PHYSICAL REVIEW VOLUME 88, NUMBER 4 NOVEMBER 15, 1952

Anelastic Measurements of Atomic Mobility in Substitutional Solid Solutions*

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(Received July 29, 1952)

A recently developed method for obtaining atomic mobility in solid solutions from the rate of anelastic relaxation makes possible the measurement of mobilities at temperatures far below those at which conventional diffusion experiments can be carried out. It is shown that the anelastic effects obtained in substitutional solid solutions are due to a phenomenon of stress-induced ordering and that the relaxation rate is determined primarily by the rate of movement of the slower atomic species. This method is applied to a series of silver-zinc solid solutions (silver rich) and the relaxation time measured as a function of temperature and concentration. The results show a slight deviation from an Arrhenius law, but a mean heat of activation may be obtained for each alloy concentration. Values for the heat of activation as a function of zinc concentration range from 36.1 kcal/mole at 15.8 atom percent zinc to 32.5 kcal/mole at 30.2 atom percent zinc. The entropy of activation, in each case, is positive and in reasonable agreement with Zener's "strain theory." A correlation of the magnitude of the anelastic effects for various specimens of the same composition with the rigidity modulus of these specimens, shows that the contribution to the torsional anelasticity from grains with ⟨111⟩ direction close to the specimen axis is much larger than from grains aligned in the ⟨100⟩ direction.

I. INTRODUCTION

THE only widely-used method for the determination of atomic mobility in metals and alloys is the diffusion experiment, which measures the manner in which a concentration gradient changes with time. It is therefore not surprising that the study of atomic mobility in metals is most often classified under the heading of "diffusion." In substitutional solid solutions, the rate of interdiffusion of two different atomic species is expressed in terms of the diffusion coefficient, D, measured in an experiment in which there is an initial chemical concentration gradient. Aside from a thermodynamic correction,[1] this diffusion coefficient is related to an appropriate atomic jump rate, Γ, by the equation

$$D=\beta a^2\Gamma, \tag{1}$$

where a is the lattice parameter and β is a numerical coefficient determined by the geometry of the lattice. (For diffusion in f.c.c. solid solutions[2] the value of β is 1/12.) The well-known experiments of Kirkendall,[3] and of da Silva and Mehl[4] show that the rate of movement of the two atomic species, say A and B, during an interdiffusion experiment are not the same, at least for several f.c.c. alloys. The "appropriate" interdiffusion jump rate, Γ, that appears in Eq. (1) may be related under suitable assumptions, to the mean frequency of jump of A atoms and of B atoms (Γ_A and Γ_B, respectively) by the relation[5]

$$\Gamma=f_B\Gamma_A+f_A\Gamma_B, \tag{2}$$

where f_A and f_B are the mole fractions of A and B, respectively. When neither of the mole fractions is much less than unity, the quantity Γ is determined, essentially, by the rate of movement of the faster diffusing component.

From statistical-mechanical considerations, it may be shown[6] that, regardless of the mechanism of the elementary atomic jump, the quantities Γ_A and Γ_B may be expressed in the form[7]

$$\Gamma_i=z\nu_i e^{-\Delta G_i/RT}, \tag{3}$$

($i=A$ or B), where z is the coordination number of the lattice (the number of nearest neighbor sites), ν_i the appropriate atom vibration frequency, R the gas constant, T the absolute temperature and ΔG_i the isothermal work required to carry the elementary diffusion process (for the appropriate type of atom) into the saddle configuration. The quantity ΔG_i is, therefore, a thermodynamic potential and may be separated into enthalpy and entropy terms according to

$$\Delta G_i=\Delta H_i-T\Delta S_i. \tag{4}$$

When Eq. (4) is substituted into (3), the quantity Γ_i assumes the form of an Arrhenius equation:

$$\Gamma_i=\Gamma_{i0}e^{-\Delta H_i/RT};\quad (\Gamma_{i0}=z\nu_i e^{\Delta S_i/R}). \tag{5}$$

If we write an analogous equation for the quantity Γ of Eq. (1), a corresponding Arrhenius equation for D is obtained:

$$D=D_0e^{-H/RT};\quad (D_0=\beta a^2z\nu e^{\Delta S/R}). \tag{6}$$

The quantities H and ΔS that appear in this equation are termed, respectively, the "heat and entropy of activation for diffusion." In view of Eq. (2) and the fact that Γ_A and Γ_B obey Eq. (5) with (in general)

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* This research has been supported in part by the ONR.

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[1] A. D. Le Claire, *Progress in Metal Physics. I* (Interscience Publishers, Inc., New York, 1949), Chapter VII (B. Chalmers, Editor).

[2] A. D. Le Claire, Phil. Mag. **42**, 673 (1951).

[3] A. D. Smigelskas and E. O. Kirkendall, Trans. Am. Inst. Mining Met. Engrs. **171**, 130 (1947).

[4] L. C. C. da Silva and R. F. Mehl, Trans. Am. Inst. Mining Met. Engrs. **191**, 155 (1951).

[5] L. S. Darken, Trans. Am. Inst. Mining Met. Engrs. **175**, 184 (1948).

[6] C. Zener, J. Appl. Phys. **22**, 372 (1951).

[7] The symbol Γ is used by Zener to represent the probability per second for an atom to jump into a specific nearest neighbor site. It, therefore, differs from the present definition by the factor z.

$\Delta H_A \neq \Delta H_B$, it is clear that Eq. (6) is only an approximation to the temperature dependence of the interdiffusion coefficient. Zener has shown[6] that it is quite reasonable to expect that the quantity ΔS, appearing in Eq. (6), will be positive. Furthermore, he shows that, if we associate a major part of the isothermal work to produce activation with elastic straining of the surrounding lattice, then

$$\Delta S \approx -(H/\mu_0)d\mu/dT, \tag{7}$$

where μ is the shear modulus (μ_0 at $T=0$).

In order to check this "strain theory" of ΔS and to obtain reliable values of H with which to compare theoretical predictions, precise measurements of D as a function of temperature are required, and over as wide a temperature range as possible. Actually, many of the values of D_0 reported in the literature are probably too low[8] by factors of 10^3 to 10^4 and the corresponding reported values of H are greatly in error. Much of the difficulty in obtaining precise values of H and D_0 is due to the limited range of temperature in which diffusion methods may be used for the study of atomic mobility. The limitations of diffusion experiments may be explained as follows. Since atom movement is a random walk problem, the mean distance that an atom travels from its starting point is proportional to the square root of the number of atomic jumps. Thus, in order that diffusion take place, even over distances of the order of 0.1 mm, the mean number of atomic jumps required is about 10^{11}. If such a large number of jumps is to take place within a reasonable time limit, the jump frequency must be very great; an experiment conducted under conditions where the mean time of stay of atoms is greater than 10^{-4} sec is a practical impossibility. Diffusion experiments are therefore limited to a narrow range of temperatures close to the melting point. The corresponding available range of values of D is usually only two to three powers of ten.

In addition to the difficulty in obtaining precise values of D_0 and H, the restriction of conventional diffusion experiments to high temperatures places important limits on the type of information that may be obtained by such methods. The following are some illustrations: (1) Diffusion in metals is generally described in terms of a vacancy mechanism.[9] If this mechanism is correct, there is much to be learned from a study of atomic movement under conditions where a nonequilibrium excess of vacancies is trapped by rapid quenching from a high temperature. If measurements are limited to high temperatures, such a vacancy excess cannot be maintained. (2) In order to study the effect of dislocations (cold work) on atomic mobility, it is necessary to carry out experiments below the recrystallization temperature. Such a temperature is too low for conventional diffusion experiments. (3) In the study of precipitation it is often desirable to measure the rate of atomic movements directly in the supersaturated solid solution. Such information cannot be obtained by diffusion experiments.

These limitations of conventional diffusion experiments can be overcome by a method that permits the measurement of atomic mobilities in a time of the order of that required for a single atomic jump, rather than for 10^{11} atomic jumps. Such a method is available through the measurement of anelastic effects resulting from stress-induced ordering in an initially disordered solid solution. The principle of the method is discussed in Sec. II, and is, briefly, as follows: The application of stress to a random solid solution will, in general, change the equilibrium configuration to a nonrandom one. Atomic redistribution must, therefore, follow the application of stress: this redistribution is accompanied by typical anelastic effects[10] such as an internal friction peak and an elastic after-effect. The relaxation time, τ, for this redistribution, obtained from the measurements, is related to an appropriate atom jump frequency, Γ_r, by

$$1/\tau = \alpha\Gamma_r. \tag{8}$$

The dimensionless proportionality constant, α, is of the order of unity, since the atomic redistribution, required in order that equilibrium be maintained, can be accomplished by a small number of atom jumps. By analogy to Eq. (5), Γ_r may be assumed to obey an equation of the form

$$\Gamma_r = z\nu e^{\Delta S_r/R} e^{-H_r/RT}, \tag{9}$$

so that the relaxation time obeys the Arrhenius equation

$$\tau = \tau_0 e^{H_r/RT}. \tag{10}$$

The appropriate jump rate, Γ_r, is, in general, not the same as the quantity Γ that appears in Eq. (1). Its relation to the individual jump rates, Γ_A and Γ_B, will be discussed in Sec. II.

This method for obtaining atomic mobility by the measurement of anelastic relaxation has been used extensively in the study of the mobility of interstitial solutes in b.c.c. lattices.[11] In the latter case, the application of stress results in the preferential occupation of certain interstitial sites at the expense of others, a form of stress-induced ordering. The details of the process are sufficiently straightforward to permit an exact calculation of the quantity α of Eq. (8); the result[12,13] is $\alpha = 3/2$. The quantity Γ_r in this case is simply the mean number of jumps, per unit time, of an interstitial atom; the mobility of the solvent atoms does not, of course, enter into consideration. The combination of the results of relaxation measurements

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[8] A. S. Nowick, J. Appl. Phys. **22**, 1182 (1951).

[9] H. B. Huntington, *Atom Movements* (American Society for Metals, Cleveland, 1951), p. 69.

[10] C. Zener, *Elasticity and Anelasticity of Metals* (The University of Chicago Press, Chicago, 1948).

[11] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949); C. Wert, Phys. Rev. **79**, 601 (1950); J. Appl. Phys. **21**, 1196 (1950).

[12] D. Polder, Philips Research Repts. **1**, 1 (1945).

[13] A. S. Nowick, chapter on "Internal friction in metals" to be published in *Progress in Metal Physics IV*.

at relatively low temperatures, with those of conventional diffusion experiments, at relatively high temperatures, makes possible very precise determination of the quantities H and D_0, of Eq. (6), for these interstitial systems. Detectable anelastic effects are obtained even for solute concentrations well below 0.01 percent.

The existence of analogous anelastic effects in substitutional solid solutions offers the possibility for a very much enlarged applicability of anelastic measurements to the study of atomic mobility. Such anelastic effects were first observed by Zener,[14] as an internal friction peak in a single crystal of alpha-brass (30 percent zinc). These measurements were only at one frequency (about 600 cps) and for only the one composition, and the origin of the effect was not explained at the time. Later Kê[15] verified the existence of such an internal friction peak in 70–30 brass at lower frequencies, and obtained a heat of activation for the relaxation process in reasonable agreement with the heat of activation for diffusion of zinc in brass. A possible mechanism for the observed anelastic effects in brass was suggested by Zener.[16] This is the mechanism of pair reorientation, which will be discussed in the next section; it will be shown that this mechanism is an oversimplification. On the basis of the concept of pair reorientation, Le Claire[2] calculates the quantity α [Eq. (8)] and interprets Γ_r as the jump frequency of zinc atoms in brass. He then correlates the anelastic measurements with conventional diffusion measurements for the case of 70–30 brass.

Inasmuch as the only previous anelastic measurements of atomic mobility in substitutional alloys are for one alloy composition, and even these measurements cover only a limited range of relaxation times, the present work is undertaken in order to obtain relaxation data over a wide range and for a series of compositions. In this way it is hoped to utilize anelastic measurements to obtain precise knowledge of the concentration and temperature dependence of atomic mobility, and to learn more about the mechanism of the relaxation process. The alpha-silver-zinc solid solutions are used, for this study, in preference to the alpha-brasses. The reason for this choice lies in the fact that the difference in atomic radii of silver and zinc is about twice the difference in the radii of copper and zinc, yet the solubility of zinc in copper and in silver is very nearly the same (in atom percent). Inasmuch as the magnitude of the anelastic effects, for a given concentration of solute, is anticipated to depend strongly on the difference in atomic radii of solute and solvent,[10,16] the effects in silver-zinc may be several times larger than in brass of the same composition. This increased magnitude is particularly desirable in dealing with relatively low concentrations of solute, when the anelastic effects tend to become very small.

The use of anelastic methods for the study of atomic mobility in substitutional solid solutions makes possible measurements at temperatures considerably below those at which conventional diffusion measurements could be carried out. As a result, the limitations of diffusion measurements, discussed earlier, can be overcome. For example, it is possible, by the relaxation method, to detect the presence of a nonequilibrium number of vacancies produced by quenching. A preliminary report of this work has appeared[17] and further details will be given in a subsequent paper. In addition to the fact that the relaxation method makes possible measurements at low temperatures, it also has the advantage that it uses an alloy of constant concentration; the interpretation of the measurements is, therefore, not complicated by the existence of a variable chemical concentration, as in interdiffusion experiments. (In this sense, the relaxation measurements are like radioactive-tracer diffusion experiments.)

The relaxation method has limitations of its own and, therefore, is not suggested as a method to replace diffusion studies, but simply to provide additional information that cannot be obtained from diffusion experiments. Among its disadvantages is the fact that it cannot be applied to pure metals and to alloys in which the two components have the same atomic radii. Even when the atomic size difference of the two components is sufficiently large, the method, as applied to substitutional solid solutions, is limited to relatively high solute concentrations, of the order of 10 percent.

II. THEORY OF STRESS-INDUCED ORDERING

A discussion of *order* concerns itself with the distribution of different atomic species in a solid solution on various lattice sites. If there is any deviation from a completely random distribution in the manner in which lattice sites are occupied, the alloy is said to show a degree of order. The well-known[18] concepts of long-range and short-range order are special cases of this definition. The application of stress to a system may result in a change in the state of order, if one already exists, or it may produce a state of order in an initially disordered solid solution. In the present case we will consider that the solution is random for zero stress. From thermodynamic reciprocity,[19] it follows that the application of stress will produce a degree of order if, and only if, the production of order is accompanied by strain. Thus, for an applied stress, σ, the instantaneous value of the appropriate strain, ϵ, is not only dependent on σ, but also on a parameter, p, which is a measure of the degree of order. The strain, at any instant, is, then, made up of two parts:

$$\epsilon=\epsilon'+\epsilon''. \tag{11}$$

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[14] C. Zener, Trans. Am. Inst. Mining Met. Engrs. **152**, 122 (1943).

[15] T. S. Kê, J. Appl. Phys. **19**, 285 (1948).

[16] C. Zener, Phys. Rev. **71**, 34 (1947).

[17] A. S. Nowick, Phys. Rev. **82**, 551 (1951).

[18] H. Lipson, *Progress in Metal Physics. II* (Interscience Publishers, Inc., New York, 1950), Chapter I (B. Chalmers, Editor).

[19] See reference 10, p. 113, or reference 13.

The quantity ϵ' is the perfectly elastic strain which obeys Hooke's law

$$\epsilon' = \sigma/M, \tag{12}$$

where M is called[10] the appropriate *unrelaxed modulus*. The *anelastic strain*, ϵ'', may be assumed proportional to p, for small values of p, or

$$\epsilon'' = \lambda p, \tag{13}$$

where λ is the constant of proportionality. For any value of σ, the quantity p assumes an equilibrium value, $\bar{p}$, if sufficient time is allowed. The quantity $\bar{p}$ may be taken to be proportional to σ, at low stress levels. Correspondingly, the equilibrium anelastic strain, $\bar{\epsilon}''$, is proportional to σ. We may write

$$\bar{\epsilon}'' = \Delta_M \sigma/M, \tag{14}$$

where Δ_M is a dimensionless constant called the *relaxation strength*, which measures the magnitude of the anelastic effect. It is reasonable to assume that, at constant stress, the quantity p approaches its equilibrium value, $\bar{p}$, according to a relaxation equation,

$$\dot{p} = -(p - \bar{p})/\tau, \tag{15}$$

where τ is the time of relaxation. The anelastic strain, therefore, also obeys the relaxation equation

$$\dot{\epsilon}'' = -(\epsilon'' - \Delta_M \sigma/M)/\tau. \tag{16}$$

When a harmonic solution is substituted into Eqs. (12) and (16), and the assumption $\Delta_M \ll 1$ introduced, the phase angle, ϕ, by which strain lags behind the stress is found to be

$$\phi = \Delta_M \omega\tau/(1 + \omega^2\tau^2), \tag{17}$$

where ω is the angular frequency with which the stress and strain vary. The quantity ϕ is a convenient measure of the internal friction;[10, 13] it is equal to the logarithmic decrement divided by π, and is also often represented by the symbol Q^{-1}, by analogy to electrical circuits. Equation (17) represents the well-known internal friction peak with maximum value at $\omega\tau = 1$. Rather than obtain the peak by variation of the frequency at constant τ, it is more convenient experimentally to observe ϕ as a function of temperature, i.e., to vary τ [see Eq. (10)] and keep ω constant. If T_m is the temperature of maximum damping, we then have

$$\tau(T_m) = 1/\omega \tag{18}$$

as the basis for the determination of τ at one particular temperature, T_m, from an internal friction peak. Although Eq. (17) is derived under the assumption $\Delta_M \ll 1$, and must be slightly modified[10] if this assumption is not valid, it may be applied without significant error up to $\Delta_M \cong 0.2$.

In order to obtain the relaxation time at different temperatures, internal friction measurements at various frequencies may be used conveniently, so long as the order of magnitude of τ is less than one second. To measure relaxation times somewhat greater than one second, static rather than oscillatory methods are best. One convenient static method is the elastic aftereffect, in which the specimen is subjected to stress and sufficient time allowed for the attainment of equilibrium. When the specimen is released the anelastic strain decays to zero exponentially, i.e., setting $\sigma = 0$ for $t > 0$ in Eq. (16), it follows that

$$\epsilon'' = \epsilon_0'' e^{-t/\tau}. \tag{19}$$

By observation of this exponential decay, τ may be obtained.

The simple relaxation Eq. (15) would be expected to hold when there is no fluctuation in the rate of atomic movement from one position to another in the crystal lattice. Actually, fluctuations in concentration result in a distribution of relaxation times, so that the internal friction peak does not strictly obey Eq. (17), but is equal to a weighted sum or integral of such terms over a narrow range of values of τ. The peak width is then greater than that predicted by Eq. (17). Similarly the elastic after-effect is no longer the simple exponential decay of Eq. (19), but a sum of such terms.

In order to relate the measured relaxation time to the atomic mobility in substitutional solid solutions in which the jump rates of the two components, Γ_A and Γ_B, are not the same, it is necessary to calculate the quantity α and to interpret the quantity Γ_r of Eq. (8). To achieve this end, it is desirable to know what is the nature of the ordering induced by stress in such a solid solution. The only suggestion, thus far, is Zener's concept of pair reorientation,[16] which may be summarized as follows: In a lattice of cubic symmetry, the elastic distortion produced by a single solute atom, which differs in size from the solvent atoms, must have cubic symmetry. On the other hand, a *pair* of solute atoms in nearest neighbor positions produces tetragonal distortion about the direction of the pair axis. Zener therefore proposes that pairs of solute atoms, which have their axes randomly distributed over permissible crystallographic directions under zero stress, will tend to be aligned preferentially when a shear or tensile stress is applied to the lattice. The total number of pairs is assumed fixed. The attempt of the lattice to maintain equilibrium when the stress is varied, results in the observed anelastic effects. This stress-induced preferential orientation of pairs of atoms is a form of stress-induced ordering. The type of order involved does not fall into the category of either long-range or short-range order, for it is assumed that the pairs themselves are formed by random fluctuation; the preference of pair axes for special directions is, nevertheless, a deviation from randomness and therefore a form of ordering. The emphasis on pairs of solute atoms also shows why large concentrations of solute are required to produce observable anelastic effects in substitutional solutions as compared to b.c.c. interstitial solid solutions. In the latter case, individual solute atoms produce tetragonal distortion.

The description of the relaxation phenomena in substitutional solutions in terms of the reorientation of solute atom pairs cannot be taken too seriously for several reasons. The "pair" concept is probably most nearly satisfactory at low solute concentrations, where most solute atoms are far apart and the number of pairs is quite small. Even in such a dilute solution, where the anelastic effects are probably too small to be observed, it may not be correct to think in terms of a fixed number of pairs of solute atoms, since a tendency toward preferential creation or dissolution of nearest neighbor pairs may occur under stress; also, the effect of next-nearest neighbors in producing relaxation effects must be considered. In actual measurements, solutions containing as high as $\frac{1}{3}$ solute atoms are used; here clusters of solute atoms considerably more complex than pairs occur with great frequency. The behavior of such clusters under stress cannot properly be taken into account in terms of a theory of reorientation of solute pairs. Finally, the theory of reorientation of "solute" atom pairs under stress focuses attention on the movement of solute atoms as the rate controlling process. Thus, Le Claire,[2] using the pair reorientation concept, considers that relaxation is controlled by the mobility of the solute (zinc) atoms in 70–30 brass. It will be seen, from the subsequent discussion, that this belief may be incorrect.

The concept of pair reorientation, therefore, seems to be an oversimplification. Even without suggesting an alternate mechanism for the observed anelasticity in substitutional solutions, we can be reasonably certain that the phenomenon is one of stress-induced ordering, controlled by atomic movements within the crystal lattice. In the first place these effects are observed in well-annealed single crystals, and the results are not structure sensitive. The possibility that the observed phenomena are related to the presence of internal surfaces or of dislocations is therefore discounted. The fact that the width of the internal friction peak corresponds closely to a single time of relaxation, also indicates that we are dealing with a volume (or bulk lattice) property. Secondly, these anelastic effects are only observed in alloys, and are, apparently, larger the greater the atomic size difference of solute and solvent atoms. Finally, the heat of activation for the process is of the same magnitude as that for volume diffusion. In view of this evidence, it seems fairly certain that the relaxation is controlled by atomic movements in the lattice, which act to produce an ordered condition of the alloy under an applied stress.

In order to evaluate theoretically the constant α of Eq. (8), and to calculate the relation between the rate determining frequency for relaxation, Γ_r, and the individual jump rates Γ_A and Γ_B, it is necessary to know more precisely the nature of the ordering induced by stress. In the absence of a detailed picture of stress-induced ordering, it is still possible to show which of the individual jump rates is rate determining under limiting conditions, and to obtain an approximate relation of more general validity. Let us assume that atomic movement occurs primarily by means of vacancies. It is reasonable to expect that the normal vacancy concentration is far too small for any relaxation effects to be observable as a consequence of a preferential distribution of the vacancies themselves. Vacancies will therefore contribute to the relaxation process only through their ability to produce a redistribution of A and B atoms. The relative probabilities for an A atom and a B atom to move into a given vacant lattice site are $f_A\Gamma_A$ and $f_B\Gamma_B$, respectively. Consider the limiting condition where one of these probabilities is much greater than the other, say, $f_B\Gamma_B \gg f_A\Gamma_A$. Then in most cases, when a B atom moves into a neighboring vacancy, the vacancy which then appears in the original site of the B atom will subsequently be filled by another B atom. In this way no contribution is made to the redistribution of atoms, necessary for the relaxation process. Only on those relatively rare occasions when an A atom makes a jump, does a redistribution in the occupation of lattice sites occur. Thus if $f_B\Gamma_B \gg f_A\Gamma_A$, the movement of A atoms is rate determining for the relaxation process. This means that the rate of relaxation is determined either by the component present in the much smaller amount, or if, as in these experiments, f_A and f_B are of the same order of magnitude, by the slower moving component. When the relative probabilities $f_A\Gamma_A$ and $f_B\Gamma_B$ are of the same order of magnitude, an approximate formula for the rate-determining factor may be obtained as follows. We define a *replacement* as the movement of a B atom into a vacant lattice site formerly occupied by an A atom, or of an A atom into a former B site. It seems reasonable to regard the replacement as the unit process that leads to atomic redistribution. It is readily shown that the probability per second, Γ_{rep}, for the occurrence of a replacement at any given lattice site is given by

$$\frac{2}{\Gamma_{\text{rep}}} = \frac{1}{f_A\Gamma_A} + \frac{1}{f_B\Gamma_B}. \tag{20}$$

In deriving this equation, the possibility that the next jump after a replacement might be the reverse of the previous jump is neglected. The correction for such a possibility is small, of the order of the reciprocal of the coordination number. From Eq. (20) the rate of replacement reduces essentially to the rate of movement of the slower component when the two atomic jump rates differ in order of magnitude, in agreement with the previous discussion. (It should be noted that the rate determining component need not be the solute.) If we assume that the rate of a replacement is essentially the relaxation rate, then Eq. (20) parallels Eq. (2). The main difference between the two cases is that the faster moving component controls the diffusion rate, while the slower component controls the relaxation rate. This fact must be considered when one attempts to relate relaxation and diffusion measurements for the same alloy.

In view of the dependence of the quantity Γ_r, in general, on both Γ_A and Γ_B, the Arrhenius equations (9) and (10) are [in the same way as Eq. (6)] only approximately valid.

III. PREPARATION OF SPECIMENS

The silver-zinc specimens used in this investigation were prepared by melting electrolytic silver and high purity zinc in graphite crucibles under charcoal. Each casting was given a homogenizing anneal, after which it was reduced in diameter by rolling and swaging. Specimens in the form of rods $\frac{1}{4}$ and $\frac{1}{8}$ inch in diameter were saved for high frequency measurements and the remainder drawn down to wire 0.032 inch in diameter, for use in the torsion pendulum. In order to grow coarse-grained specimens a special annealing procedure was used for both the wire and rod specimens: the specimens were sealed in vacuum and heated from 220°C to 700°C over a period of two days, then left at 700°C for five days. To obtain a final grain size larger than the specimen diameter, it was necessary to start with vacuum remelted silver, so as to remove traces of oxygen.

The percent of silver in the various specimens was determined by conventional gravimetric analysis.

IV. EXPERIMENTAL METHODS

The "high frequency" internal friction measurements are obtained using equipment similar to that described by Kê,[20] but modified in details. This method uses a magnetic drive and pickup; an audio-oscillator supplies the driving power and a tuned amplifier serves as a detector. Soft iron pole pieces are attached to flattened ends of the specimens, facing downward, so that flexural vibrations are produced. The fundamental frequency of the $\frac{1}{4}$-inch specimens (about 4 inches long) is about 1300 cps, while that of the $\frac{1}{8}$-inch specimens (about 6 inches long) is about 300 cps. Specimens are supported horizontally at the nodes of vibration. Internal friction is obtained from the half-width of the amplitude resonance curve for forced vibration. All measurements are made in air, at temperatures below 450°C. The fact that the measurements did not change with time indicates that no appreciable zinc loss took place during the experiments and that the surface oxidation that occurred did not affect the measurements. This latter result is not surprising in view of the fact that the internal friction is interpreted as arising from volume atomic mobility.

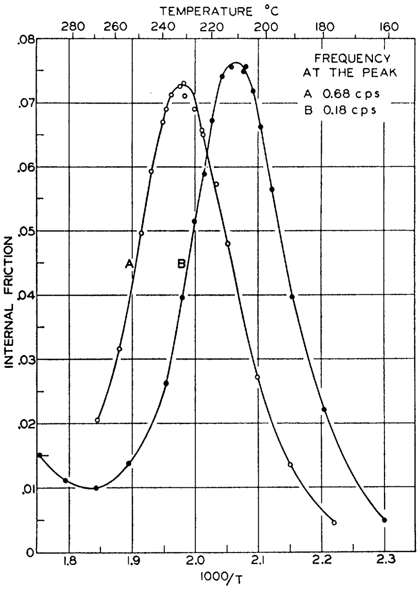

FIG. 1. Internal friction as a function of temperature, at two different frequencies, for a 70–30 silver-zinc solid solution.

The "low frequency" internal friction measurements are obtained in a torsion pendulum, in which the wire specimens serve as the suspension, by the free decay method. This apparatus is well known.[21] The frequency range of 0.2 to 2.0 cps is conveniently obtained by varying the inertia number.

Elastic after-effect measurements are made in the same apparatus as the low frequency internal friction, so modified that in place of the inertia member there is an arrangement that permits the twisting of the wire through a few degrees and its release at any desired time. The measurements consist in the determination of the residual strain after the wire is released, as a function of time. If the anelastic behavior were describable in terms of a single time of relaxation [Eq. (16)], the elastic after-effect would obey Eq. (19). One could then obtain τ in several ways—as the time for the anelastic strain to fall to $1/e$ of its initial value, from the slope of a plot of log strain against time, or from the inflection point in a plot of linear strain *versus* log time. The last method is particularly convenient because it does not require a knowledge of the initial deflection of the wire and of the final position after relaxation is complete. (The latter is especially hard to determine when grain-boundary relaxation occurs in addition to the stress-induced ordering phenomenon.) Actually, the anelastic behavior cannot be described in terms of a single time of relaxation, but shows a distribution of relaxation times, as discussed in Sec. II. Under these circumstances, it is readily shown that the time at the point of inflection, in a plot of strain against log time, is equal to a properly weighted average of the distribution of relaxation times. Thus, the average τ is best obtained by this method. Similarly, in the internal friction measurements, the time of relaxation, as

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[20] T. S. Kê, J. Appl. Phys. **20**, 1226 (1949).
[21] T. S. Kê, Phys. Rev. **71**, 533 (1947).

obtained from Eq. (18), represents the same weighted average of the distribution of relaxation times.

The measurement of temperature in both the high frequency and torsion apparatus is by means of a calibrated chromel-alumel thermocouple placed close to the center of the specimen. The variation of temperature over the length of the wire in the torsion equipment is about 2°C at 300°C. The temperature is controlled within $\pm\frac{1}{2}$°C by means of an electronic proportioning temperature controller.

Measurements of the rigidity modulus are obtained from the frequency of torsional vibration of wires at various temperatures. The modulus is proportional to the square of the vibration frequency, except for a small correction for thermal expansion of the wires as the temperature is varied. The rigidity modulus is always measured at temperatures below those at which the internal friction becomes appreciable, to avoid the contribution attributable to relaxation.[10]

In all measurements of internal friction and rigidity modulus the maximum shear strain is less than 10^{-5}. Under such conditions, internal friction and vibration frequency are found to be independent of the amplitude of vibration.

V. EXPERIMENTAL RESULTS

A. Relaxation Measurements

The anticipated large relaxation effects in silver-zinc alloys are readily demonstrated by low frequency internal friction measurements. Figure 1 shows the results of measurements in a torsion pendulum at two different frequencies, on a specimen containing 30 atomic percent zinc. The height of these internal friction peaks is about seven times the height of peaks observed[15] in 70–30 brass at similar frequencies. From the frequency and temperature at the maximum, the corresponding relaxation time is obtained from Eq. (18). A series of peaks are obtained at essentially the same frequency for different silver-zinc solid solutions; these data are shown in Fig. 2. The result of decreasing the concentration of zinc is a rapid decrease in the peak height, and a shift of the peak to higher temperatures. The latter effect means that, at a given temperature, the relaxation time is lower the higher the concentration of zinc. The change in the height of the peak with concentration is to be expected because the degree of ordering induced by stress should fall off rapidly as the concentration of zinc decreases, regardless of the mechanism of the ordering. From Fig. 2 it appears as if the peak height, and therefore the relaxation strength, Δ_M, varies approximately as the square of the concentration of zinc. It should be noted that when the height of the peak is sufficiently small (curve D of Fig. 2) grain-boundary relaxation[21,10] contributes to the internal friction at high temperatures and distorts the "mobility" peak. Such grain boundary effects are at a minimum in Fig. 2 because the specimens from which these data are obtained are prepared in such a way (described in Sec. III) as to produce grains larger than the specimen diameter. In such specimens the grain boundary internal friction occurs at higher temperatures and is smaller in magnitude than the corresponding effects in finer grained specimens.

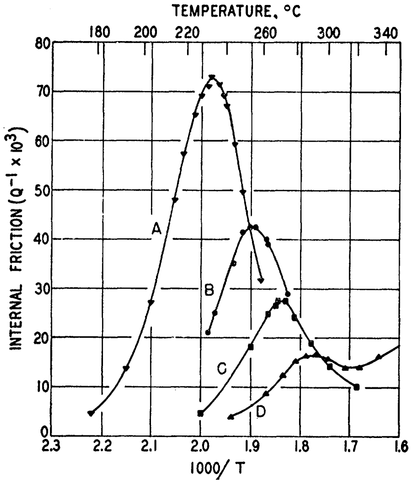

Fig. 2. Internal friction measurements, at a frequency of about 0.7 cps, for a series of silver-zinc solid solutions. The atomic percent zinc in the four alloys is 30.2, 24.2, 19.3, and 15.8, corresponding to the curves A to D, respectively.

Measurements were also obtained for finer grained specimens, obtained when the silver used in preparation of the alloys was not vacuum remelted, and also when lower final annealing temperatures were used. In addition to the fact that the grain boundary internal friction in these specimens is more pronounced, so that the curves even for the 70-30 composition assume a shape somewhat like that of curve D of Fig. 2, the height of the mobility peak is also observed to be lower in these finer grained specimens. For example, for 70-30 silver-zinc, peak heights ranging from 0.04 to 0.073 are observed, the highest peaks being obtained from the coarsest grained specimens. On the other hand, the location of the internal friction peak at a given frequency, which determines the relaxation time, is found to be the same for all specimens of the same composition within experimental error. Apparently, the relaxation strength may depend on factors other than the composition, but the relaxation time is completely insensitive to structural differences which arise from the method of preparation.

The range of values of relaxation time that may be obtained by internal friction measurements in the torsion pendulum are very limited. In order to measure much shorter relaxation times (at higher temperatures) the high frequency measurements are employed; to measure much larger values of τ, the elastic after-effect method is used. Typical measurements of the elastic after-effect, for the same specimen as used for Fig. 1, are presented in Fig. 3. The method of plotting the

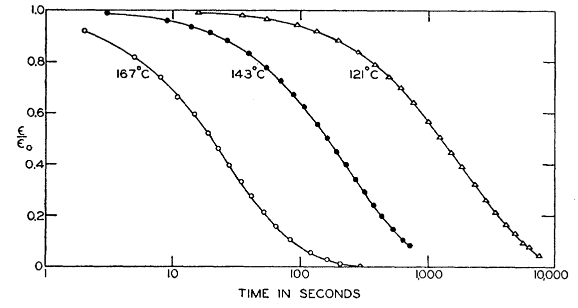

FIG. 3. Typical elastic after-effect measurements, at three temperatures, on the same specimen used for Fig. 1. The relaxation time, in each case, is the value of the time at the inflection point.

data is that described in the last section; the time of relaxation is taken as the time to reach the inflection point.

By the use of low and high frequency internal friction and elastic after-effect measurements, it is possible to cover a range of relaxation times from 10^{-4} to about 2000 seconds, i.e., more than seven logarithmic cycles. The combined data for relaxation time as a function of the reciprocal of the absolute temperature is given in Fig. 4, for solid solutions of four different compositions. The dependence on concentration is very striking; a ten percent increase in the atomic percent zinc increases the relaxation time at a given temperature by about a factor of ten. A straight line is drawn for each composition, but it is clear that there is a regular deviation from a simple Arrhenius law. This deviation means that the effective heat of activation is a function of temperature. It has been customary to assume that H is a constant in diffusion studies (except when grain boundary diffusion plays a significant role), but this assumption is only used because the precision and range of conventional diffusion data does not permit one to detect such deviations. The slopes of the straight lines shown in Fig. 4 give a mean value for the heat of activation over the temperature range of these experiments. These mean values, H_r, and the corresponding mean intercepts, τ_0 [see Eq. (10)], are given in Table I, for the various compositions. Examination of the values of the intercepts shows that the four straight lines when extrapolated to $T^{-1}=0$, meet almost at a point, within one-tenth of a logarithmic cycle. Consequently, the variation of relaxation time (and, therefore, of atomic mobility) with concentration is attributable almost entirely to the quantity H_r, and practically not at all to the quantity τ_0 of Eq. (10). The values H_r are plotted as a function of concentration, in Fig. 5. Within the precision of the measurements a straight line may be drawn through these four points. It is interesting to note that this line extrapolates to 40.2 kcal/mole at zero concentration, and not to 46 kcal/mole, the value obtained from self-diffusion of pure silver.

Knowing the values of the heat of activation, we may compare the widths of the observed internal friction peaks with the theoretical width at half-maximum,

$$\delta(1/T)=2.62R/H,$$

which may be obtained from Eqs. (17) and (10). In this way we have a measure of the extent of deviation from a single time of relaxation. It is found that the observed peaks are 15 to 20 percent wider than the theoretical value. This is about the same magnitude as the deviation from a single time of relaxation in the study of the mobility of interstitial solutes.[22]

B. Measurements of Rigidity Modulus

Relative values of the rigidity modulus at room temperature are obtained for the various wire specimens used in the relaxation experiments already described. These include those specimens of the same composition that had been given different treatments in preparation, resulting in differences both in grain size and in the heights of the observed internal friction peaks. A correlation is found to exist between the rigidity modulus and the height of the internal friction peak, the highest values of the modulus being observed for the specimens that show the lowest peaks. The range of variation of the rigidity modulus, observed for

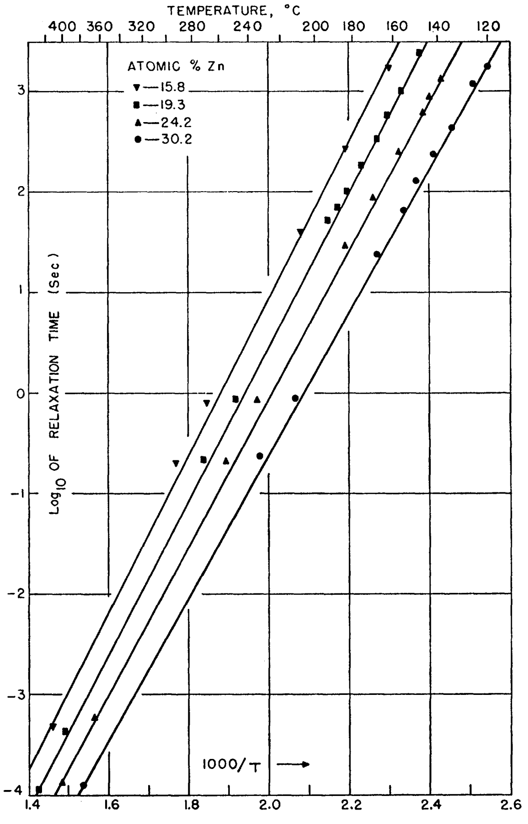

FIG. 4. The variation of the time of relaxation for stress-induced ordering with temperature, for a series of silver-zinc solid solutions.

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[22] See C. Wert and C. Zener, reference 11.

different specimens of the same concentration, is 16 percent. Such large variations in the modulus cannot be accounted for by differences in such factors as dislocation density or by the presence of impurities, but is undoubtedly a consequence of differences in the degree of preferred orientation of the grains that compose the specimen.

Inasmuch as Eq. (7) for the entropy of activation, ΔS, involves the quantity $\mu_0^{-1}(d\mu/dT)$, this quantity is obtained experimentally for the various alloys, by measurement of the temperature dependence of the frequency of torsional vibration between room temperature and 200°C. Above 200°C relaxation effects produce deviations from the linearity of the curve of rigidity modulus *versus* temperature. The values of $\mu_0^{-1}(d\mu/dT)$ are practically the same for all specimens of a given composition, i.e., not dependent on the degree of preferred orientation. These values are listed in Table I; the value obtained from measurements on a wire of high purity silver are also included for comparison. Within the error of the measurements, the tabulated values may be regarded as independent of the concentration of zinc.

VI. DISCUSSION

The measurements of relaxation time as a function of temperature and composition show that the atomic mobility in silver-zinc solid solutions is strongly concentration dependent. The only previous data for concentration dependence of atomic mobility are obtained by Matano analysis of the results of an intermetallic diffusion experiment.[23] Such data are never precise enough to make possible a reliable determination of the heat of activation as a function of concentration. The present experiments trace the strong concentration dependence of the relaxation time to the variation of the mean heat of activation with zinc concentration, and indicate that the quantity τ_0, Eq. (10), is practically independent of concentration.

In view of the concentration dependence of the mean activation energy, it is not surprising that the curves of Fig. 4 are not straight lines, and also that the anelastic effects are not describable in terms of a single time of relaxation. Both of these facts may be explained in terms of statistical fluctuations in concentration throughout the solid solution, leading to a statistical distribution in the values of the activation energy and, correspondingly, in the relaxation times. Another factor that may contribute to the deviation of the curves of Fig. 4 from straight lines has already been discussed in Sec. II, i.e., the fact that the relaxation frequency depends on both Γ_A and Γ_B (Eq. (5)), while ΔH_A and ΔH_B are, in general, not equal.

TABLE I. Results obtained from relaxation and rigidity measurements on silver-zinc alloys.

Atomic percent Zn	H_r kcal/mole	$-\log_{10}\tau_0$ (τ_0 in sec)	$\mu_0^{-1}(d\mu/dT)$ (°K$^{-1}\times10^4$)	α
0	—	—	4.4	—
15.8	36.1	14.75	4.3	0.26
19.3	35.2	14.84	4.3	0.34
24.2	33.8	14.76	4.4	0.34
30.2	32.5	14.78	4.6	0.42

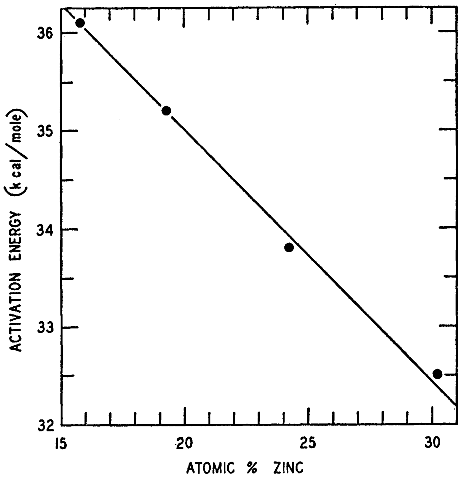

FIG. 5. The dependence of the mean activation energy, for the relaxation process in silver-zinc alloys, on concentration.

The present experiments have obtained H_r and τ_0 for different compositions of silver-zinc alloys. It is therefore important that some attention be given to the interpretation of these measured quantities. The relaxation time is related, by means of Eq. (8), to an appropriate jump frequency, Γ_r. In view of the discussion of Sec. II, it appears that we may regard Γ_r essentially as the jump frequency of the slower component of the solid solution, provided that one component moves considerably slower than the other. H_r is then very nearly equal to the larger of the two quantities ΔH_A and ΔH_B. To give a complete interpretation to the quantity τ_0 requires a knowledge of the numerical constant α of Eq. (8). In the absence of a theoretical calculation for α, an attempt will be made to estimate its value empirically. Combining Eqs. (8), (9), and (10) we obtain

$$1/\tau_0 = 12\alpha\nu e^{\Delta S_r R}, \qquad (21)$$

where the coordination number, z, is set equal to 12, for f.c.c. alloys. A reasonable value for ν may be obtained from the Debye frequency, while ΔS_r may be estimated from Eq. (7). In calculating ΔS_r, we make use of our experimental result that, within the precision of measurement the quantity $\mu_0^{-1}(d\mu/dT)$ is independent of concentration for these silver-zinc alloys. Equation (7) may then be reduced to

$$\Delta S_r/\Delta S_{\mathrm{Ag}} \cong H_r/H_{\mathrm{Ag}},$$

where ΔS_{Ag} and H_{Ag} are the values obtained from

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[23] See, for example, F. N. Rhines and R. F. Mehl, Trans. Am. Inst. Mining Met. Engrs. **128**, 185 (1938).

measurements[24] of self-diffusion in pure silver: $H_{\mathrm{Ag}}=45.9$ kcal/mole, $\Delta S_{\mathrm{Ag}}=9.5$ cal/mole per °K. Comparison of the experimental values of τ_0 (Table I) with the values of $\nu e^{\Delta S_r/R}$ calculated in the manner just described, yields the values of α listed in the final column of Table I. Inasmuch as the formula used for the calculation of ΔS_r is only approximate, and the quantity ΔS_r appears in an exponent in Eq. (21), the numerical values obtained by this calculation should not be taken too seriously and are probably only correct within a factor of 2 or 3. The importance of these results, however, lies in the fact that they may be regarded as self-consistent with the expectation that α is of the order of magnitude unity, and that ΔS_r is greater than zero and given approximately by Zener's strain theory, i.e., Eq. (7). The fact that α is somewhat less than unity is also reasonable, since it means that the relaxation frequency is somewhat less than the rate-controlling jump frequency. These results, therefore, are further indication that the interpretation of the relaxation phenomena in terms of stress-induced ordering is correct.

There is another method by which the constant α may be estimated empirically: by direct comparison of relaxation data with high temperature diffusion measurements. The obstacles to such a comparison are first, the lack of suitable diffusion data, and second, the difficulty in correcting for the appropriate jump frequency. The only diffusion data for silver-zinc alloys[25] are obtained by the evaporation method (in the temperature range 650°C to 850°C); the fact that data obtained by the same authors for copper-zinc alloys are in poor agreement with the results of more conventional diffusion experiments, indicates that the silver-zinc diffusion data is probably not reliable.[26] As for the corrections required, the earlier discussion has shown that the effective frequency in intermetallic diffusion [the quantity Γ of Eqs. (1) and (2)] is not generally the same as the effective frequency in relaxation (the quantity Γ_r); in fact, whereas Γ is essentially the mobility of the faster diffusing component, Γ_r is that of the slower component. It is, therefore, difficult to make a reliable comparison between intermetallic diffusion and relaxation data. Le Claire[2] has made such a comparison for 70–30 brass and found that the value of α is close to unity; in correcting for the effective frequency, however, he assumed that the movement of zinc atoms (the faster component) controlled the rate of relaxation. Much more reliable information could be obtained by comparison of the relaxation results with data from diffusion experiments in which radioactive tracers of each component are diffused, in turn, through binary solid solutions of constant chemical concentration. Such tracer experiments, when carried out for a series of solid solutions will give Γ_A and Γ_B separately as functions of temperature and concentration. Unfortunately, such data are not yet available.

The measurements of rigidity modulus of various wire specimens have enabled us to trace differences in the heights of internal friction peaks of specimens of the same composition to differences in the degree of preferred orientation of the grains. There are no data available for the elastic moduli of single crystals of silver-zinc alloys, but examination of such data for copper, silver, and gold shows that in all cases the shear modulus for the ⟨100⟩ direction is considerably larger than that for the ⟨111⟩ direction. It seems reasonable to expect that this same condition applies to the silver-zinc alloys. Then, the fact that the larger moduli are observed for specimens that show the lower peaks leads to the conclusion that grains for which the ⟨111⟩ direction lies close to the wire axis show much greater anelastic effects in a torsion experiment than those aligned in the ⟨100⟩ direction. Single crystal measurements are contemplated to verify this conclusion and to determine the ratio of the relaxation strengths for the ⟨100⟩ and ⟨111⟩ directions. Such information will aid in determining the nature of the stress-induced ordering.

The fact that the degree of preferred orientation, and therefore the relaxation strength, is so sensitive to the prior heat treatment of the specimen means that the apparent dependence of peak height on the square of the concentration, as indicated by Fig. 2, should not be taken too seriously. In fact, rough considerations, based on a comparison of the data for elastic modulus as measured by Köster and Rauscher[27] with the rigidity data obtained in these experiments indicate that the peak height for a given orientation may vary more nearly linearly with the concentration of zinc.

In conclusion, the author wishes to express his gratitude to Mr. A. Vernon and Mr. R. Sladek for assisting with the measurements, to Dr. N. Nachtrieb for the chemical analyses, and particularly to Dr. W. Bergmann for the preparation of the specimens and for the numerous experiments that he conducted to obtain sufficiently coarse-grained specimens.

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