Theory of Vacancy Formation in Internally Stressed Crystals under Pressure

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The equilibrium vacancy concentration in crystals, subject to hydrostatic pressures, or internal stress systems, or both, is calculated. The dependence of vacancy concentration on stresses is due to four major effects: (i) Work done by or against the externally applied hydrostatic pressure, as the volume of a crystal increases when an atom is removed from its interior to form a vacancy, and is redeposited on the crystal surface. (ii) The change in elastic energy of a stressed crystal because the vacancy with its immediate vicinity constitutes an elastically "soft" region. (iii) Work done by or against the normal stress components of the internal stress system as the material around the vacancy relaxes by V_R , the volume of relaxation. (iv) The change of localized modes of lattice vibrations, reacting to the strains in the vicinity of the vacancy. In addition, the zero point energy of the local modes is changed by strains, and an electrical interaction exists so as to attract vacancies to regions of compression. However, the latter two terms are negligible.

A theoretical formula is derived to take account of the named major effects, and is applied to dislocations in otherwise stress free isotropic crystals. It is found that in f.c.c. metals at high temperatures the frequency effect is dominant, causing vacancies to be repelled from regions of compression. A logical consequence of this results is that edge and mixed dislocations cannot climb readily, even though attracting vacancies. Some rather puzzling previous experimental observations may be explained on the basis of this result.

Derivation of the Basic Formula

Previously, the following equation has been derived¹⁾ for f_0 , the equilibrium vacancy concentration in a stress free crystal:

$$\ln f_{0} = -\frac{1}{kT} \left\{ U'(0) - U(0) + \frac{h}{2} \sum_{l} [\nu'_{l}(0) - \nu_{l}(0)] \right\} \\
+ \sum_{l} \ln \frac{\nu'_{l}(0)}{\nu_{l}(0)} \tag{1}$$

where U'(0) - U(0) is the difference in potential energy between a crystal containing one vacancy, and a reference crystal, alike in all respects except that it does not contain a vacancy. The symbols $\nu'_l(0)$ and $\nu_l(0)$ denote the frequencies of the *l* th normal mode, in the crystal containing the vacancy and in the reference crystal respectively. The symbols *h*, *k* and *T* have their usual meaning, namely Planck's constant, Boltzmann's constant and the absolute temperature. By inference, the equilibrium vacancy concentration, $f(\tau)$, in a -crystal subject to stresses τ_{ij} is given by

$$\ln f(\tau) = -\frac{1}{kT} \left\{ U'(\tau) - U(\tau) + \frac{h}{2} \sum_{l} [\nu'_{l}(\tau) - \nu_{l}(\tau)] + p \Delta V \right\} + \sum_{l} \ln \frac{\nu'_{l}(\tau)}{\nu_{l}(\tau)} . \quad (2)$$

When subtracting Eq. (1) from Eq. (2), the vacancy enhancement factor, $f(\tau)/f_0$, due to the application of a stress is found as

$$\ln \frac{f(\tau)}{f_0} = -\frac{1}{kT} \left\{ \Delta U(\tau) - U \Delta(0) + \frac{h}{2} \sum_{l} \left[\Delta \nu_l(\tau) - \Delta \nu_l(0) \right] + p \Delta V \right\} + \sum_{l} \left[\ln \frac{\nu'_l(\tau)}{\nu_l(\tau)} - \ln \frac{\nu'_l(0)}{\nu_l(0)} \right].$$
(3)

Here $\Delta U(\tau)$ is the potential energy difference between an internally stressed crystal containing a vacancy and its similarly stressed vacancy free reference crystal, while $\varDelta U(0)$ is the corresponding quantity for the unstressed state. No effect of externally applied forces appears in the expression for $\Delta U(\tau)$ for the reason that the extra elastic energy stored in an imperfect externally stressed crystal is completely compensated for by extra work done on the crystal by the surface forces. However, the crystal changes its volume by $\Delta V = v - V_R$, the difference between one atomic volume, v, and the volume of relaxation of a vacancy, V_R , when one atom is removed from its interior and is redeposited on its surface.

In the presence of an externally applied hydrostatic pressure, p, work is thereby done against this pressure, and this is the origin of the term $p\Delta V$ in Eq. (3). The other terms are $\Delta \nu_l(\tau) = \nu'_l(\tau) - \nu_l(\tau)$ and $\Delta \nu_l(0) = \nu'_l(0) - \nu_l(0)$.

The expression $\Delta U(\tau) - \Delta U(0)$ consists of two major parts (i) E_{Int} , the difference in stored elastic energy between a stressed crystal containing a vacancy and its similarly stressed vacancy free reference crystal, which is due to the fact that a vacancy causes an elastically "soft" region in the crystal and therefore is drawn towards regions of high stress, regardless of sign, and (ii) the pressure work, $1/3 \tau V_R$, with τ the sum of the normal stress components of the internal stress system at the position of the vacancy, expended as the material relaxes V_R on removing an atom. It is to be remembered that V_R is a negative quantity, *i.e.* the pressure work term is a linear function of strains and causes vacancies to migrate away from regions of dilatation and into regions of compression.

In an earlier investigation, Eshelby²) has derived E_{Int} , for the case of an ellipsoidal inclusion with modulus of rigidity, μ' , and compressibility κ' instead of μ and κ as in the rest of the material. It is, for a spherical inclusion of volume Ω ,

$$E_{Int} = \frac{\Omega}{2} \left[\frac{A}{g\kappa} \tau^2 + \frac{B}{2\mu} * \tau_{ij} * \tau_{ij} \right]. \quad (4)$$

Here $A = (\kappa' - \kappa) / [(\kappa - \kappa') \alpha - \kappa]$ with $\alpha = (1+\sigma)/3(1-\sigma)$, σ being Poission's ratio, and $B = (\mu' - \mu)/[(\mu - \mu')\beta - \mu]$ with $\beta = 2(4-5\sigma)/15(1-\sigma)$. Further, τ is the sum of normal stress components of the internal stress system, as before, while $*\tau_{ij} = \tau_{ij} - 1/3\tau\delta_{ij}$ is the deviatoric part of the internal stress components, with δ_{ij} Kronecker delta.

In order to apply this formula to vacancies, it is necessary to assign specific values to Ω , the volume surrounding a vacancy within which the elastic constants are significantly altered, to κ'/κ and to μ'/μ . This is possible without undue ambiguity when using a result by Dienes³⁾ that an atomic fraction c of vacancies causes an equal fractional change of Young's modulus, E, *i.e.* that E'/E=1-c. Since c may be expressed as $c=v/\Omega$, v being one atomic volume, this means that μ'/μ and κ'/κ are always close to unity, whether Ω is thought to encompass only the first-neighbor shell around the vacancy, or many. If, further, σ is constant, one has $\mu'/\mu = \kappa'/\kappa = g$ and with g close to unity, $A \cong B \cong 1-g$ for all values of σ . Since $c = v/\Omega$, and $g = \mu'/\mu =$ 1-c according to Dienes³⁾ one thus finds $\Omega A \cong$ $\Omega B \cong v$. From thereon the application of Eq. (4) is straightforward.

The pressure work term, $1/3\tau V_R$, is simple to evaluate since, on considering the motion of the atoms in the immediate vicinity of a vacancy, it becomes apparent that the effective value of V_R is never far from v/2, *i.e.* never far from one half of an atomic volume.

The part $h/2\sum_{l} [\Delta \nu_{l}(\tau) - \Delta \nu_{l}(0)]$ of Eq. (3) reflects the change of zero point energy of the vibrational modes of the crystal. It can be shown that this is negligible.

In the remaining part of Eq. (3), the "frequency term" $\sum_{l} [\ln \nu'_l(\tau) / \nu_l(\tau) - \ln \nu'_l(0) / \nu_l(0)] = C$ appears to be the most interesting. It is almost exclusively governed by changes in localized modes of vibrations at the vacancy when stresses are applied. One finds that this effect causes vacancies to be repelled from regions of compression, attracted to regions of dilatation, and that it is linear in the strains. It thus opposes the pressure work term.

The theoretical treatment of *C* is somewhat involved and rests on the application of Gruneisen's relationship for the relative change of vibrational frequencies, $\delta\nu/\nu_0$, due to relative changes of volume, $\delta V/V_0$, namely $\delta\nu/\nu_0 =$ $-\gamma \delta V/V_0$, where $\gamma \cong 2$ is the Gruneisen constant. The final result obtained is

$$C = \gamma Z \kappa_1 \left[\frac{1}{V_0} \int_{Orystal} \varepsilon d\vec{r} - \varepsilon \right] + \frac{3\Omega}{v} \gamma (1 - \kappa_1) \varepsilon.$$
 (5)

Besides the symbols defined above, including V_0 , the volume of the crystal in the unstressed state, this equation contains Z, the number of nearest neighbor atoms to the vacancy, ε , the sum of the normal strains due to internal and external stresses, and $\kappa_1 = \kappa/[\kappa - (\kappa - \kappa')\alpha]$ with $\alpha = (1+\sigma)/3(1-\sigma)$, as introduced before. Also, as we saw already, $g=1-c=1-v/\Omega$ which is always close to unity. Moreover, $\kappa_1 \cong 2-p$ for g near unity and thus $3\Omega(1-\kappa_1)/v=-3$. If this is correct, C becomes the dominant of all contributions to $\ln(f(\tau)/f_0)$ in internally stressed crystals at high temperatures.

In addition to the contributions discussed

already, $\Delta U(\tau)$ contains an electric interaction energy. This is due to the fact that vacancies carry a net negative charge, and regions of dilatation and of compression carry a net negative and a positive charge respectively. Cottrell, Hunter and Nabarro⁴ have previously investigated this effect for the case of noble metals. They concluded that the resulting interaction energies are insignificant.

In summary, then, the ratio of the equilibrium vacancy concentration in internally stressed crystals subject to an external hydrostatic pressure, divided by that in stress free crystals is given by

$$\ln \frac{f(\tau)}{f_0} \simeq -\frac{1}{kT} \left\{ p \varDelta V + \frac{v}{2} \left[\frac{\tau^2}{g\kappa} + \frac{*\tau_{ij} * \tau_{ij}}{2\mu} \right] - \frac{v\tau}{6} \right\} - 2Z \left[\frac{1}{V_0} \int \varepsilon d\vec{r} - \varepsilon \right] + 6\varepsilon \quad (6)$$

provided the various parameters are evaluated as discussed.

Application of the Formula to Dislocations

One of the most suitable problems for the application of the above theory is the distribution of vacancies at dislocations. This is one case in which stresses and strains reach values sufficiently high to cause significant deviations of $f(\tau)/f_0$ from unity.

No particular difficulties are encountered when calculating the equilibrium vacancy distribution in the elastic stress field of dislocations. It is found that outside of a distance of about 20Å from a dislocation axis in typical metals the value of $f(\tau)/f_0$ is close to unity.

Much more interesting is the behavior of $f(\tau)/f_0$ at closer distance from dislocation axes, but the treatment of this region is complicated by the fact that linear elasticity theory breaks down in it. The radius of the region in which linear elasticity theory is not obeyed, *i.e.* the radius of the dislocation cores, is defined as $r_0 = A_D/\tau_{crit}$. It is $A_D = A_S = \mu b/2\pi$ for screw dislocations, and $A_D = A = \mu b/2\pi (1-\sigma)$ for edge dislocations, where σ is Poisson's ratio, and $\tau_{crit} = \mu/g$ is the theoretical shear strength of the crystal. The parameter g assumes its highest value of $g \cong 30$ for close packed metals and is lower for all other types of crystals.

Utilizing the known value of the energy of dislocation cores, being about 1 eV per atomic

plane, allows to define and estimate the magnitude of what may be called the "equivalent core stress". This is found to be about $2\tau_{crit}$ in average, and between $3\tau_{crit}$ and $6\tau_{crit}$ as a maximum value. The average strain in a dislocation core, on the other hand, is composed of two parts: (i) An overall dilatation due to non-linearity, amounting to about one atomic volume per atomic plane. (ii) The strain of about $(b/2)/2r_0$, arising because the dislocation core of total width $2r_0$ may be regarded as the boundary between an unslipped region and a region slipped by b; of which b/2 is the deformation of the plane above the slip plane, and b/2 that of the plane below it. It is estimated that the maximum strain is not far from twice the average strain in the core.

With the above values it is shown that, in typical metals, the interaction energy, E_{Int} , is small under all circumstances, contrary to the findings of Bullough and Newman⁵⁾. The pressure work term is not negligible and may reach 1/3 eV at the center of an edge dislocation in a typical f.c.c. metal. Finally the frequency term, *C*, always opposes the pressure work term, and, at intermediate temperatures, is of comparable magnitude.

Discussion

From the preceding calculations it appears that the interaction energy due to the relaxation around a vacancy, as well as the equivalent binding energy due to the frequency effect are both much larger than all other contributions to the binding energy between vacancies and dislocations. These two terms are linearly related to compressional and dilatational stresses, respectively strains, but have opposite sign. Moreover, the pressure work term gives rise to a binding energy, resulting in an enhancement of vacancy concentration in the compressed parts of the core which decreases with increasing temperature. The frequency effect, by contrast, lowers the vacancy concentration in the compressed regions, and increases it in the dilated regions, such that vacancy enhancement factor is constant, independent of the Thus, the overall vacancy temperature. enhancement factor due to both processes combined goes through a minimum at some intermediate temperature. Below this temperature range, the vacancies are attracted to the regions of compression, above it they are increasingly repelled from the regions of compression and are instead attracted to regions of dilatation.

As a result, dislocations are expected to lose almost all of their vacancy atmospheres at intermediate temperatures. At both, high and low temperatures, the net increase in relative vacancy concentration in the cores of edge dislocations becomes significant. However, edge dislocations are not expected to climb readily at high temperatures, in spite of their vacancy atmosphere, because, in order for climb to occur, vacancies must enter the compressed region of the core. On the other hand, conditions might well be favorable for pipe diffusion along the dilated part of the core. The discussed characteristics diminish as the angle between the Burgers vector and the dislocation axis decreases and, consequently, the normal stress components diminish.

If the above results are accepted, several hitherto rather puzzling observations are thereby explained. These have previously been discussed in considerable detail⁶⁾ and

point to the fact that edge dislocations are not ready sources and sinks for vacancies, particularly not at high temperatures.

A detailed account of this research is to be published elsewhere.

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DISCUSSION

Krumhansl, J. K.: Would you comment briefly on the type of dilatation field which you assumed in computing the contribution of localized modes?

Girifalco, L. A.: We used a general strain matrix. The localized modes were taken as vectors directed towards the center of the vacancy. The strain dyadic was then dotted into the frequency vectors to appropriately change its length and orientation.

Seeger, A.: Using Grüneisen's constant in estimating the changes in the vibrational free energy is equivalent to using quadratic elasticity theory. Should not also all the other second-order contributions be included in the calculation, *e.g.* the quadratic contribution to the stress-field of the dislocation?

Girifalco, **L. A.**: It would certainly be more rigorous to use second order elasticity theory. However, using Grüneisen's constant is analogous to using linear elasticity with temperature dependent elastic constants. The frequency effect becomes comparable to the linear elastic effects only when the strains are high near the vacancy and low far from the vacancy. This is not the result of the order of the approximation, but merely of the functional form of the strain field.

Sines, G.: In many phenomena in which the interaction energy appears, such as diffusion and some dislocation-point defect interactions, the energy appears as a multiple of 1/kT. I suggest that it would be useful to also express the interaction in this manner.

Girifalco, L. A.: We were interested in binding energies and therefore expressed our results in these terms.