be the controlling factor, arguing that transport by vapor along the interface between the wire and the alloy might give the movement of the wires observed. We have now investigated all types of markers including various wares, powders and foils. All of them move and by the same amount; even those which are wetted and which actually dissolve partially show the same amount of movement.'

It is clear from the start that the Kirkendall experiment cannot be explained naturally in terms of the diffusion mechanism if this is assumed to be exclusively of the interchange type, that is, if one of the possible mechanisms studied by Zener is assumed to predominate completely. For in this case an atom which shifts its position would always do so by moving from one normal position to another and would always be replaced at once by another atom. As a result the lattice array would be maintained completely intact, except for the local expansion or contraction that arises from the variation of the average size of the unit cell with composition, which does not appear to be sufficient to explain the Kirkendall effect.

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* As yet unpublished work reported at Cleveland Meeting of A.S.M., October 1949.

On the other hand, the Kirkendall experiment can be explained on the basis of the diffusion mechanism if one assumes that this mechanism is not of the type involving direct interchange. The first treatment of this type was made by Darken (1948), who showed that the Kirkendall effect is exactly what one should expect if each atom can be assigned its own diffusion coefficient, if this diffusion coefficient is unequal for the two constituents, and if the loss or gain in mass of a given element of volume of the system as a result of the unbalance in diffusion rates of the two constituents is compensated by a change in volume which keeps the volume per atom constant. Seitz (1948) subsequently showed that an unbalance of the type suggested by Darken is not at variance with the theory of vacancy diffusion, as suggested by Birchenall & Mehl (1947). Still more recently, Bardeen (1949) has demonstrated the relationship between the work of Darken and Seitz for a simple system and has shown that Darken's equations automatically follow in the case of this system if it is assumed that the density of vacancies in any region of the alloy is maintained at the equilibrium value in spite of the presence of vacancy currents. A somewhat more general treatment is given in the Appendix. Bardeen's connective analysis is developed there with fewer assumptions. It is shown that Darken's diffusion equations are to be expected if either vacancy or interstitial diffusion (or a combination of both) is the prevailing mechanism.

To summarize: The existing evidence concerning the Kirkendall experiment, if interpreted in the most natural way in terms of the diffusion mechanism, indicates that the mechanism suggested by Zener cannot be the exclusive one. On the contrary, this evidence supports either the vacancy mechanism or the interstitial mechanism. There is always the possibility that the interchange mechanism contributes a fraction to the diffusion mechanism; in this case it may prove difficult to use the Kirkendall experiment to determine the fraction.

(2) *Diffusion in dilute solid solutions*

It is a well-known fact that the activation energy for diffusion of a small addition of one element in another is often substantially less than the activation energy for self diffusion in the solvent. To quote from among the best examples, the activation energies for diffusion of small amounts of zinc or tin in copper are 38 and 45 kg.cal., whereas the activation energy for self-diffusion in copper is about 48 kg.cal. (see, for example, Barrer (1941) and Smithells (1949, p. 390)). The activation energy for diffusion of gold in lead is only 13 kg.cal., whereas the self diffusion coefficient in lead is 38 kg.cal. However, it is possible that this example is not a good one since the atomic diameter of lead is about 20 % larger than that of gold. There is a chance that the diffusion is interstitial. It should also be mentioned that in cases other than those associated with lead, the measured diffusion coefficients do not show quite as great differences as one might expect from the differences in activation energy mentioned above, because there seems to be a tendency for the coefficient of the Boltzmann factor in the usual expression for the diffusion coefficient to decrease as the activation energy decreases. The cases involving lead, however, are very striking.

The fact that foreign atoms diffuse faster can be explained relatively easily on the basis of the vacancy or interstitial mechanism, as Johnson (1939) and Wagner (1938) have pointed out; it is only necessary to assume that vacancies or interstitial atoms have a higher statistical probability of being found near the solute atoms than near the normal atoms at some distance from the solute. On the other hand, it is not easy to see why the foreign atom should have such a large influence upon the activation energy for direct exchange, particularly if such exchange involves the cooperative action of four or more atoms, as proposed by Zener.

It is possible, of course, that the mechanism for diffusion of dilute solute atoms is different from that for the bulk material. If this viewpoint is taken, however, it is to be noted that the activation energies for this 'special' process is of the same order of magnitude as the activation energies for bulk diffusion. It is difficult to believe that this similarity is purely a matter of coincidence in lieu of evidence that is much better than anything that has been put forward to date.

(3) *Evidence from salts*

Although the evidence accumulated from the analysis of transport phenomena in salts probably should not be admitted in a discussion that centers about the behavior of metals, it is perhaps worth noting that the existence of vacancies has now been established with practically no ambiguity in the case of the alkali halides.* It now seems almost certain that the normal electrolytic currents and diffusion currents are associated with the migration of positive-ion and negative-ion vacancies. Moreover, the discoloration associated with the F bands in these salts can be associated with negative-ion vacancies which have captured an electron. Since vacancies play such an important role in these materials, it is difficult to believe that their introduction in the theory of metals can be regarded as merely a matter of fashion, particularly when so many other independent lines of evidence, both theoretical and experimental, support the same conclusion.

4. Additional proposed experiments

Inasmuch as it seems to be very difficult to enhance the density of vacancies by quenching in a way which affects the properties that usually are measured in

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* See Seitz (1946), Estermann, Leivo & Stern (1949). Of great importance are as yet unpublished measurements of D. E. Mapother and R. J. Maurer on simultaneous measurements of diffusion and electrolytic conductivity.

'conventional' experiments, it seems natural to ask if there are other methods of enhancing the density. A rather obvious answer is provided by consideration of the salts. It is possible to enhance the density of vacancies in the monovalent salts by adding a divalent impurity. We evidently cannot expect to use the identical principle in the case of metals because the fields of the inner shells are balanced by free electrons instead of by other ions, as in the salts. On the other hand, it is quite possible, as emphasized in paragraph (2) of the previous section in connection with Johnson and Wagner's interpretation of the low activation energy for migration of dilute solute atoms, that impurity atoms frequently introduce vacancies into metals. For example, it is possible that vacancies accompany the introduction of a small amount of zinc in pure copper or the introduction of gold into lead. This suggests two experiments: (1) The measurement of density and lattice parameter in alloys containing of the order of 0·1 % of a solute to see if there are appreciable numbers of vacancies. Lipson *et al.* (1941) have made such an analysis for the Ag–Zn system with negative results, but the situation should be surveyed more broadly. (2) A study of self-diffusion of the solvent atoms in a homogeneous alloy containing small amounts of a solute which is suspected of introducing vacancies because the activation energy for diffusion of the solute is much lower than the activation energy of self-diffusion of the solvent, or better still, because of results obtained from experiments of type (1). The first type of experiment should lead to observable results only if the probability that an impurity has a vacancy associated with it is at least 0·01, whereas the second type of experiment may provide a much more sensitive test.

It is interesting to consider the equations governing the density of vacancies in a dilute solid solution. We shall designate the solvent atoms by A and the solute by B, and assume that there are N sites in the specimen of which n_a are occupied by A atoms, n_b are occupied by isolated B atoms, n_v are occupied by vacancies which are not near B atoms. It will also be assumed that there are n_p pairs of B atoms and vacancies in close association or 'paired', and that the pair can be oriented in s independent ways. If we assume that the relevant contribution to the entropy arises from mixing, the entropy S of the system is

$$S = \boldsymbol{k} \log \frac{N!\, s^{n_p} (N-2n_p)!}{n_a!\, n_b!\, n_v!\, n_p!\, (N-n_p)!}, \tag{4}$$

in which $\boldsymbol{k}$ is Boltzmann's constant. If ϵ_b is the energy of solution of a B atom, measured relative to the solid phase of pure B, ϵ_v is the energy required to form a vacancy in the lattice of A, and ϵ_p is the energy required to form a pair consisting of a B atom and an associated vacancy, the energy of the system relative to the ground state of pure A which contains neither B atoms nor vacancies is

$$E = n_b \epsilon_b + n_v \epsilon_v + n_p \epsilon_p. \tag{5}$$

The differential of the free energy $A = E - TS$ is

$$dA = (\epsilon_b + \boldsymbol{k}T \log n_b/N)\, dn_b + (\epsilon_v + \boldsymbol{k}T \log n_v/N)\, dn_v + (\epsilon_p + \boldsymbol{k}T \log n_p/sN)\, dn_p, \tag{6}$$

in which Stirling's approximation has been employed in the evaluation of terms of the type $\log n!$, and it has been assumed that n_b, n_v and n_p are all small compared with n_a.

The most interesting equilibrium problem to consider is that in which there is a fixed number of B atoms present, so that $n_b + n_p = N_b$, a constant. In this case $dn_b = -dn_p$, and the conditions for equilibrium are

$$\left.\begin{aligned} \epsilon_v + \boldsymbol{k}T \log n_v/N &= 0, \\ (\epsilon_b - \epsilon_p) + \boldsymbol{k}T \log s(N_b - n_p)/n_p &= 0. \end{aligned}\right\} \tag{7}$$

The first of these equations gives the customary expression for the number of free vacancies under the assumption that the mixing entropy is the most important source of entropy. The second yields the relation

$$(N_b - n_p)/n_p = \exp\left[(\epsilon_p - \epsilon_b)/\boldsymbol{k}T\right]. \tag{8}$$

If $\epsilon_p - \epsilon_b$ is negative, that is, if less energy is required to place a B atom in the lattice with a vacancy than without one, all of the B atoms will have vacancies attached to them at sufficiently low temperatures under conditions in which the vacancies come to equilibrium. Conversely, none of the B atoms will have vacancies attached to them at low temperatures if $\epsilon_p - \epsilon_b$ is positive. The first case evidently is one in which the impurities should give a measurable change in density because of the presence of vacancies.

Even if $\epsilon_p - \epsilon_b$ is not negative, it may prove possible to obtain a specimen in which each impurity has a vacancy attached to it by quenching rapidly from elevated temperatures, provided the quantity $\epsilon_p - \epsilon_b - \epsilon_v$ is negative. For in this case the vacancies will be energetically more stable when bound to an impurity atom than when free in the lattice, and may become trapped at the impurity atoms while attempting to diffuse to edge dislocations. In other words, appropriately chosen impurities may make it possible to freeze in far more vacancies than would be possible in a pure metal having a reasonable number of edge dislocations. Seith & Keil (1933), who studied diffusion in lead which contained additions of gold and silver, found changes in the self-diffusion coefficient of lead when the alloy was quenched rapidly. These effects may be associated with the freezing-in of vacancies by a process similar to this.

APPENDIX

Darken has derived an expression for the chemical diffusion coefficient and for the velocity with which markers attached to the lattice move, on the basis of the assumption that each atom has an intrinsic diffusion coefficient for migrating in the presence of a chemical gradient, and the assumption that a process akin to plastic flow occurs to maintain the normal density of the alloy at each region. The equations of Darken will be re-examined in this Appendix on the basis of the three types of mechanism of diffusion, namely, vacancy, interstitial and direct exchange mechanisms. A general formulation of the vacancy case was developed earlier (Seitz, 1948); however, as Bardeen has pointed out, this formulation may lead to relations other than Darken's, depending upon the assumptions which are made regarding the fate of the vacancy current. Bardeen showed, with use of a simple model, that Darken's equations are obtained if it is assumed that the vacancies are maintained at equilibrium in each region. The treatment given here is more general than Bardeen's in two respects: first, it will be tied in more closely with the material of the earlier paper (Seitz, 1948) and hence made more nearly independent of the model employed; secondly, the case of interstitial migration will be included.

It is perhaps well to emphasize that no attempt will be made here to examine Darken's thermodynamical relations between the chemical and radioactive diffusion coefficients when the latter are determined in a chemically homogeneous specimen. Bardeen has derived these with the use of his simple model. We have tried unsuccessfully to generalize his derivation and believe at present that Darken's thermodynamical relations are valid only in the very special case treated by Bardeen.

Consider first the currents which accompany vacancy diffusion in the presence of a chemical gradient. We shall follow an approach which is somewhat different from, although as general as, that employed before (Seitz, 1948). We shall assume that we are dealing with two neighboring crystallographic planes, (1) and (2), and that the planar densities of A atoms, B atoms and of vacancies in the two planes are, respectively n_{a1}, n_{a2}, n_{b1}, n_{b2}, n_{v1} and n_{v2}. These six quantities are interrelated by the equations

$$n_{a1}+n_{b1}+n_{v1}=n_{a2}+n_{b2}+n_{v2} \tag{9}$$

in a region where the crystal is perfect. As long as n_{v1} and n_{v2} are small, n_{b1} and n_{b2} are specified when n_{a1} and n_{a2} are given. We shall designate by $\pi_a(n_{a1}, n_{a2})$ and $\pi_b(n_{a1}, n_{a2})$ the probabilities per unit time that a vacancy in plane (1) will interchange places with an A atom and a B atom, respectively, in plane (2). The total rate at which the vacancy jumps is

$$\pi(n_{a1}, n_{a2})=\pi_a(n_{a1}, n_{a2})+\pi_b(n_{a1}, n_{a2}). \tag{10}$$

It is evident that the quantity $p(n_{a1}, n_{a2})$ employed in the previous paper is related to π_a and π_b by the equation

$$p(n_{a1}, n_{a2})=\pi_a(n_{a1}, n_{a2})/\pi(n_{a1}, n_{a2}). \tag{11}$$

The vacancy current I_v which flows from plane (1) to plane (2) is

$$I_v=n_{v1}\pi(n_{a1}, n_{a2})-n_{v2}\pi(n_{a2}, n_{a1}), \tag{12}$$

which, if expanded to the first order in the interplanar spacing λ, is

$$I_v=-\pi(n_a)\frac{dn_v}{dx}\lambda+n_v\left(-\frac{\partial\pi}{\partial\xi}+\frac{\partial\pi}{\partial\eta}\right)\lambda\frac{dn_a}{dx}, \tag{13}$$

in which $n_a=\frac{1}{2}(n_{a1}+n_{a2})$, $\pi(n_a)=\pi(n_a, n_a)$ and ξ and η are defined by the relations

$$\left.\begin{aligned}\frac{\partial\pi}{\partial\xi}&\equiv\frac{\partial\pi(n_{a1}, n_{a2})}{\partial n_{a1}}\,n_{a1}=n_{a2}=n_a,\\ \frac{\partial\pi}{\partial\eta}&\equiv\frac{\partial\pi(n_{a1}, n_{a2})}{\partial n_{a2}}\,n_{a1}=n_{a2}=n_a.\end{aligned}\right\} \tag{14}$$

We see from (13) that a vacancy current will, in the general case, be induced to flow in the system even if the vacancy gradient is zero. In other words, a single vacancy, finding itself in a region in which a chemical gradient exists, will drift preferentially in one direction because of the anistropy of its environment. If vacancies could neither disappear nor be generated in the interior of the specimen, this current would flow to the boundary of the specimens or, if this is impossible as a result of geometrical factors, a vacancy gradient would be established which would eventually compensate for the pumping action of the chemical gradient. When this point is reached, there might be an excess of vacancies in one region of the specimen, relative to the equilibrium density that would prevail there if equilibrium could be obtained, and a deficiency in another region.

Actually, as we have seen in §2, edge dislocations should provide sources and sinks for vacancies which are sufficient to maintain equilibrium over regions of the order of 10^{-4} cm. or less on an edge, provided the temperature at which the investigation is being carried out is sufficiently high that the jump frequency for interchange of atoms is not appreciably smaller than 1 per sec. This condition is usually met in practice.

The currents of A and B atoms between the atomic planes (1) and (2) are

$$\begin{aligned}I_a&=n_{v2}\pi_a(n_{a2}, n_{a1})-n_{v1}\pi_a(n_{a1}, n_{a2})\\ &=\pi_a\frac{dn_v}{dx}\lambda+n_v\left(\frac{\partial\pi_a}{\partial\xi}-\frac{\partial\pi_a}{\partial\eta}\right)\lambda\frac{dn_a}{dx},\end{aligned} \tag{15}$$

$$I_b=\pi_b\frac{dn_v}{dx}\lambda+n_v\left(\frac{\partial\pi_b}{\partial\xi}-\frac{\partial\pi_b}{\partial\eta}\right)\lambda\frac{dn_a}{dx}. \tag{16}$$

If dn_v/dx in these equations is replaced by I_v from (13), one readily finds

$$I_a=-p(n_a)\,I_v+n_v\pi(n_a)\left[\frac{\partial p}{\partial\xi}-\frac{\partial p}{\partial\eta}\right]\lambda\frac{dn_a}{dx}, \tag{17}$$

$$I_b=-(1-p(n_a))\,I_v-n_v\pi(n_a)\left[\frac{\partial p}{\partial\xi}-\frac{\partial p}{\partial\eta}\right]\lambda\frac{dn_a}{dx}, \tag{18}$$

which are identical with the equations obtained in the previous paper.

Let us assume that the vacancy gradient dn_v/dx can be expressed as a function of the chemical gradient in the simple manner

$$\frac{dn_v}{dx}=\frac{dn_v}{dn_a}\frac{dn_a}{dx}; \tag{19}$$

that is, that the concentration of vacancies in a given region is determined primarily by the chemical composition. This evidently will be the case if n_v has the equilibrium value corresponding to the local chemical composition, for in this event dn_v/dn_a will be given by

$$\frac{dn_v}{dn_a}=-\frac{n_v}{kT}\frac{d\mu_v'}{dn_a}, \tag{20}$$

in which μ_v' is the chemical potential of a vacancy, exclusive of the component arising from mixing, $\boldsymbol{k}$ is Boltzmann's constant and T is the absolute temperature. It is interesting, however, to consider the more general relation (19).

If (19) is valid, I_v, I_a and I_b may be written in the form

$$I_v=(D_a-D_b)\frac{dc_a}{dx}, \tag{21a}$$

$$I_a=-D_a\frac{dc_a}{dx}, \tag{21b}$$

$$I_b=D_b\frac{dc_a}{dx}, \tag{21c}$$

where $c_a=n_a/\lambda$ and

$$\left.\begin{aligned} D_a&=-\pi_a\frac{dn_v}{dn_a}\lambda^2-n_v\left(\frac{\partial\pi_a}{\partial\xi}-\frac{\partial\pi_a}{\partial\eta}\right)\lambda^2,\\ D_b&=\pi_b\frac{dn_v}{dn_a}\lambda^2+n_v\left(\frac{\partial\pi_b}{\partial\xi}-\frac{\partial\pi_b}{\partial\eta}\right)\lambda^2.\end{aligned}\right\} \tag{22}$$

If the vacancy current (21a) condenses and produces strain by the shortening of the planes associated with edge dislocations, the region where the gradient is dc_a/dx will undergo a mass displacement of the type postulated by Darken, with the velocity

$$v=\frac{1}{c}I_v=\frac{1}{c}(D_a-D_b)\frac{dc_a}{dx}, \tag{23}$$

in which c is the concentration of atoms. This displacement will take place relative to a region of the specimen where the concentration gradient is zero. Equations (21b), (21c) and (23) are precisely those of Darken and will lead to the consequences of his treatment of the subject. In particular, the chemical diffusion coefficient is given by the expression

$$D_c=(f_bD_a+f_aD_b), \tag{24}$$

in which f_a and f_b are the fractions of A and B atoms.

From the standpoint of lattice geometry, the lattice imperfection which is the inverse counterpart of a lattice vacancy is an interstitial atom which moves by jumping into a normal lattice site and forces the atom that is there into a neighboring interstitial site. This entity has the same type of phase-like existence as a vacancy or a dislocation, since the pattern can move without having a fixed atom move with it. We shall term it an *interstitialcy.* If the calculations of Huntington and Seitz have meaning, interstitial diffusion in normal substitutional alloys would occur by means of interstitialcies rather than by the migration of specific atoms in interstitial positions, since the activation energy for the former process is lower. Actually vacancy diffusion is preferred, but it is valuable to follow through the analogy.

The case in which diffusion takes place by the migration of interstitialcies can be formulated in a way very similar to that used for vacancies. Without loss of generality, we may assume that the gradient in concentration is normal to one of the principal crystallographic planes. We shall also assume that the interstitial sites lie midway between these planes, as presumably would be the case in the face-centered cubic lattice if diffusion were normal to the octahedral planes. We shall consider three successive principal planes, normal to the concentration gradient, and designate them by (a), (b) and (c). The interstitial plane between (a) and (b) will be designated by (1) and that between (b) and (c) by (2). We shall consider the currents associated with jumps of the interstitialcies between planes (1) and (2), analogous to the jumps of vacancies between neighboring lattice planes. The compositional environment in the neighborhood of the interstitial plane (1) will be somewhat different from that in the neighborhood of plane (2) because of the concentration gradient. We may express this fact by associating with each interstitial plane a parameter which describes the composition in the nearest regular lattice planes and which will vary from interstitial plane to interstitial plane when there is a gradient in chemical composition. This parameter may, for example, be taken to be the average number of A atoms in the two neighboring regular planes. We shall adopt this procedure and shall designate the corresponding variable associated with the kth interstitial plane by n_{ak}.

The interstitial atom associated with a passing interstitialcy at any point in its migration may be either an A atom or a B atom. This characteristic of diffusion by interstitialcies has no analogue in vacancy diffusion. We shall designate the density of A type and B type interstitialcies in the $\boldsymbol{k}$th interstitial plane by $n_{ik}(a)$ and $n_{ik}(b)$. If an interstitialcy is A type in plane (1), it may either remain A type in going to plane (2) or may transform to B type; conversely, an interstitialcy that is B type in plane (1) may either remain B type or transform to A type in the transition. We shall designate by $\pi_{aa}(n_{a1}, n_{a2})$ the probability per unit time that an interstitialcy which is A type in the interstitial plane (1) will make a transition to interstitial plane (2) when the concentrations of A atoms in the vicinity of planes (1) and (2) are described by n_{a1} and n_{a2}, respectively, and will remain A type. The corresponding probabilities for an interstitialcy which changes from A type to B type in the transition, and for one which is B type and either remains the same or changes to A type, are $\pi_{ab}(n_{a1}, n_{a2})$, $\pi_{bb}(n_{a1}, n_{a2})$ and $\pi_{ba}(n_{a1}, n_{a2})$, respectively.

The total interstitialcy current flowing between planes (1) and (2) evidently is

$$\begin{aligned} I_i=n_{i1}(a)&\left[\pi_{aa}(n_{a1},n_{a2})+\pi_{ab}(n_{a1},n_{a2})\right]\\ &+n_{i1}(b)\left[\pi_{bb}(n_{a1},n_{a2})+\pi_{ba}(n_{a1},n_{a2})\right]\\ &-n_{i2}(a)\left[\pi_{aa}(n_{a2},n_{a1})+\pi_{ab}(n_{a2},n_{a1})\right]\\ &-n_{i2}(b)\left[\pi_{bb}(n_{a2},n_{a1})+\pi_{ba}(n_{a2},n_{a1})\right],\end{aligned} \tag{25}$$

in which the terms with positive sign correspond to transitions from plane (1) to plane (2) and those with negative sign correspond to transitions in the reverse direction. By analogy with the case of vacancy diffusion, this evidently may be expanded in terms of the interatomic distance and expressed in the form

$$I_i=\pi_a(n_a)\frac{dn_i(a)}{dx}\lambda+\pi_b\frac{dn_i(b)}{dx}+\left\{n_i(a)\left[\frac{\partial\pi_a}{\partial\xi}-\frac{\partial\pi_a}{\partial\eta}\right]\lambda+n_i(b)\left[\frac{\partial\pi_b}{\partial\xi}-\frac{\partial\pi_b}{\partial\eta}\right]\lambda\right\}\frac{dn_a}{dx}, \tag{26}$$

where $$\pi_a=\pi_{aa}+\pi_{ab}, \quad \pi_b=\pi_{bb}+\pi_{ba}, \tag{27}$$

$\pi_a(n_a)$ is the value of π_a when $n_{a1}=n_a$, and the derivatives with respect to ξ and η have the same connotation as in the case of vacancy diffusion.

In an entirely analogous way, the contribution to the currents of I_a and I_b of A atoms and B atoms between planes (1) and (2) arising from transitions from (1) and (2) can be expressed in the form

$$\left.\begin{aligned}I_a\colon\quad & n_i(a)\,[\pi_{aa}(n_{a1},n_{a2})+\tfrac{1}{2}\pi_{ab}(n_{a1},n_{a2})]\\ & \qquad +n_i(b)\,\tfrac{1}{2}\pi_{ba}(n_{a1},n_{a2}),\\ I_b\colon\quad & n_i(b)\,[\pi_{bb}(n_{a1},n_{a2})+\tfrac{1}{2}\pi_{ba}(n_{a1},n_{a2})]\\ & \qquad +n_i(a)\,\tfrac{1}{2}\pi_{ab}(n_{a1},n_{a2}).\end{aligned}\right\} \tag{28}$$

Factors of $\frac{1}{2}$ are introduced in cases in which the interstitialcy changes from A type to B type, and vice versa, because transitions of this type contribute equally to both types of current.

Expressions for the current I_a and I_b may be derived by subtracting from these quantities those corresponding to jumps from plane (2) to plane (1) and expanding in powers of λ. It is evident that the currents will satisfy the relation

$$I_i=I_a+I_b, \tag{29}$$

which is the counterpart of the relation

$$I_v=-I_a-I_b \tag{30}$$

in the case of vacancy diffusion.

If $n_i(a)$ and $n_i(b)$ can be expressed in terms of the chemical composition, that is, in terms of n_a, as would be the case if the concentration of interstitialcies is maintained at equilibrium locally, the derivatives $dn_i(a)/dx$ and $dn_i(b)/dx$ can be expressed in terms of dn_a/dx, and there will be relations of the form

$$I_a=-D_a\frac{dc_a}{dx}, \quad I_b=D_b\frac{dc_a}{dx}, \quad I_v=-(D_a-D_b)\frac{dc_a}{dx} \tag{31}$$

analogous to (21).

The flow of the interstitial current will be accompanied by an expansion of the material into which the current flows, so that relative to a region in which there is no chemical gradient a point fixed in the material will move with velocity

$$v=-\frac{1}{c}I_i, \tag{32}$$

analogous to (23). As previously, the chemical diffusion coefficient will have the value

$$D_c=f_bD_a+f_aD_b. \tag{33}$$

The velocity v appearing in (23) and (32) is the velocity with which markers that are attached to the material will move relative to regions of the system in which there is no concentration gradient, that is, the velocity which is observed in the Kirkendall experiment. The existence of such motion implies that D_a and D_b are unequal, for it is proportional to the difference D_a-D_b. In any interchange mechanism, such as any member of the family proposed by Zener, D_a and D_b must be equal, since the currents of A atoms and B atoms must balance exactly. In other words, whenever the Kirkendall experiment yields a positive result, Zener's mechanism cannot be the only one.

One interesting consequence of Darken's equations is the fact that chemical diffusion is allowed even when the vacancies or interstitialcies prefer to move only one type of atom. That is, D_c is finite even when one of the pair D_a or D_b is zero or at least very small. If a study of the Kirkendall effect shows that in any instance the measured values of v and D_c can be correlated on the assumption that either D_a or D_b is negligible, we shall have an unambiguous case in which diffusion occurs either by vacancies or interstitials alone. This case could probably occur only when both atoms are present to a very high density so that there is essentially an almost continuous network of each type.

Darken has postulated that the diffusion coefficients D_a and D_b which appear in any of the forms of diffusion theory should be expressible in terms of the radioactive diffusion coefficients D_a^* and D_b^* through relations of the type

$$D_a=D_a^*\frac{d(\mu_a/kT)}{d\log c_a}, \quad \frac{D_a}{D_b}=\frac{D_a^*}{D_b^*}, \tag{34}$$

in which μ_a is the chemical potential of an A atom. As mentioned in the early part of this Appendix, Bardeen has derived these relations on the basis of vacancy theory with the use of a simplified model in which it is assumed that the probability that a vacancy will replace an A atom in jumping into a given plane is proportional to the density of A atoms in that plane. As Bardeen has stressed, this assumption is exceedingly restrictive. It is probably not more general than the assumption that it is possible to separate the mixing entropy from other sources of entropy, which seems to be equivalent to assuming that A and B atoms behave as if they were chemically identical, although this identical behavior may depend upon the composition. We have attempted to see if the relations (34) could be derived on the basis of a more general model than that employed by Bardeen, but have not succeeded.

The writer is deeply indebted to Dr R. Shuttleworth for many interesting and valuable discussions of this topic.

Note added in proof: I am indebted to Prof. Mehl for an opportunity to read Da Silva's thesis. This investigator has appreciated independently many of the points made here. It should be added that this work seems to show that vacancies strongly prefer to diffuse through the zinc lattice in 70–30 brass.

References

Bardeen, J. (1949). *Phys. Rev.* **76**, 1403.

Barrer, R. M. (1941). *Diffusion in and through Metals.* Cambridge University Press.

Birchenall, C. E. & Mehl, R. F. (1947). *Trans. Amer. Inst. Min.* (*Metall.*) *Engrs*, **171**, 143.

Breckenridge, R. G. (1948). *J. Chem. Phys.* **16**, 959.

Breckenridge, R. G. (1949). *Phys. Rev.* **75**, 1282.

Darken, L. S. (1948). *Trans. Amer. Inst. Min.* (*Metall.*) *Engrs*, **175**, 184.

Estermann, I., Leivo, W. J. & Stern, O. (1949). *Phys. Rev.* **75**, 627.

Huntington, H. B. (1942). *Phys. Rev.* **61**, 325.

Huntington, H. B. & Seitz, F. (1942). *Phys. Rev.* **61**, 315.

Huntington, H. B. & Seitz, F. (1949). *Phys. Rev.* **76**, 1728.

Johnson, R. P. (1939). *Phys. Rev.* **56**, 814.

Kê, T. (1948). *J. Appl. Phys.* **19**, 285.

Lipson, H., Petch, N. I. & Stockdale, D. (1941). *J. Inst. Met.* **67**, 79.

Maier, M. S. & Nelson, H. R. (1942). *Trans. Amer. Inst. Min.* (*Metall.*) *Engrs*, **147**, 39.

Nabarro, F. R. N. (1948). *Strength of Solids.* Report of a conference held at Bristol in July 1947. London: Physical Society.

Rollin, B. D. (1939). *Phys. Rev.* **55**, 231.

Seith, W. & Keil, A. (1933). *Z. phys. Chem.* B, **22**, 350.

Seitz, F. (1946). *Rev. Mod. Phys.* **18**, 384.

Seitz, F. (1948). *Phys. Rev.* **74**, 1513.

Smigelskas, A. D. & Kirkendall, E. O. (1947). *Trans. Amer. Inst. Min.* (*Metall.*) *Engrs*, **171**, 130.

Smithells, C. J. (1949). *Metals Reference Book.* New York: Interscience.

Steigman, J., Shockley, W. & Nix, F. C. (1939). *Phys. Rev.* **56**, 13.

Stockdale, D. (1940). *J. Inst. Met.* **66**, 287.

Straumanis, M. E. (1949). *Acta Cryst.* **2**, 82.

Wagner, C. (1938). *Z. Phys. Chem.* B, **38**, 325.

Zener, C. M. (1947). *Phys. Rev.* **71**, 34.

Zener, C. M. (1950). *Acta Cryst.* **3**, 346.

Acta Cryst. (1950). **3**, 363

Über die Kristallstruktur des Natriumthioantimonats, $Na_3SbS_4.9H_2O$ (Schlippe'sches Salz)

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Powder diagrams of $Na_3SbS_4.9H_2O$ show the crystals to be cubic with $a = 11{\cdot}96 \pm 0{\cdot}02$ A., $n = 4$. The space group was taken to be $P2_13\text{–}T^4$, and atomic positions were assigned by trial-and-error methods based on considerations of co-ordination and on a comparison of observed and calculated intensities for 118 reflexions. The four Sb atoms are tetrahedrally surrounded by S at 2·37 A. Eight of the Na atoms are surrounded by 6 H_2O at $2{\cdot}46 \pm 0{\cdot}03$ A., and the remaining 4 Na by 3 S at 2·91 A. and 3 H_2O, both octahedra about Na being deformed. The S–H_2O distances lie between 3·15 and 3·52 A.

Einleitung

Im Jahre 1821 entdeckte Schlippe ein Salz, das nach ihm benannt wurde. Die Zusammensetzung des Salzes wurde von Rammelsberg (1841) festgestellt. Kristallographisch wurde es von Rammelsberg (1855, p. 201), Marbach (1856) und Wyrouboff (1886) untersucht. Röntgenographisch wurde es von Hui (1933) ($a = 11{,}835$ A., T^4) und Verhulst (1933) ($a = 12{,}02$ A., T^1) bearbeitet.

Eigenschaften

Die Kristalle lassen sich aus einer Lösung von Sb_2S_5 und S in NaOH als hellgelbe Tetraeder (*Gmelins Handbuch*..., 1928, Band 21, S. 974) gewinnen. Die Kristalle haben die Tendenz sich nach [111] zu strecken. Der Bruch ist muschelig. Zirkularpolarisation wurde von Wyrouboff festgestellt. Marbach misst, für die Wellenlänge $\lambda = 556\ m\mu$, $\alpha = 2{,}67°$. Ramaneffekt wurde beobachtet und gemessen (Feher & Morgenstern, 1937).

Röntgenographische Methoden

Die Gitterkonstante wurde durch Indizierung der Pulveraufnahmen mittels Cu $K\alpha$ (1,539 A.) und Fe $K\alpha$ (1,935 A.) Strahlung bestimmt.

$$a = 11{,}96 \pm 0{,}02 \text{ A.}$$

Die Dichte auf $n = 4$ bezogen ergibt sich als $\rho = 1{,}867$ g.cm.$^{-3}$, während sie in der Literatur mit $\rho = 1{,}864$ g.cm.$^{-3}$ angegeben ist. Drehkristallaufnahmen um [001] und [111] ergeben die systematische Abwesen-