# Stress Induced Preferential Orientation of Pairs of Solute Atoms in Metallic Solid Solution*

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(Received October 7, 1946)

In a non-stressed cubic crystal the axes of pairs of adjacent solute atoms are randomly orientated along the several permissible crystallographic directions. It is shown that in the presence of a stress the equilibrium orientation is no longer random, but that certain directions become preferred, and it is further shown that the continual striving of the crystal to maintain equilibrium causes it to manifest all the characteristic anelastic effects, stress relaxation, internal friction, etc. In particular, its internal friction will be anomalously high in that temperature range where the time of relaxation for the establishment of equilibrium is comparable with the period of oscillation. The theory is developed for the dependence of anelastic effects upon temperature and upon crystallographic orientation, and it is found that in b.c.c. crystals these effects vanish for a tensile stress applied along one of the ⟨100⟩ axes. The magnitude of the anelastic effects associated with this stress induced preferential orientation may be very large. Thus in alpha-brass past experiments indicate that under optimum conditions the associated internal friction is at least 20 times as large as that due to all other causes.

NO real metal is perfectly elastic in the sense that stress and strain are single-valued functions of one another. The application of a constant stress is always followed by one or more types of relaxation, such as the relaxation of temperature fluctuations, of shear stress across viscous regions, etc., and consequently by a gradual creep, which in most cases is recoverable. These relaxations are also responsible for stress relaxation when a constant strain is applied, for a variation of the elastic moduli with frequency, and for internal friction. That property of a metal in virtue of which stress and strain are not unique functions of one another in the pre-plastic range has been called anelasticity. The various sources of anelasticity have recently been reviewed by the author.[1] In the present paper an analysis is given of one source of anelasticity which has heretofore been overlooked, the relaxation of the preferential orientation of pairs of solute atoms.

The solute atoms in a solid solution usually have a different size from that of the solvent atoms, and therefore give rise to an elastic distortion of the lattice. When the solution is of the substitutional type, and when the lattice has cubic symmetry, the distortion produced by each isolated solute atom will also have cubic symmetry. When two solute atoms are adjacent to one another, the distortion of the lattice by the pair will no longer have cubic symmetry. Thus if the solute atoms are larger than the solvent atoms, the lattice will be extended more along the axis of the pair than along any other axis. When the average stress throughout the crystal is zero, the pair axes will be randomly distributed over the several permissible crystallographic directions. When, however, a stress is applied to a crystal, the equilibrium distribution of pair axes is no longer random. Thus if the solute atoms are larger than the solvent atoms, and a tensile stress is applied, the solute pairs will tend to be oriented preferentially along those permissible axes which make the least angle with the tensile axis. This preferential distribution of pair axes will, however, require some time to be established, and consequently strain lags behind stress, i.e., the crystal is anelastic.

The internal friction in an alpha-brass (solid solution of zinc in copper) crystal was observed by the author[2] in 1942 to be anomalously high with a narrow temperature band in the vicinity of 400°C. The observations are reproduced in Fig. 1. At that time no explanation was given of this anomaly. Recently an interpretation was advanced based on the assumption that the equilibrium distribution of zinc atoms was non-uniform,[1] an assumption which has no corroborative support. In view of the above considerations, it looks as though the anomaly shown

* This research was supported by ORI (Contract No. N6ori-20-IV).

[1] C. Zener, Metals Tech. (Aug. 1946).

[2] C. Zener, Trans. A.I.M.E. 152, 122 (1943).

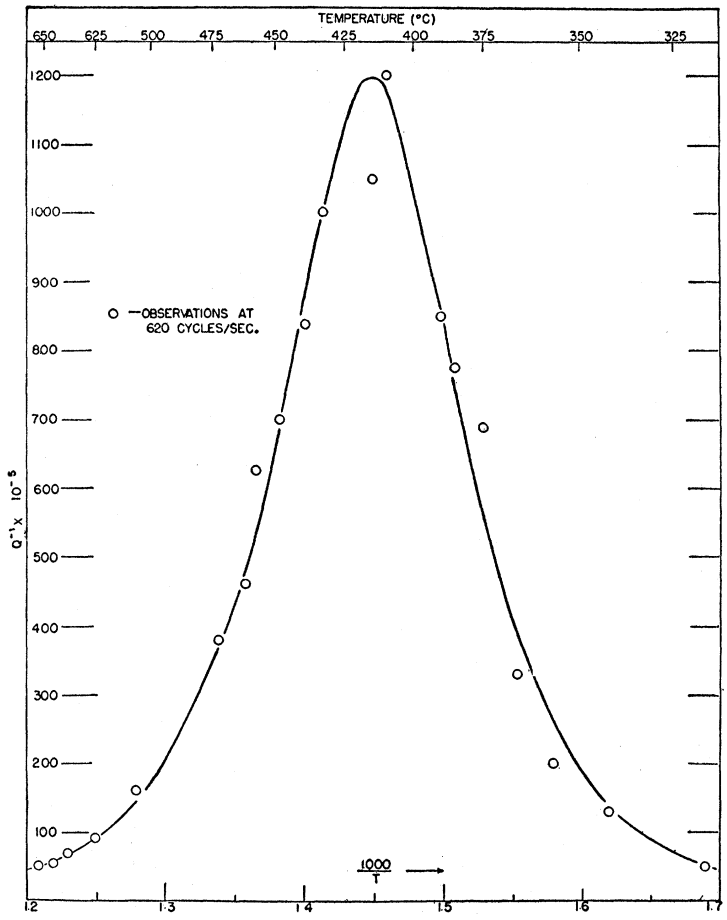


FIG. 1. Internal friction of alpha-brass crystal (After Zener, reference 2).

in Fig. 1 is a manifestation of the stress induced preferential orientation of pair axes, and that all solid solution crystals will show similar anomalies. The temperature variation of the internal friction is explained as follows. At low temperatures the time of relaxation $\tau$ for the establishment of equilibrium distribution of pair axes is very long compared with the period of vibration $P$. The distribution of pair axes therefore remains essentially unaltered during vibration, strain is essentially in phase with stress, and hence the internal friction is extremely low. At very high temperatures the time of relaxation $\tau$ is very short compared with the period $P$, and consequently the distribution of pair axes is at every instant essentially the equilibrium distribution. Strain is again essentially in phase with stress, and so the internal friction is again very small. Only in the intermediate temperature range, where

$$\tau \backsimeq P, \tag{1}$$

and hence where the pair axis distribution is neither constant nor equivalent to the equilibrium distribution, does strain lag behind stress appreciably, and hence is the internal friction large.

If the rate at which the distribution of pair axes tends to approach the equilibrium distribution is proportional to the difference between the instantaneous and equilibrium distribution, it may be shown[1] that the internal friction ($Q^{-1}$) varies with the angular frequency of measurement $W$ as

$$Q^{-1} = \Delta_E \frac{\tau\omega}{1+\tau^2\omega^2}. \tag{2}$$

Here $\Delta_E$ is defined in terms of the unrelaxed and

relaxed Young's moduli, $E_U$ and $E_R$, respectively, by

$$\Delta_E = (E_U - E_R)/E_R, \tag{3}$$

and is called the relaxation strength. The observations on the brass crystal were found to obey this formula provided $\tau$ was assumed to vary with temperature through a heat of activation type of relation, i.e.,

$$\tau = \tau_0 e^{H/RT}. \tag{4}$$

In Section I an analysis is given of the manner in which the relaxation strength varies with temperature and with the material constants of the metal. In Section II an analysis is given of the manner in which the relaxation strength varies with the crystallographic orientation, and a comparison is given of the relaxation strengths in the case of a pure tensile test, $\Delta_E$, and in a pure torsion test, $\Delta_G$.

The theory of the anelasticity arising from the preferential orientation of pair axes is formally very similar to that arising from the stress induced macroscopic diffusion of solute atoms studied by Gorsky,[3] and to the stress induced preferential distribution of the interstitial carbon and nitrogen atoms in alpha-iron studied by Snoek[4] and Polder.[5]

## I. TEMPERATURE DEPENDENCE OF RELAXATION STRENGTH

In this section we shall compute the relaxation strength for a particular case where the crystal axes are so oriented as to simplify the computations. The influence of crystal orientation is reserved for the next section.

An f.c.c. lattice will be considered in which a tensile stress is applied along the [111] direction. The pair axes of the solute atoms may lie along any of the six ⟨110⟩ directions. Of these six directions three [011], [101], [110] have a direction cosine of $(2/3)^{\frac{1}{2}}$ with respect to the [111] axis, while three, [0$\bar{1}$1], [$\bar{1}$01], [$\bar{1}$10], are normal to the [111] direction. If the solute atoms are larger than the solvent atoms, a tensile stress along the axis of the specimen will therefore tend to orient the pair axes from the second group, the $n$ group, into the first, the $p$ group, of the ⟨110⟩ directions.

The tensile strain $\epsilon$ will be regarded as a function of the tensile stress $\sigma$, the temperature $T$, and the number of pair axes in the $p$ group per unit volume $n_p$. The tensile strain could also be regarded as a more complex function of atomic distribution, such as the relative orientation of next nearest neighbors. However, it is anticipated that only a small error will be introduced by neglecting the correlation in positions of pairs of solute atoms which are not nearest neighbors. According to the present assumption, a variation in the tensile strain is specified by

$$d\epsilon = E_U^{-1} d\sigma + \alpha dT + (\partial\epsilon/\partial n_p) dn_p. \tag{5}$$

Here $E_U$ is the isothermal unrelaxed tensile elastic modulus, i.e., the tensile modulus when $n_p$ remains unchanged, and $\alpha$ is the linear thermal expansion coefficient when $n_p$ remains unchanged. We shall now compute the change in the elastic modulus occasioned by $n_p$ changing in such a way as to maintain equilibrium. Under equilibrium conditions

$$n_p = n e^{-U/kT}/(1+e^{-U/kT}),$$

where $n$ is the number of pairs per unit volume, and $U$ is the work necessary to transfer a pair axis from an $n$ to a $p$ direction, the transfer being performed at constant strain and at constant temperature. If, as is normally the case, $U/kT$ is small compared with unity, the above equation reduces to

$$n_p = n/2 - nU/4kT. \tag{6}$$

It remains to obtain an estimate of $U$. It is anticipated that $U$ will not depend appreciably upon temperature. It will therefore be estimated by considerations at the absolute zero temperature where thermal effects are absent. The change in energy per unit volume is then given by

$$dE = \sigma d\epsilon + U dn_p.$$

The differential of $E - \sigma\epsilon$ is therefore

$$-\epsilon d\sigma + U dn_p.$$

Since this is a perfect differential,

$$\partial U/\partial\sigma = -\partial\epsilon/\partial n_p.$$

We now introduce the assumption that $U$ is a

[3] W. Gorsky, Physik. Zeits. Sowjetunion 8, 457 (1935).
[4] J. Snoek, Physica 6, 591 (1939); 8, 711 (1941); 9, 862 (1942); Chemisch Weekblad 39, 454 (1942).
[5] D. Polder, Phillips Res. Rep. 1, 1 (1945).

function only of $\sigma$, and is independent of $n_p$. We thereby exclude any effects arising from the mutual interaction of neighboring pairs of atoms, an interaction which may, in certain cases, be of importance, perhaps even leading to an ordered arrangement of the pairs at zero stress. This assumption leads to

$$U=-(\partial\epsilon/\partial n_p)\sigma. \tag{7}$$

When we now substitute Eqs. (6) and (7) into Eq. (5), we obtain

$$E_R^{-1}-E_U^{-1}=n(\partial\epsilon/\partial n_p)^2/4kT,$$

and therefore, from Eq. (3),

$$\Delta_E=nE_U(\partial\epsilon/\partial n_p)^2/4kT. \tag{8}$$

An estimate of the relaxation strength $\Delta_E$ will now be given for the case of alpha-brass with 30 percent zinc. In this solution[6]

$$\partial\epsilon/\partial C=0.071,$$

where $C$ is the zinc concentration. Upon using this value, and upon taking $n$ as identical with the number of zinc atoms per unit volume, and upon replacing $(\partial\epsilon/\partial n_p)$ by $r(\partial\epsilon/\partial n)$, we obtain for the relaxation strength at 400°C

$$\Delta_E=0.075r^2.$$

It is anticipated that the numerical coefficient $r$ will be less than, but of the order of magnitude of, unity. In the crystal examined $\Delta_E$ was[2] 0.025, a value whose order of magnitude is in agreement with the above theoretical computation.

## II. ORIENTATION DEPENDENCE OF RELAXATION STRENGTH

In an experimental study of the anelasticity arising from stress induced preferential orientation of pair axes it is highly desirable that single crystals be used in order to avoid the anelasticity associated with the viscous[7] grain boundaries. Since it is difficult to grow a set of single crystals all of the same orientation, it is desirable that a theoretical formula be at hand which gives the dependence of the relaxation strength upon crystal orientation.

In the type of relaxation we are here considering no relaxation will be induced in cubic crystals by pure hydrostatic pressures. The relaxation under an arbitrary stress system may therefore be represented in terms of the relaxation in the two shear moduli $c_{44}$ and $(c_{11}-c_{12})/2$. The relaxation strengths of these two moduli will be denoted by $\delta$ and $\delta'$, respectively. Thus

$$\delta=\{(c_{44})_U-(c_{44})_R\}/(c_{44})_R. \tag{9}$$

In order to compute $\Delta_E$ and $\Delta_G$ in terms of $\delta$ and $\delta'$, use will be made of the following formulae for the tensile and shear moduli:[8]

$$E^{-1}=s_{11}-[2(s_{11}-s_{12})-s_{44}]\phi, \tag{10}$$

$$G^{-1}=s_{44}+2[2(s_{11}-s_{12})-s_{44}]\phi, \tag{11}$$

where

$$\phi=\gamma_1^2\gamma_2^2+\gamma_2^2\gamma_3^2+\gamma_3^2\gamma_1^2, \tag{12}$$

with $\gamma_1$, $\gamma_2$, $\gamma_3$ being the direction cosines of the specimen axis with respect to the principal axes of the specimen. We now subtract $E_U^{-1}$ from $E_R^{-1}$, and divide by $E_U^{-1}$. The right-hand member will now be transformed from the $s$'s to the $c$'s. Towards this end we introduce the notation

$$s=s_{44}, \qquad c=c_{44},$$

$$s'=2(s_{11}-s_{12}), \quad c'=(c_{11}-c_{12})/2,$$

and observe that

$$s=1/c; \quad s'=1/c'; \quad s_{11}+2s_{12}=1/(c_{11}+2c_{12});$$

$$\delta\equiv(c_U-c_R)/c_R=(s_R-s_U)/s_U;$$

$$\delta'\equiv(c'_U-c'_R)/c'_R=(s'_R-s'_U)/s'_U.$$

Upon dividing the right-hand member by $ss'$, and upon using these relations, we obtain

$$\Delta_E=\frac{c\delta'/3-(c\delta'-c'\delta)\phi}{\dfrac{c_{44}(c_{11}+c_{12})}{2(c_{11}+2c_{12})}-(c-c')\phi}. \tag{13}$$

In a similar manner one obtains

$$\Delta_G=\frac{c'\delta+2(c\delta'-c'\delta)\phi}{c'+2(c-c')\phi}. \tag{14}$$

It remains to determine which, if any, of the two unknown quantities $\delta$ and $\delta'$ are zero in cubic lattices. In b.c.c. lattices the axes passing through nearest neighbors lie along one of the

[6] E. A. Owen and L. Pickup, Proc. Roy. Soc. **140**, 179 (1933).

[7] See the coming paper by T. S. Kê.

[8] E. Schmid and W. Boas, *Kristallplastizität* (Berlin, 1935), p. 23.

four ⟨111⟩ directions. Pairs of solute atoms lying along these four directions will be affected equally by a shear stress $\sigma_{xx}-\sigma_{yy}$ across the (110) planes, but unequally by a shear stress $\sigma_{xy}$ across a (001) plane. The first type of shear stress will therefore not cause a preferred orientation of pair axes, i.e., $\delta'$ is identically zero, and therefore the $\Delta_E$ due to interaction of nearest neighbors is zero when a tensile stress is applied along one of the principal axes. On the other hand, the shear stress $\sigma_{xy}$ will tend to cause a preferred orientation, and hence $\delta$ is not zero. These conclusions may be arrived at in a more elegant manner. Let $n_{111}, n_{\bar{1}11}\cdots$ be the number of pairs of solute atoms with axes lying along the directions [111], [$\bar{1}$11], $\cdots$. The potential energy of the lattice can then contain three interaction terms which are linear in the $n$'s and in the strains. One interaction term will contain the product of the sum of the $n$'s and of the sum $\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz}$. This term will cause no relaxation, and hence will not be further considered. The remaining two terms represent interaction of the orientation variables with shear strains. These terms must have the same symmetry as the lattice. One term is

$$\alpha\{n_{111}(\epsilon_{yz}+\epsilon_{zx}+\epsilon_{xy})+n_{\bar{1}11}(\epsilon_{yz}-\epsilon_{zx}-\epsilon_{xy})+n_{1\bar{1}1}(-\epsilon_{yz}+\epsilon_{zx}-\epsilon_{xy})+n_{11\bar{1}}(-\epsilon_{yz}-\epsilon_{zx}+\epsilon_{xy})\}.$$

No interaction term can be formed of the $\epsilon_{xx}$, $\epsilon_{yy}$, $\epsilon_{zz}$ strains, other than that representing a uniform dilation, which has the cubic symmetry of a cubic lattice.

In f.c.c. lattices the axes passing through nearest neighbors lie along one of the six ⟨110⟩ directions. These pairs are affected unequally by both types of shearing stress, and hence both $\delta$ and $\delta'$ are different from zero. This conclusion is vindicated by the existence of two shear interaction terms which satisfy the symmetry relations. These are

$$\beta\{(n_{011}+n_{0\bar{1}1})(2\epsilon_{xx}-\epsilon_{yy}-\epsilon_{zz})+(n_{101}+n_{\bar{1}01})(2\epsilon_{yy}-\epsilon_{zz}-\epsilon_{xx})+(n_{110}+n_{\bar{1}10})(2\epsilon_{zz}-\epsilon_{xx}-\epsilon_{yy})\}$$

and

$$\gamma\{(n_{011}-n_{0\bar{1}1})\epsilon_{yz}+(n_{101}-n_{\bar{1}01})\epsilon_{zx}+(n_{110}-n_{\bar{1}10})\epsilon_{xy}\}.$$

PHYSICAL REVIEW VOLUME 71, NUMBER 1 JANUARY 1, 1947

# Quantized Space-Time

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(Received May 13, 1946)

It is usually assumed that space-time is a continuum. This assumption is not required by Lorentz invariance. In this paper we give an example of a Lorentz invariant discrete space-time.

THE problem of the interaction of matter and fields has not been satisfactorily solved to this date. The root of the trouble in present field theories seems to lie in the assumption of point interactions between matter and fields. On the other hand, no relativistically invariant Hamiltonian theory is known for any form of interaction other than point interactions.

Even for the case of point interactions the relativistic invariance is of a formal nature only, as the equations for quantized interacting fields have no solutions. The uses of source functions, or of a cut-off in momentum space to replace infinity by a finite number are distasteful arbitrary procedures, and neither process has yet been formulated in a relativistically invariant manner. It may not be possible to do this.

It is possible that the usual four-dimensional continuous space-time does not provide a suitable framework within which interacting matter and fields can be described. I have chosen the idea that a modification of the ordinary concept of space-time may be necessary because the "elementary" particles have fixed masses and associated Compton wave-lengths.

The special theory of relativity may be based on the invariance of the indefinite quadratic form

$$S^2=c^2t^2-x^2-y^2-z^2, \quad (1)$$