K atoms are located between the chains in positions which are not equivalent, but both K atoms are surrounded by seven Cl atoms, six in the corners of a distorted trigonal prism and one on a lateral face. The *c* axis of the structure is parallel to the trigonal axis of the prism around K (I) and to one of the base edges of the trigonal prism around K (II). The calculated distances are listed in Table 4.

Table 4. *Calculated distances in* K_2CuCl_3

(Values in A. Maximum error about 0·04 A.)

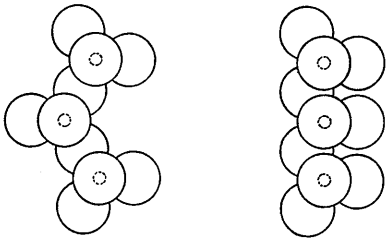
Cu–Cl (I) in the same symmetry plane	2·31
Cu–Cl (II) in the same symmetry plane	2·32
Cu–Cl (III) in different symmetry planes	2·43
K (I)–Cl (II) in the same symmetry plane	3·20
K (I)–Cl (II) in different symmetry planes	3·18
K (I)–Cl (III) in different symmetry planes	3·22
K (I)–Cl (I) in different symmetry planes	3·27
K (II)–Cl (III) in the same symmetry plane	3·23
K (II)–Cl (III) in the same symmetry plane	3·18
K (II)–Cl (I) in the same symmetry plane	3·18
K (II)–Cl (II) in different symmetry planes	3·22
K (II)–Cl (I) in different symmetry planes	3·12
Cu–Cl distance in CuCl	2·34
K–Cl distance in KCl	3·14

The chains have some analogy with the SiO_3 chains in the pyroxenes, but still there is a typical difference, resulting in greater compactness of the $CuCl_3$ chain (Fig. 7). In a $CuCl_3$ chain of the type of the SiO_3 chain in the pyroxenes the Cu–Cu distance would be larger.

The structure satisfies the electrostatic valence rule (Pauling, 1939, p. 364): the sum of the strength of the electrostatic bonds to Cl I and to Cl II is: $\frac{5}{7}+\frac{1}{4}=0{\cdot}96$, and to Cl III: $\frac{4}{7}+\frac{2}{4}=1{\cdot}07$.

The chains are in agreement with the observed optical behaviour (largest refractive index in the needle direction).

It is a great pleasure to us to thank Prof. Dr A. E. van Arkel, Leiden, for suggesting and stimulating this investigation and for reading the manuscript.



(*a*) (*b*)

Fig. 7. (*a*) Chain in pyroxenes (idealized). Small circles are Si, large circles O. (*b*) Chain in K_2CuCl_3 (idealized). Small circles are Cu, large circles Cl.

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Relation between Residual Strain Energy and Elastic Moduli*

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It is shown that the presence of residual strain energy necessarily results in a lowering of the overall tensile and shear moduli, and a quantitative relation is derived between the density of residual strain energy and the decrease in tensile and shear moduli. An interpretation is thereby given to the recent observations of Köster that solute atoms of only a small solubility lower the tensile modulus when they are atomically dispersed.

Introduction

The inspiration for the present paper has been derived from the recent study of Köster & Rauscher (1948) regarding the influence of solute atoms in solid solution upon the tensile elastic modulus of metals. Köster has found that alloying elements always reduce the tensile elastic moduli of Cu, Ag, and Au provided the maximum solubility of the alloying elements is less than 20 atomic %. He further found a rough correlation between the maximum solubility and the rate at which the elastic modulus decreases with increasing concentration, the lower the solubility the greater the rate at which the elastic modulus decreases. The general trends are indicated in Fig. 1 for alloying elements in copper.

It would appear at first sight as if no correlation whatsoever should exist between the limit of solubility and the decrease in elastic modulus. Closer examina-

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tion reveals, however, a possible common physical origin of both the limit of solubility and the decrease in elastic modulus. One of the primary factors which limit solubility is the difference in size between solute and solvent atoms (Hume-Rothery, 1945, pp. 59–63). A difference in size results in an introduction of strain energy whenever a solute atom is added to the lattice, which strain energy reduces the solubility of the solute atoms at any given temperature. We are, therefore, led to investigate whether strain energy *per se* has an influence upon the elastic modulus.

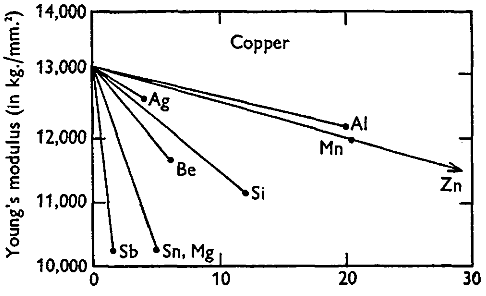

Fig. 1. Köster's data on effect of alloying elements in solid solution upon elastic modulus.

Analysis

The general nature of the relation between residual strain energy and the overall tensile or shear modulus may readily be obtained. We first note that under most conditions the residual strain energy is primarily shear-strain energy as opposed to dilation-strain energy. Thus in an elastically isotropic medium the shear-strain energy associated with a uniaxial tension is as high as eight times the dilation-strain energy when Poisson's ratio has the typical value of $\frac{1}{3}$, and the strain induced by a pressure acting upon the surface of a small spherical cavity is exclusively pure shear strain. We next note that when the tensile modulus E is expressed in terms of the bulk modulus K and the shear modulus G,

$$E^{-1}=\tfrac{1}{9}K^{-1}+\tfrac{1}{3}G^{-1}. \tag{1}$$

E is found, for typical values of Poisson's constant, to be eight times as sensitive to changes in G as to the same relative change in K. The tensile modulus will thus depend upon the various physical parameters in essentially the same manner as does the shear modulus.

From the above we conclude that it suffices to find the nature of the relation between the residual shear-strain energy and the overall shear modulus. Towards this end we shall consider a cylindrical specimen to be simultaneously subjected to a torque τ applied at the two ends, and to a hydrostatic pressure p applied over the entire surface. The specimen will be considered as polycrystalline with a random orientation of the individual crystallites, and hence may be regarded as macroscopically isotropic. Under these conditions an increment in energy δE of the specimen becomes

$$\delta E=-p\,\delta v+\tau\,\delta\phi+T\,\delta S,$$

where ϕ is the angle of twist, and v is the volume, S the entropy, of the entire specimen. Since we shall wish to regard as independent variables the quantities, p, ϕ and T, we form the following perfect differential:

$$\delta(E+pv-TS)=v\,\delta p+\tau\,\delta\phi-S\,\delta T. \tag{2}$$

Since the left member, and hence also the right member, is a perfect differential, the following relation is satisfied,

$$(\partial S/\partial\phi)_{p,T}=-(\partial\tau/\partial T)_{p,\phi}. \tag{3}$$

From symmetry considerations alone we see that each member of (3) is zero when ϕ itself is zero. In order to obtain an equation which is non-trivial when ϕ is zero we divide each side of (3) by τ. We now denote by ϵ the work done by the torque in twisting the specimen from equilibrium to ϕ, the pressure and temperature remaining constant. The resulting equation may then be written as

$$(\partial S/\partial\epsilon)_{p,T}=-(\partial\ln\tau/\partial T)_{p,\phi}. \tag{4}$$

When we now introduce the rigidity G of the specimen, defined by the equation

$$\tau=G\phi,$$

the right-hand member of (4) may be rewritten as

$$-d\ln G/dT,$$

where in taking the derivative it is implicitly assumed that the pressure is maintained constant. In order to obtain an equation involving the change in overall shear modulus with residual shear-strain energy, we shall find it necessary to change the form of the left member of (4) by means of several approximating assumptions. Our first assumption is that the temperature is sufficiently high so that all the normal modes of vibration have their classical energy. This assumption leads to the following equation:

$$(\partial S/\partial\epsilon)_{p,T}=-3Nk\,d\ln\bar{\nu}/d\epsilon,$$

where N is the total number of atoms in the specimen, and $\bar{\nu}$ is the geometrical mean of all the frequencies of the normal modes of vibration. In forming the derivative in the right member it is implicitly assumed that the pressure and temperature are to be held constant. These two transformations reduce (4) to

$$d\ln\bar{\nu}/d\epsilon=(3Nk)^{-1}\,d\ln G/dT. \tag{5}$$

Our next approximation concerns the manner in which the mean frequency $\bar{\nu}$ is related to the elastic coefficients. Now $\bar{\nu}$ is proportional to the square root of some mean of the elastic coefficients. When cognizance is taken of the fact that in an isotropic medium there are twice as many transverse waves as longitudinal waves, we see that only a minor error is introduced by replacing the mean elastic coefficient by just the shear coefficient μ. The mean frequency $\bar{\nu}$ is likewise proportional to the sixth root of the volume, as may be seen by combining the two equations

$$\bar{\nu}\sim cV^{-\frac{1}{3}}\quad\text{and}\quad c\sim(\mu V/M)^{\frac{1}{2}},$$

where c is the velocity of the shear waves, and M is the mass of the specimen. Our present approximation therefore leads to

$$d\ln\bar{\nu}/d\epsilon = \tfrac{1}{2}\,d\ln\mu/d\epsilon + \tfrac{1}{6}\,d\ln V/d\epsilon. \qquad (6)$$

The second term is analyzed in the Appendix, and is found to be an order of magnitude smaller than the first term. Substitution of (6) into (5) then leads to the following approximate equation:

$$d\ln\mu/d\epsilon \simeq (\tfrac{3}{2}Nk)^{-1}\,d\ln G/dT. \qquad (7)$$

Before the above equation can be applied to our present problem, the left member must be reinterpreted. According to our derivation, ϵ is the strain energy introduced by an axial torque, and μ is the shear coefficient for shear heat waves averaged over all directions of propagation and over all directions of polarization. While the shear coefficients of the heat waves are independent of direction of propagation when no torque is present, they are not necessarily the same in the presence of a finite torque. It is clear that the left member of (7) will remain unaltered if we now let μ refer to a single pair of planes of maximum shear stress, rather than to an average over all orientation, provided we simultaneously regard ϵ as shear-strain energy in which the planes of maximum shear stress are randomly distributed, rather than as shear-strain energy in which only one pair of planes of maximum shear stress is present. Such a random distribution of planes of maximum shear stress occurs, for example, when the shear-strain energy arises from the presence of solute atoms. This new interpretation of the differential coefficient $d\ln\mu/d\epsilon$ is now in a form that is directly applicable to our problem.

In the derivation of (7) ϵ and N were defined as the total shear-strain energy and the total number of atoms within the specimen. This equation remains unaltered if we now regard ϵ and N both as referring to unit volume rather than to the entire specimen.

Discussion

We have in (7) a method for computing the effect of shear-strain energy upon the overall shear coefficient. The differential coefficient $d\ln G/dT$ is just the temperature coefficient of the rigidity modulus obtained by a static method, or by a dynamical method using an auxiliary inertia arm, provided no attempt is made to correct for those changes in dimensions which accompany a change in temperature. This differential coefficient has been measured by Kê for several metals in his recent studies of relaxation phenomena in metals. His data are reproduced in Table 1.

Table 1. *Temperature coefficient of rigidity modulus*

Metal	Ta	Fe	Al	α-Brass
Reference	Kê (1948*a*)	Kê (1948*b*)	Kê (1947)	Kê (1948*c*)
$(G^{-1}_{23^\circ\mathrm{C}}\,dG/dT)\times 10^6$	−180	−260	−515	−293
$\beta\times 10^6$	19	23	72	60

The negative sign of the temperature coefficient of G insures us that residual shear-strain energy will reduce the overall shear coefficient μ. Before proceeding to a quantitative test of our theory, we shall first introduce one further approximation which will change (7) into a form in which we can utilize the large amount of data upon the temperature coefficient of μ. We note that G may be written as the product of a geometrical factor and of μ. This geometrical factor has the dimensions of volume. Hence

$$d\ln G/dT = d\ln\mu/dT + \beta, \qquad (8)$$

where β is the cubic thermal expansion coefficient. By reference to Table 1 we see that β is nearly an order of magnitude less than the first term in the right member of (8), and hence only a slight error will be made in neglecting β. When this approximation is introduced, the substitution of (8) into (7) leads to

$$d\mu/d\epsilon = (\tfrac{3}{2}Nk)^{-1}\,d\mu/dT. \qquad (9)$$

This approximate equation may be given a very simple interpretation, namely, that the variation of μ with strain energy arising from residual stresses is identical with the variation of μ with the strain energy introduced by thermal vibrations.

Extensive measurements of the temperature variation of the Young's modulus E of different metals have recently been presented by Köster (1948). An estimate of the temperature variation of μ may then be obtained from the approximate equation

$$d\mu/dT = \tfrac{3}{8}\,dE/dT, \qquad (10)$$

the factor of $\tfrac{3}{8}$ corresponding to a typical Poisson ratio of $\tfrac{1}{3}$. Table 2 for $d\mu/d\epsilon$ has been constructed by the substitution of Köster's data into (10) and (9).

Table 2. *$d\mu/d\epsilon$ for cubic metals*

Metal	$-d\mu/d\epsilon$	Metal	$-d\mu/d\epsilon$
Ag	13	Mo	12
Al	10	Ni	12
Au	5·3	Pb	8·6
Ba	5·0	Pd	4·4
Ca	5·8	Pt	4·4
Cu	7·3	Rh	27
Fe	12	Ta	10
In	23	W	12
Ir	28		

The above analysis is in qualitative agreement with Köster's observation upon the influence of atomically dispersed solute atoms upon the elastic tensile modulus, in that the negative sign of $d\mu/d\epsilon$ will lead to a decrease in μ with increasing solute concentration provided the solute atoms introduce considerable strain energy. We shall now make a quantitative comparison of the results of the above analysis with Köster's data. Since only a rough estimate may be made of the strain energy introduced by solute atoms, the best that can be hoped for is agreement in order of magnitude.

In estimating the strain energy introduced by solute atoms, we shall consider the matrix as elastically isotropic and as continuous, thereby allowing use of standard elasticity theory. We then equate the strain energy associated with a single solute atom to the work required to expand (or contract) a spherical cavity within the continuous matrix from an initial radius equal to the radius of a solvent atom, to a final radius equal to that of the solute atom. When cognizance is taken of the fact that the bulk modulus of a spherical cavity is $(\frac{4}{3}\mu)$, we obtain for the strain energy associated with a single solute atom

$$\delta\epsilon = 8\pi\mu R\,(\delta R)^2,$$

where R is the radius of the solvent atom, and δR is the difference in the radii of the solvent and solute atoms. The number of solute atoms per unit volume may be taken as $3c/4\pi R^3$, where c is the atomic concentration of the solute atoms. We thereby obtain the following estimate for the strain energy per unit volume:

$$\epsilon = 6\mu(\delta R/R)^2 c.$$

Substitution of this relation between ϵ and c in (9) leads to

$$\mu^{-1}d\mu/dc = 4(\delta R/R)^2\,(Nk)^{-1}\,(d\mu/dT). \qquad (11)$$

The above estimated value of $\mu^{-1}d\mu/dc$ is compared in Table 3 with Köster's observed values in the case where the matrix is copper. While Köster's data actually give us $E^{-1}dE/dc$, we may consider this as equivalent to $\mu^{-1}d\mu/dc$. It is seen that in every case the estimated values of $\mu^{-1}d\mu/dc$ are of the same order of magnitude as are the observed values. For those solute atoms which are larger than the matrix atoms, we expect the value of $\mu^{-1}d\mu/dc$ to be larger the larger the solute atom. This is seen to be indeed the case.

Table 3. *Comparison with experiment*

(Copper as solvent)

Solute atom	R* (A.)	$-\mu^{-1}\,(d\mu/dc)$	
		Est.	Obs.
Sb	1·614	3·2	12
Mg	1·60	2·8	4
Sn	1·582	2·6	4
Ag	1·441	0·75	1·6
Al	1·40	0·43	0·4
Zn	1·374	0·27	0·5
Cu	1·275	—	—
Be	1·125	0·62	2·0

* Hume-Rothery (1945, pp. 47–55).

APPENDIX

In (6) the second term in the right member was neglected in comparison with the first term. This step will now be justified. In order that we may compare two dimensionless quantities, the right member is written as

$$d\mu/d\epsilon + \tfrac{1}{3}\mu d\ln V/d\epsilon, \qquad \text{(i)}$$

the numerical factor $\frac{1}{2}\mu^{-1}$ being omitted.

The second term in (i) has already been evaluated by the author (Zener, 1942) in his study on the influence of plastic deformation on overall lattice expansion. The final result may be obtained directly from (2) by following the procedure utilized in the derivation of (4), except that now the cross-differentials are to be taken between the first two terms in (2). Upon replacing τ by $M\phi$, and upon noting that M is the product of μ and of a geometrical factor having the dimensions of volume, we obtain

$$dV/d\epsilon = -K^{-1} + d\ln\mu/dp.$$

The last term will now be estimated through the assumption that μ is the elastic coefficient which controls the mean frequency $\bar{\nu}$ of all the normal modes of vibration. From the relation

$$d\ln\mu = 2d\ln\bar{\nu} - \tfrac{1}{3}d\ln V,$$

previously used in (5), we have

$$d\ln\mu/dp = K^{-1}\,(2\gamma - \tfrac{1}{3}),$$

where γ is Grüneisen's constant. Upon letting ϵ now refer to shear-strain energy per unit volume, we obtain finally for the expression (i)

$$d\mu/d\epsilon + (2\mu/3K)\,(\gamma - \tfrac{2}{3}). \qquad \text{(ii)}$$

Upon taking $\frac{3}{8}$ as the typical value of μ/K, and upon observing that γ lies between 1 and 3 for most metals (Mott & Jones, 1936, p. 318), we see that the second term in (ii) is usually less than $\frac{1}{2}$, and hence, from Table 2, the first term is an order of magnitude greater than the second term.

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