MECHANICAL PROPERTIES AND IMPERFECTIONS IN CRYSTALS*

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I. Introduction

The main purpose of this chapter is to call the attention of rheologists to a relatively new and rapidly expanding field. It is generally understood by now that crystal imperfections of various kinds are responsible for many interesting and important features of the mechanical properties of solids. Conversely, one can learn a great deal about imperfections in crystals from a systematic study of their mechanical properties.

Instead of an exhaustive review, which is hardly possible in a short

* Under contract with the U. S. Atomic Energy Commission.
[1] E. Schmid and W. Boas, "Plasticity of Crystals," F. A. Hughes, London, 1952.
[2] F. Seitz, "Physics of Metals," McGraw-Hill, New York, 1943.
[3] F. Seitz, Phil. Mag. Suppl. 1, 43 (1952).
[4] A. H. Cottrell, "Dislocations and Plastic Flow in Crystals," Oxford Univ. Press, New York, 1953.
[5] W. T. Read, "Dislocations in Crystals," McGraw-Hill, New York, 1953.
[6] C. Kittel, "Introduction to Solid State Physics," Wiley, New York, 1953.
[7] C. S. Barrett, "Structure of Metals," McGraw-Hill, New York, 1952.
[8] Plastic Deformation of Crystalline Solids, Carnegie-ONR Conference. U. S. Department of Commerce, PB 104604, 1950.

article, some representative topics will be treated in order to give the reader a picture of the types of problems which have been studied. A general bibliography is given in footnotes 1 to 17. It is assumed that the reader is familiar with the general features of dislocation theory discussed in other chapters in this book. In Section II a brief discussion is given of imperfections in crystals. In Section III the associated mechanical properties are discussed arranged in order of complexity from elastic moduli through anelastic phenomena to plastic deformation.

II. Imperfections in Crystals

A general definition of crystal imperfections may be given as follows: any departure from perfect periodicity in a crystalline lattice constitutes an imperfection. Obviously, on the basis of this definition, a perfect crystal (apart from zero point vibrations) can only exist at absolute zero since thermal vibrations of the atoms represent imperfections (phonons). For the present purpose thermal vibrations will not be considered as imperfections nor shall we be concerned with excitons, electrons, and holes. The classification given here is, therefore, more restricted than that of Seitz.[11] Attention will be focussed on the following types of imperfections:

1. IMPURITY ATOMS

Foreign atoms may be introduced into a crystal by a variety of methods, either into interstitial positions or as substitutes for normal atoms of the lattice. At high concentrations alloys and mixed crystals are formed.

2. ORDER-DISORDER TRANSITIONS

In a crystal consisting of two or more types of atoms these atoms may be arranged randomly or in order on the lattice sites. Above a certain temperature thermal agitation will keep the atoms in a disordered state, i.e., randomly arranged on the fixed lattice sites. Below the transition temperature

[9] Report of a Conference on the Strength of Solids, University of Bristol. Physical Society, London, 1948.

[10] C. Zener, "Elasticity and Anelasticity of Metals." Univ. of Chicago Press, Chicago, 1948.

[11] Shockley, J. H., Hollomon, R. Maurer, and F. Seitz (eds.), "Imperfections in Nearly Perfect Crystals." Wiley, New York, 1952.

[12] R. Smoluchowski, J. E. Meyer, and W. A. Weyl (eds.), "Phase Transformations in Solids." Wiley, New York, 1951.

[13] F. R. N. Nabarro, *Phil. Mag.* Suppl. 1, 271 (1952).

[14] F. C. Frank, *Phil. Mag.* Suppl. 1, 91 (1952).

[15] N. F. Mott, *Proc. Phys. Soc. (London)*, **B64,** 729 (1951).

[16] N. F. Mott, *Phil. Mag.* **43,** 1151 (1952); **44,** 742 (1953).

[17] A. H. Cottrell, "Progress in Metal Physics" (B. Chalmers, ed.), Vol. 1, Butterworths, London, 1949; Vol. 4, Pergamon, London, 1953.

ordering may take place, provided the decrease in internal energy due to ordering is not outweighed by the decrease in entropy. In these cases the irregular arrangement of the different types of atoms on the lattice sites constitutes the imperfection. Many order-disorder alloys have been investigated.[18]

3. VACANT LATTICE SITES (VACANCIES)

There exist in a crystal in thermal equilibrium a number of vacant lattice points. A finite concentration of vacancies is a thermodynamic requirement at any temperature above absolute zero.[19, 20] A non-equilibrium number of vacancies may be "frozen-in" by quenching or created by fast particle bombardment.[21] In the alkali halides vacant positive- and negative-ion sites are normally generated in equal numbers. These imperfections are commonly called Schottky defects, because Schottky first suggested this mechanism of electrolytic conductivity.[22]

4. INTERSTITIAL ATOMS

This imperfection is created by squeezing an extra atom into the lattice with the extra atom located on a nonlattice site. It is a counterpart of the vacancy and the comments above apply equally well to this imperfection. Vacancies and interstitials may be produced simultaneously in pairs either thermally or by fast particle bombardment by moving a normal atom into an interstitial position and leaving a vacancy behind. These latter imperfections are usually called Frenkel defects.[23]

5. CLUSTERS OF IMPERFECTIONS

It is known that vacancies, and also probably interstitials, tend to combine into pairs or larger clusters.[3, 11, 24-27] Foreign atoms, of course, may tend to precipitate. These clusters are expected to have properties which

[18] For reviews see: F. C. Nix and W. Shockley, *Revs. Mod. Phys.* **10**, 1 (1938); H. Lipson, *in* "Progress in Metal Physics" (B. Chalmers, ed.), Vol. 2, p. 1. Butterworths, London, 1952.

[19] N. F. Mott and W. Gurney, "Electronic Processes in Ionic Crystals." Clarendon Press, Oxford, 1950.

[20] J. Frenkel, "Kinetic Theory of Liquids." Oxford Univ. Press, London, 1946.

[21] For recent review see: G. J. Dienes, *Ann. Rev. Nucl. Sci.* **II**, 187 (1953); *J. Appl. Phys.* **24**, 666 (1953).

[22] W. Schottky and C. Wagner, *Z. physik. Chem.* **IIB**, 163 (1930); W. Schottky, *Z. physik. Chem.* **29B**, 353 (1935).

[23] J. Frenkel, *Z. Physik* **35**, 652 (1926).

[24] F. Seitz, *Revs. Mod. Phys.* **18**, 384 (1946).

[25] G. J. Dienes, *J. Chem. Phys.* **16**, 620 (1948).

[26] J. R. Reitz and J. L. Gammel, *J. Chem. Phys.* **19**, 894 (1951).

[27] J. H. Bartlett and G. J. Dienes, *Phys. Rev.* **89**, 848 (1953).

are quite different from those associated with isolated atomic imperfections. Apart from precipitates very little is known about the properties of these clusters.

6. DISLOCATIONS

These imperfections are discussed in detail in other chapters of this book. The interactions of dislocations with the above imperfections are the processes which determine most of the plastic properties of imperfect crystals.

III. Effect of Imperfections on Mechanical Properties

1. ELASTIC CONSTANTS

The elastic constants of solids are best understood theoretically since they are calculable from first principles although very few such calculations have been performed.[28-31] The elastic moduli of a crystal are given by the second derivatives of the elastic potential energy per unit volume with respect to the strains. Thus, if the interatomic potential functions are known for the crystal the moduli can be calculated. The mathematical techniques are worked out in considerable detail.[32-34] However, when imperfections are present, one does not know how the potential functions are modified or how one should average over the crystal to derive the modified bulk properties of such a heterogeneous substance. At the present time, therefore, theoretical methods are not available for calculating the desired properties from first principles and all interpretation must be done on a semitheoretical basis.

Consider first substitutional impurity atoms in an otherwise perfect lattice. Ordinary substitutional alloys are excellent examples of this situation and a considerable body of experimental information is available for polycrystalline materials. The experiments of Köster and Rauscher[35] on a large number of binary systems show clearly that a wide diversity of behavior is observed when Young's modulus is plotted as a function of composition. It is unlikely that any single factor could account for the experimental results.

[28] K. Fuchs, *Proc. Roy. Soc. (London)* **A153,** 622 (1936); **A157,** 444 (1936).

[29] D. S. Leigh, *Phil. Mag.* **42,** 139 (1951).

[30] R. Landsoff, *Z. Physik* **102,** 201 (1936).

[31] P. O. Löwdin, A Theoretical Investigation into some Properties of Ionic Crystals. Thesis, Uppsala, 1948.

[32] M. Born, *J. Chem. Phys.* **7,** 591 (1939).

[33] R. Furth, *Proc. Cambridge Phil. Soc.* **37,** 34 (1941); *Proc. Roy. Soc. (London)* **183,** 84 (1945).

[34] M. M. Gow, *Proc. Cambridge Phil. Soc.* **40,** 151 (1944).

[35] W. Köster and W. Rauscher, *Z. Metallkunde* **39,** 111 (1948).

Zener[36] considered theoretically one aspect of this problem, namely, the long-range elastic strain resulting from distortion around the impurity atoms. Using elasticity theory Zener showed that the long-range elastic strain always leads to a decrease in the modulus, regardless of whether the impurity atom is smaller or larger than the solvent. As intimated above Zener's theory only accounts for part of the experimental observations since it does not take into account any changes in chemical bonding. Further, if the strains around the impurity atom are large, elasticity theory is not applicable near the impurity.

In addition to the above size effect there are electronic or chemical effects. The alteration of the binding force which occurs upon replacing a solvent atom by a solute atom is accompanied, of course, by a change in the interatomic potential functions and hence by a change in the moduli. One should apply the band theory of solids to this problem, but this is very difficult and has only been discussed qualitatively.[37] On a phenomenological basis one can proceed with some simplifying assumptions in the following manner. Assume that the interatomic forces are central and act between nearest neighbors only. Then the potential energy, V, of an alloy in random distribution may be written as

$$V = x^2 V_{AA}(r) + (1 - x)^2 V_{BB}(r) + 2x(1 - x) V_{AB}(r) \qquad (1)$$

where x = atomic fraction of component A, V_{AA}, V_{BB}, and V_{AB} are the interaction energies between neighboring A, B, and AB atoms, respectively. The elastic moduli are then given by the second derivatives with respect to r with suitable coefficients to take into account the type of crystal lattice.[28, 38] The derivatives are to be evaluated at the equilibrium volume existing in the alloys. It is evident that both an increase and a decrease in moduli is possible depending on the relative magnitudes of V_{AA}, V_{BB}, and V_{AA}, and the corresponding volume change. This is then one way of expressing the chemical or bonding effect and it has been used with some success by Shibuya[39] for various alloys. Considerable further progress can be made as data become available on single crystals of alloys since essentially all the parameters can be evaluated from the three elastic moduli. There is a surprising lack of data in the literature on single crystals.

Thus, as far as impurity atoms are concerned at least three factors must be taken into account in analyzing the changes in the elastic moduli: (1) large distortion around the impurity, (2) long-range elastic distortion, and (3) chemical or bonding effect.

[36] C. Zener, *Acta Cryst.* **2**, 163 (1949); see also J. D. Eshelby, *J. Appl. Phys.* **25**, 255 (1954).

[37] A. D. N. Smith, *J. Inst. Metals* **80**, 477 (1951–2).

[38] G. J. Dienes, *Phys. Rev.* **86**, 228 (1952).

[39] Y. Shibuya, *Sci. Repts. Tôhoku Univ.* **A3**, 645 (1951).

The approach represented by equation (1) may also be applied to some simple order-disorder transformations. Shibuya has used this approach with some success.[40] Experimentally it is known that both AuCu and AuCu$_3$ exhibit a decrease in moduli upon disordering.[35] Unfortunately, data on single crystals, which are needed for a quantitative analysis, are only available for ordered AuCu$_3$.[41] Presumably, the moduli increase upon ordering because of the change of the kind of nearest neighbors, i.e., the distribution of Au-Au, Cu-Cu, and Au-Cu bonds, as well as because of the contraction in volume.

The study of the change in the elastic constants due to the presence of vacancies and interstitials has not progressed very far as yet. On the basis of a simple theory, based on the repulsive interactions of the closed ion shells in close packed metals, Dienes[42] concluded that the presence of interstitial atoms will result in an appreciable increase in the moduli. The repulsive potential is of an exponential nature and varies extremely rapidly with interatomic distance. As the interaction distance is shortened by creating an interstitial the energy of the system increases sharply on the repulsive side of the potential curve while the creation of vacancies results essentially in the destruction of some normal interactions. Thus, one expects the influence of the interstitials to outweigh heavily the effect of the vacancies. Experimental confirmation of this analysis is not yet at hand.

Another effect should be discussed briefly although it belongs to the topic of interaction of dislocations with imperfections. This is the change in the elastic response of a dislocation produced by the presence of impurity atoms or imperfections. Mott[43] has pointed out that the presence of a network of dislocations leads to a decrease of the rigidity modulus since under a small shear stress a dislocation line AB locked at A and B responds elastically to the shear stress. Friedel[44] has extended the calculation to solid solutions assuming that the dislocations are pinned down by the solute atoms. According to this picture the addition of solute atoms will always at first increase the shear modulus by shortening the free dislocation length. Reasonable agreement was obtained with the experiments of Bradfield and Pursey.[45] Implications of the elastic response of the dislocations at small amounts of cold work have been discussed by Smith.[46]

[40] Y. Shibuya, *Sci. Repts. Tôhoku Univ.* **A1,** 161 (1949).

[41] S. Siegel, *Phys. Rev.* **57,** 537 (1940).

[42] G. J. Dienes, *Phys. Rev.* **86,** 228 (1952); **87,** 666 (1952); see also N. R. F. Nabarro, *Phys. Rev.* **87,** 665 (1952).

[43] N. F. Mott, *Phil. Mag.* **43,** 1151 (1952).

[44] J. Friedel, *Phil. Mag.* **44,** 444 (1953).

[45] G. Bradfield and H. Pursey, *Phil. Mag.* **44,** 437 (1953).

[46] A. D. N. Smith, *Phil. Mag.* **44,** 453 (1953).

2. ANELASTIC PHENOMENA

As one proceeds from the simple to the more complex mechanical properties one encounters next the group of phenomena which is characterized by the time dependence of stress and strain. Internal friction, recoverable creep, stress relaxation, and elastic aftereffect at low stress levels are typical experimental observables. A sound phenomenological description exists for these phenomena in terms of linear differential equations relating stress, strain, and their time derivatives. Stress and strain are still linearly related and the material obeys the Boltzmann superposition principle. The fundamentals are well described by Zener[10] for metals and Alfrey[47] for high polymers. An excellent modern review has been published by Nowick[48] in which the basic atomic rearrangements responsible for anelasticity (as well as static hysteresis and amplitude-dependent internal friction) are discussed in detail.

In this article one typical case will be discussed in detail which illustrates many of the features of anelasticity phenomena which depend on the motion of lattice imperfections. Consider a crystal of α-iron (body-centered cubic) which contains a low concentration of interstitial carbon atoms in solution. The interstitial positions, namely the centers of the faces and edges, have tetragonal symmetry. In a stress-free crystal the interstitial atoms are distributed isotropically but in the presence of stress the equilibrium distribution is no longer isotropic. For example, a tensile stress along the (100) axis will induce a preferential distribution in which each interstitial atom has a greater probability of being in an interstitial position whose tetragonal axis is along the (100) axis than along either of the other two $\langle 100 \rangle$ axes. The continual striving of the metal to maintain an equilibrium distribution will give rise to time-dependent mechanical responses. This is a typical example of stress-induced ordering for which the general requirement is that a change in the state of order result in the production of strain. The associated physical changes will be observable provided the interstitial atoms have sufficient mobility to achieve the new equilibrium configuration within the time-scale used in the experiment. It has been shown[48] that the behavior of such a material is very well approximated by the behavior of the "standard linear solid" which is characterized by a single time of relaxation. The behavior of the standard linear solid is governed by the differential equation

[47] T. Alfrey, "Mechanical Behavior of High Polymers." Interscience, New York, 1948.

[48] A. S. Nowick, in "Progress in Metal Physics" (B. Chalmers, ed.), Vol. 4, pp. 1–71. Pergamon, London, 1953.

$$\dot{\epsilon}'' = -\left(\frac{1}{\tau_r}\right)(\epsilon'' - \Delta_M\epsilon') \tag{2}$$

where $\epsilon'' =$ non-elastic strain, $\epsilon' =$ elastic strain, $\Delta_M =$ relaxation strength, and $\tau_r =$ relaxation time.

When a harmonic solution is substituted into (2) the result is

$$\frac{\epsilon''}{\epsilon'} = \frac{\Delta_M}{1 + i\omega\tau_r} \tag{3}$$

and separation into real and imaginary parts yields for the internal friction and the dynamic modulus

$$\Phi = \Delta_M \frac{\omega\tau_r}{1 + \omega^2\tau_r^2} \tag{4}$$

$$M = M'\left(1 - \frac{\Delta_M}{1 + \omega^2\tau_r^2}\right) \tag{5}$$

The internal friction curve, plotted as Φ vs $\log(\omega\tau)$, is symmetrical with the peak value equal to $\Delta_M/2$ at $\omega\tau = 1$. The internal friction peak caused by interstitial solutes was first interpreted correctly by Snoek.[49]

The retardation time for internal friction is simply related to the mean time of stay, τ, of an atom at a given lattice site for the b.c.c. lattice, namely,

$$\tau = \tfrac{3}{2}\tau_r$$

The diffusion coefficient of interstitial carbon in α-iron is given by[50, 51]

$$D = \frac{a^2}{24}\frac{1}{\tau}$$

where D is the diffusion coefficient and a is the lattice parameter. From the position of the peak at any given temperature τ_r, and, therefore, D is immediately calculable. At lower temperatures, it is more convenient to measure the elastic aftereffect which is the decay of the nonelastic strain after removal of stress and is given by the solution of equation (2) putting $\epsilon' = 0$. By a combination of these methods D can be measured over a very wide temperature range and in a temperature region which is inaccessible to conventional diffusion techniques because of the tremendously long time required for bulk diffusion compared to the atomic jumps measured by anelasticity. The carbon diffusion data, representing a combination of techniques, are shown in Fig. 1. Not only is agreement observed among the various methods but it is also evident that unusually precise data have been obtained over a very wide temperature range.

[49] J. Snoek, *Physica* **6**, 591 (1939).
[50] C. A. Wert, *Phys. Rev.* **79**, 601 (1950).
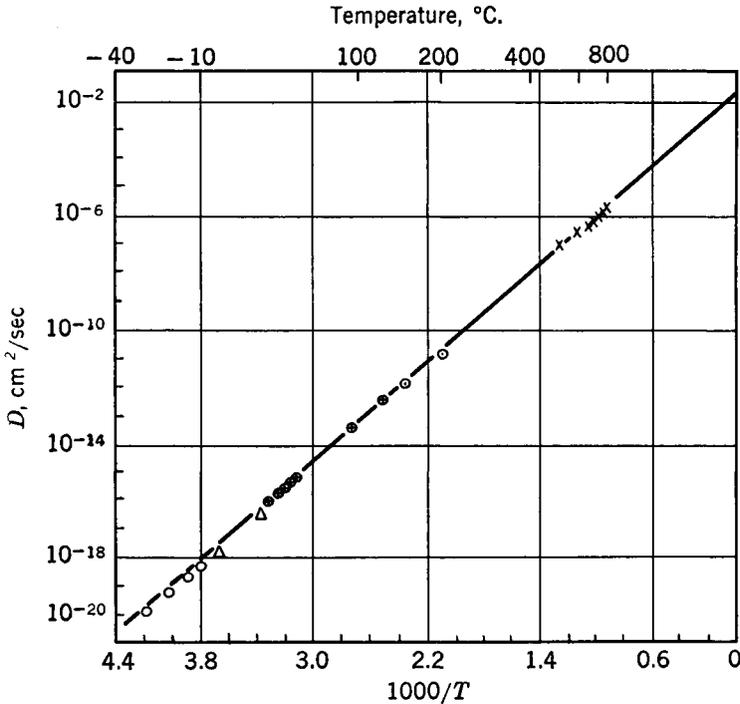[51] C. Wert and C. Zener, *Phys. Rev.* **76**, 1169 (1949).

FIG. 1. Diffusion coefficient of C in α-iron as a function of $1/T$. The data are identified as follows: $\bigcirc$, $\triangle$—elastic after effect; $\oplus$—internal friction; $\odot$—precipitation measurements; $\times$—bulk diffusion measurements. (*After C. Wert*[50]).

The case of internal friction resulting from interstitial carbon in iron was discussed in detail because it represents a clear case where one understands the underlying mechanism of the anelastic mechanical response. Further, in addition to understanding the mechanical response, these studies show that a great deal can be learned by such techniques about various solid-state processes, in this case interstitial diffusion. Many other anelastic phenomena have been studied and are understood in a more or less satisfactory manner. For these the reader is referred to Nowick's[48] article. The writer belives that the example treated here may be considered to be a prototype for many others.

3. PLASTIC PROPERTIES

Dislocation theory and the interaction of dislocations with other dislocations are treated elsewhere in this book. This section is concerned mainly with the interaction of dislocations with other lattice imperfections. The interaction occurs by means of the stresses created in the crystal by the presence of the dislocations and the other imperfections. There is a further interplay which will not be emphasized in this treatment. The interaction

of dislocations during their motion may create vacancies and interstitials and conversely, dislocations can also absorb these lattice imperfections. While some features of this process will be discussed, namely the interplay between mechanical stresses and concentration of vacancies in high-temperature creep and diffusion, the reader is referred to recent papers by Seitz[3] and Mott[16, 43] for a thorough treatment.

a. Interaction of Dislocations and Impurity Atoms

The interaction of dislocations with impurities has been studied in considerable detail. The theory, mainly developed by Mott and Nabarro,[52-54] will be reviewed briefly. Impurity atoms, in any state of dispersion, create internal stresses, σ_i, in the crystal. These stresses impede the motion of dislocations and can be overcome only if the applied stress is larger than some average of the internal stresses. Dislocation lines are known to be flexible and can, therefore, to some extent bend around regions of high stress. Consequently, the proper averaging of the internal stresses is the crux of the problem, and this average will depend on the scale of dispersion of the impurity atoms. The limiting radius of curvature, r, to which a dislocation can be bent by internal stress, σ_i is given by

$$ r = \frac{\alpha \mu a}{\sigma_i} \tag{6} $$

where a is the interatomic distance, μ is the shear modulus and α is a constant of the order of $\frac{1}{2}$. Let Λ be the distance between the impurity particles. Then Λ also represents the distance between the centers of stress, i.e., it can be thought of as the wavelength of σ_i.

In a solid solution $\Lambda \sim a/c^{1/3}$, where c is the atomic concentration of solute. Since $\Lambda \ll r$ the dislocations will not be deviated appreciably by the local stresses and the appropriate value for σ_i is the volume average. If the misfit of the foreign atom in the lattice is ϵ, evaluated as $\epsilon = 1/a\, da/dc$, then the tangential strain at a distance r is given by $\epsilon\, a^3/r^3$ and the shear stress by $\mu\epsilon\, a^3/r^3$. The volume average of σ_i is then given by

$$ \sigma_i = \frac{\int_a^\Lambda \left(\frac{\mu\epsilon a^3}{r^3} \right) 4\pi r^2\, dr}{\int_a^\Lambda 4\pi r^2\, dr} \cong \mu\epsilon c \log \frac{1}{c} \tag{7} $$

[52] N. F. Mott and F. R. N. Nabarro, *Proc. Phys. Soc. (London)* **52,** 86 (1940); Report of a Conference on the Strength of Solids, University of Bristol, pp. 1–20. Physical Society, London, 1948.

[53] N. F. Mott, *J. Inst. Metals.* **72,** 367 (1946).

[54] F. R. N. Nabarro, *Proc. Phys. Soc. (London)* **58,** 669 (1946).

The angle turned along a length Λ of the dislocation line is very small and such a loop will not move independently through the distance of order Λ because the amplitude of such a loop is also small. Consequently, a longer piece of dislocation consisting of several loops will have to move as a whole. When this is taken into account it can be shown[55] that the yield stress of the material is given, in terms of σ_i, by

$$\sigma = \frac{\sigma_i}{2} \left(\frac{\Lambda \sigma_i}{\alpha \mu a} \right)^{1/3} \tag{8}$$

substitution for σ_i and Λ gives

$$\sigma = \frac{1}{2} \mu \epsilon^{4/3} c \left[\frac{c^{2/3} (\log c)^4}{\alpha} \right]^{1/3} \tag{9}$$

In the concentration range 10^{-3} to 10^{-2} a good approximation to (9) is given by

$$\sigma = 2.5 \ \mu \epsilon^{4/3} c \tag{10}$$

Dependence on ϵ and c is in rough agreement with experiment but the factor $2.5 \ \mu$ is too large. The theory can be further refined, for example, by allowing for the temperature dependence of the yield stress. Another complicating factor arises from differences in the valency of the solute. When the valency difference is large the solute atoms have a greater hardening effect, for the same size factor, than those whose valency is near to that of the solvent.[56, 57]

Consider next slip in precipitation hardened alloys. In this case one expects $\Lambda \cong \alpha \mu a / \sigma_i$, i.e., the dislocation can avoid the obstacles by being bent into loops whose wavelength is of the order of Λ. Thus, each loop can move largely independently of the others and the effective internal stress is given by the arithmetic average. Let the crystal contain N particles per unit volume of radius r_0 and misfit ϵ. The average distance from a point in the matrix to the particle is about $\frac{1}{2} N^{-1/3}$ and, therefore, the average shear stress is given by

$$\sigma_i = \mu (8 \epsilon r_0^3 N)$$

But $r_0^3 N \cong \frac{3}{4} c / \pi$ and therefore

$$\sigma_i \cong 2 \ \mu \epsilon c \tag{11}$$

[55] N. F. Mott, *in* "Imperfections in Nearly Perfect Crystals" (W. Shockley *et al.*, eds.), pp. 173–197. Wiley, New York, 1952.

[56] J. E. Dorn, P. Pietrowsky, and T. F. Tietz, *Trans. Am. Inst. Mining Met. Engrs.* **118**, 933 (1950).

[57] N. P. Allen, T. H. Schofield, and A. E. L. Tate, *Nature* **168**, 378 (1951).

It can be shown further that thermal agitation will have a very small effect on σ_i so that (11) represents the yield stress σ. The corresponding Λ, obtained from $\Lambda = \alpha a/2\epsilon c$ by putting $\epsilon \sim \frac{1}{5}$, $c \sim \frac{1}{40}$, $\sigma_i \sim \mu/100$, turns out to be about 50 atomic spacings in excellent agreement with experiment. It is known experimentally that the maximum hardness occurs at about this stage of precipitation.

If the alloy is overaged, so that Λ becomes large compared to $\alpha\mu a/\sigma_i$, the alloy becomes "soft". Orowan[58] proposed an explanation by suggesting that the obstacles can be by-passed by bending the dislocations. In order to accomplish this the dislocation line must be bent into loops of radii of the order of $\Lambda/2$. The stress required is given by

$$\sigma = \frac{2\alpha\mu a}{\Lambda} \tag{12}$$

showing that the stress decreases with increasing Λ. If $\Lambda > 2\,\alpha\mu a/\sigma_i$ then $\sigma < \sigma_i$ and the yield strength for the Orowan process is smaller than that estimated for the fully aged alloy. The maximum yield stress occurs for $\Lambda \sim \alpha\mu a/\sigma_i$.

A different type of interaction between a dislocation and an impurity atom has been studied in detail by Cottrell,[59, 60] who suggested that impurity atoms may diffuse to the neighborhood of dislocations and lock them into position. In order for this effect to occur the free energy for the process must be favorable at a temperature where diffusion of the impurity atoms can occur. Physically the suggestion is roughly as follows: In the neighborhood of a dislocation the lattice is compressed on the upper side of the dislocation and expanded on the lower side. A solute atom, which is larger than the solvent atom, will be attracted to the region of dilation since stress will be relieved by locating the solute atom in this region. Similarly, a solute atom which is smaller than the solvent atoms will be attracted to the region of compression.

The above interaction can be investigated quantitatively within the approximation of elasticity theory. The interaction energy for a solute atom in a stress field is given by

$$V = -\tfrac{4}{3}\pi\epsilon r^3(\sigma_x + \sigma_y + \sigma_z) \tag{13}$$

where ϵ is the misfit of the solute atom and the σ's are the normal stresses.

[58] E. Orowan, Symposium on Internal Stresses, p. 451. Institute of Metals, London, University of Bristol, pp. 30–38. Physical Society, London, 1948; 1947.

[59] A. H. Cottrell, Report of a Conference on the Strength of Solids, see also J. S. Koehler, *J. Appl. Mechanics* **14**, 217 (1947).

[60] A. H. Cottrell, Plastic Deformation of Crystalline Solids, Carnegie-ONR Conference, pp. 60–76. U. S. Department of Commerce, PB 104604, 1950.

The interaction energy is determined by the change in volume, $4\pi\epsilon r^3$, and by the hydrostatic pressure of the stress field, $-\frac{1}{3}(\sigma_x + \sigma_y + \sigma_z)$. Let the solute atom be situated at a point of polar coordinates R, α from a positive edge dislocation. The stress field of the dislocation at x, y is given by

$$\sigma_x = \frac{-\mu\lambda}{2\pi(1-\nu)} y \frac{3x^2 + y^2}{(x^2 + y^2)^2}$$

$$\sigma_y = \frac{\mu\lambda}{2\pi(1-\nu)} y \frac{x^2 - y^2}{(x^2 + y^2)^2} \tag{14}$$

$$\sigma_z = \nu(\sigma_x + \sigma_y)$$

where λ is the slip distance in the dislocation and ν is Poisson's ratio. The interaction energy is then given by

$$U = \frac{4}{3}\left(\frac{\mu\epsilon r^3\lambda}{R}\right)\left(\frac{1+\nu}{1-\nu}\right)\sin\alpha \tag{15}$$

which is positive on the upper side of the dislocation for a large solute atom and negative on the other side in agreement with the physical discussion given above.

If interaction with screw dislocations is of importance one has to calculate the anisotropy of the solute atom distortion. The reason is that a screw dislocation has no hydrostatic component and the solute atom can interact with it only if it produces nonspherical distortion and therefore is able to relieve shear stresses.

Interpretation of the yield point[60] is probably the most interesting application of these ideas. The experimental facts may be summarized as follows: The yield point is characterized by abrupt plastic flow at the critical stress (upper yield point) which continues at the same or lower stress (lower yield point). A specimen which has yielded (overstrained) shows no yield point upon immediate retesting. The yield point may be developed again upon annealing. These effects are only observed when small amounts of certain impurities are present in the crystal. Typical results for single crystals of zinc containing nitrogen are shown in Fig. 2.

Cottrell's interpretation, based on the interaction of dislocations and impurity atoms, attributes the yield point to the segregation of solute atoms near the dislocations. Because of the associated binding energy the force needed to break the dislocations away from their anchored positions is larger than the force needed to keep them in motion once they have been freed. This explains the abrupt start of plastic flow. A crystal freshly strained past the yield point contains free dislocations and hence shows no yield point. During aging or annealing, however, the solute atoms diffuse back to the dislocations again locking them in position. The presence of
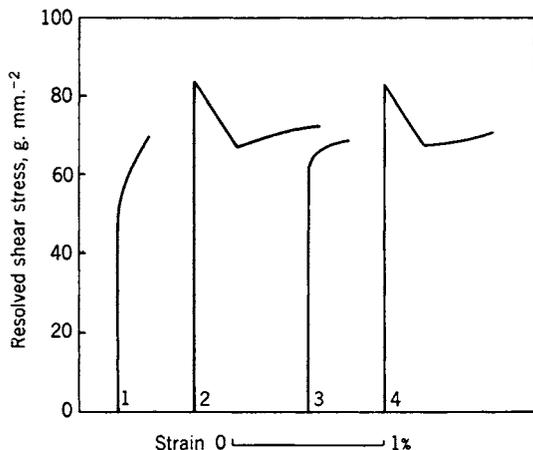
FIG. 2. Yielding in a single crystal of zinc containing nitrogen. (1) Initial test; (2) after three strain-aging treatments, each of 0.3% extension followed by 40 min. at 180°C.; (3) measured immediately after (2); (4) after seven strain-aging treatments. (*After Cottrell*[60]).

anisotropy in hexagonal metals such as zinc favors nonsymmetrical distortion around the impurity atom so that both edge and screw dislocations may be anchored. Similarly, the tetragonal distortion around carbon and nitrogen in iron favors the development of a yield point. Yield points have been observed primarily in such crystals. Cottrell[60] has also extended these ideas qualitatively to take into account the role of grain boundaries and internal stresses in polycrystalline media and the conditions for yield propagation. An important characteristic of Cottrell locking is that the stress required to move an impurity anchored dislocation is highly temperature- and time-dependent. The reason is that the forces around the locking atoms are of short range and in the presence of an applied stress only a short length of a loop need be detached to create an unstable situation leading to low activation energies.[61] The yield point stress is, therefore, more strongly dependent on temperature than the flow stress in agreement with experiment.[61]

b. *Effect of Nuclear Radiation*

It is well known by now[21] that fast neutron or charged particle bombardment may create a high nonequilibrium concentration of vacancies and interstitial atoms which will remain "frozen-in" in the lattice at sufficiently low temperature. In many ways one expects their interaction with dislocations to be similar to that of impurity atoms. The critical shear

[61] A. H. Cottrell and B. A. Bilby, *Proc. Phys. Soc. (London)* **62,** 19 (1949).

stress of metals, for example, is increased by a large factor upon pile irradiation. In single crystals of copper, for example, the critical shear stress increased from 0.241 to 2.0 kg./mm.^{2} for an integrated neutron exposure of about 2×10^{18} neutrons/cm.^{2}.[62] The shape of the stress-strain curve after irradiation is similar to that produced by solid solution hardening. Further, critical shear stress vs bombardment curves also indicate strong similarity to hardening by dissolved impurities.

In spite of the qualitative similarities, however, radiation hardening cannot be described quantitatively in terms of the theory of solid solution hardening. Comparison of radiation hardening to those impurities which are well described by the theory (for example, α-brass) indicates that unreasonably large distortions would have to be ascribed to the interstitial atoms to explain the results. Thus, one may have to postulate that interstitial atoms and/or vacancies are present in the form of clusters which may be effective enough to raise the critical shear stress to the observed levels.

Large changes in hardness of irradiated alkali halide crystals have also been observed recently.[63, 64] Systematic studies of altered mechanical properties and correlation with optical measurements, along the lines started by Westervelt,[64] represent promising approaches.

c. Order-Disorder Transformations

The influence of the degree of order on structure-sensitive mechanical properties has not been studied extensively either experimentally or theoretically. Many hardness measurements are reported in the literature but very little fundamental information can be derived from changes in this physical property. In a few cases stress-strain curves have been determined. A typical example is shown in Fig. 3 for ordered and disordered AuCu$_3$ taken from the work of Sachs and Weerts.[65] Upon disordering the critical shearing stress is seen to rise by about a factor of 2 although the work-hardening capacity of the disordered alloy is considerably less than that of the ordered one.

The ordered alloy has a lower critical shear stress because long-range order alters the distribution of dislocations in such a way that they regroup into pairs, each pair having a Burger's vector equal to twice that for the disordered lattice.[66] The driving force for this grouping is provided by the

[62] T. H. Blewitt and R. R. Coltman, *Phys. Rev.* **82,** 769 (1951); see also reference 21.

[63] Yin-Yuan Li, *Acta Metallurgica* **1,** 455 (1953).

[64] D. Westervelt, *Acta Metallurgica* **1,** 754 (1953).

[65] G. Sachs and J. Weerts, *Z. Physik* **62,** 473 (1930).

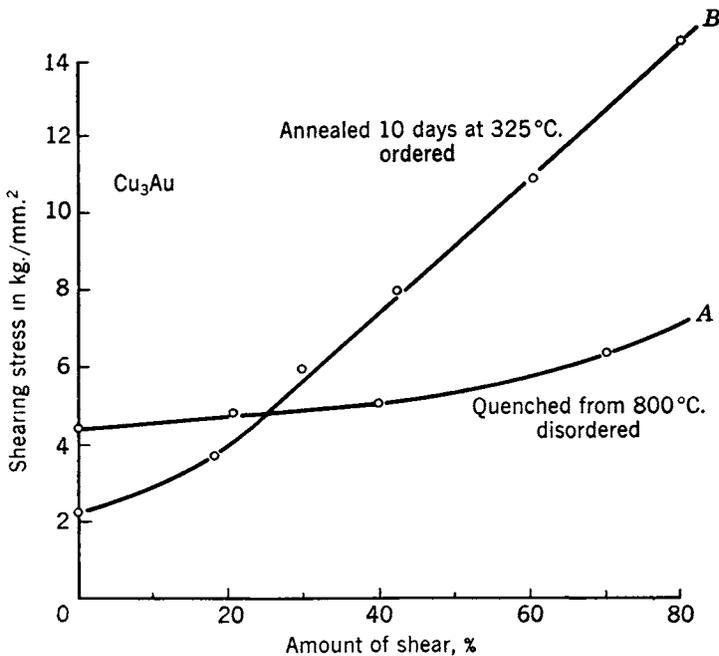[66] J. C. Fisher, *Acta Metallurgica* **2,** 9 (1954).

FIG. 3. Stress-strain curves for single crystals of Cu₃Au in the ordered and disordered states. (*After Sachs and Weerts*[65]).

long-range order itself because each single dislocation would be the edge of a surface of misfit. The pair is in equilibrium under zero stress since the motion of the dislocation recreates the ordered structure.

Fisher has pointed out recently[66] that short-range order has the opposite effect. Dislocation motion destroys the order by creating an interface of positive energy γ. The stress increment resulting from short-range order hardening may be estimated from the relation $\sigma = \gamma/a$, which for reasonable values of γ leads to considerable hardening. In contrast, dislocation motion in a completely random solid solution recreates random matching across the glide plane and the behavior should be essentially the same as in a pure metal. As the temperature is lowered below the critical temperature in an order-disorder system long-range order is developed and the critical shear stress is lowered in agreement with experiment. As long-range order is destroyed by plastic deformation rapid hardening of the ordered alloy is expected and observed.

d. *Creep and Diffusion*

In this section some mechanical properties will be discussed which are closely related to the presence of lattice imperfections but are not controlled
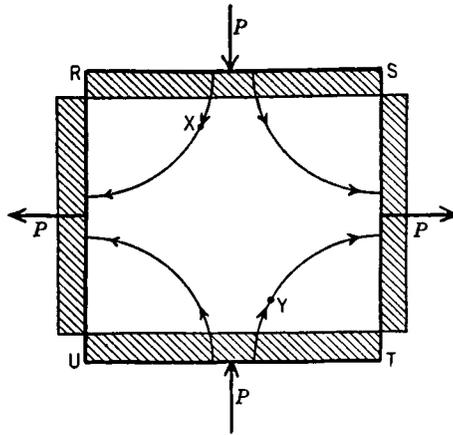
FIG. 4. A block of metal under shear stress P. If the block creeps under the stress, atoms at X and Y move in opposite directions. (*After Nabarro*[69]).

by the motion of dislocations. This section is by no means a survey of the complex field of creep and diffusion. Rather, some special cases will be considered to serve again as examples of the role played by imperfections in determining some of the mechanical responses.

A rather simple type of creep is observed in metals near the melting point. The researches of Udin and co-workers[67, 68] have established the essential features of this high-temperature response to shearing stress. These workers have found that lightly loaded wires of copper, gold, and silver deform viscously at high temperatures. This conclusion is reached from the fact that strain vs time curves at any given stress are linear and at low stresses the strain at a given time is proportional to the applied stress. At higher stresses an additional slip mechanism comes into play. Thus, a specific viscous creep component has been successfully isolated under these experimental conditions. The activation energy for this viscous creep is in good agreement with the activation energy for self-diffusion.

These experiments find their interpretation in mass transport resulting from the migration of vacancies within the crystal grains caused by the applied shearing stress. The possibility of viscous creep resulting from such vacancy migration was suggested by Nabarro[69] and the theory was worked out in a more refined manner by Herring.[70] The basic idea is as follows:

[67] H. Udin, A. J. Shaler, and J. Wulff, *Trans. Am. Inst. Mining Met. Engrs.* **185,** 186 (1949).

[68] F. H. Buttner, E. R. Funk, and H. Udin, *Trans. Am. Inst. Mining Met. Engrs.* **194,** 401 (1952).

[69] F. R. N. Nabarro, Report on a Conference on the Strength of Solids, University of Bristol, pp. 75–91. Physical Society, London, 1948.

[70] C. Herring, *J. Appl. Phys.* **21,** 437 (1949).

Consider a block of metal under shear stress P as shown in Fig. 4. The external stress will be relieved if the metal diffuses along the arrows. Vacancies, which are believed to be responsible for self-diffusion in metals,[71] will flow in the opposite direction. Because of the normal pressures on surfaces RS and UT the concentration of vacancies will be low in the neighborhood of these surfaces and the vacancies will diffuse toward them from RU and ST under their own concentration gradient and the specimen creeps by mass transfer.

The final equation, derived by Herring for the conditions of the experiment discussed above, reads[70]

$$\eta = \frac{2kTRL}{3BD\Omega_0} \qquad (16)$$

where η = viscosity, L = distance between grain boundaries, R = radius of the grains, B = constant, known function of L/R, D = diffusion coefficient, and Ω_0 = atomic volume of the atoms.

The experimental results discussed above are in good agreement with equation (16). It has already been pointed out that the activation energy of η is the same as that of D which is to be expected from equation (16) since the other terms are essentially temperature independent. The variation of η with R is also confirmed. Further, viscosities calculated from diffusion coefficients by means of equation (16) were found to be in good agreement with the experimentally measured values. This agreement may be taken as a confirmation of the Nabarro-Herring mechanism, particularly since there are no adjustable constants in equation (16).

There is another interesting interaction between applied stress and the motion of vacancies. It has already been mentioned that the interaction of dislocations during plastic deformation is expected to result in the formation of vacant lattice sites.[3, 16, 43] If this be the case then, since the rate of self-diffusion is directly proportional to the number of vacancies,[71] enhanced diffusion should result from the application of stress. Such enhanced diffusion has been observed recently by Buffington and Cohen.[72] These workers found a large increase in the coefficient of self-diffusion of iron at 890° C. when the specimen was deformed at various strain rates. Their results were describable by the equation

$$\frac{D_s}{D_u} = 1 + 50\dot{\epsilon} \qquad (17)$$

[71] For a reveiw see for example: F. Seitz, *in* "Phase Transformation in Solids" (R. Smoluchowski, ed.), pp. 77–149. Wiley, New York, 1951.

[72] F. S. Buffington and M. Cohen, *Trans. Am. Inst. Mining Met. Engrs.* **194**, 859 (1952).

where D_s = diffusion coefficient under stress, D_u = diffusion coefficient unstressed, and $\dot{\epsilon}$ = natural strain rate in hour^{-1}.

The supersaturation of vacancies obtainable during deformation at elevated temperatures is expected to depend on the strain rate rather than on the strain itself. The reason is that production and annealing are occurring at the same time and, therefore, the excess concentration of defects is proportional to the rate of production at any fixed elevated temperature. The above findings are, therefore, consistent with the vacancy mechanism of diffusion.

Nomenclature

D	Diffusion coefficient	ϵ'	Elastic strain
D_s	Diffusion cofficient under stress	ϵ''	Non elastic strain
L	Distance between grain boundaries	$\dot{\epsilon}$	Natural strain rate in hour^{-1}
M	Dynamic modulus	η	Viscosity
N	Number of particles per unit volume	Λ	Distance between the impurity particles
P	Shear stress	Λ	Distance between the centers of stress
R, α	Polar coordinates	Λ	Wave length of dislocation loop
R	Radius of the grains	λ	Slip distance in dislocation
U	Energy of interaction	μ	Shear modulus
V	Potential energy	ν	Poisson's ratio
a	Interatomic distance, (lattice parameter)	σ	Yield stress
c	Atomic concentration of solute	σ_i	Internal stresses
r	Radius	τ	Mean time of stay
x	Fraction of component A	τ_r	Relaxation time
γ	Energy of interface	ϕ	Internal friction
Δ_M	Relaxation strength	Ω_0	Atomic volume of the atoms
ϵ	Strain; misfit of foreign atom	ω	Frequency