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On the Zener Effect in Alloys I.
The Size Factor.

by

J. M. SIVERTSEN**

Technical Report No. 6

September 15, 1962

Contract Nonr 710(29)

DEPARTMENT OF METALLURGY
INSTITUTE OF TECHNOLOGY
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**Associate Professor, University of Minnesota

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ABSTRACT

The problem of the stress-induced ordering of solute atoms, the so-called Zener effect, is considered. In this work the effect of the difference in solute-solvent atom sizes is considered. Starting with this size factor the tensor anelastic strain is computed. Then by the thermodynamic theory for relaxation processes, due Meixner and others, the relaxation strength, Δ_M, is calculated as a function of orientation. The results of the calculation suggest that the size factor is not necessarily the most important contribution in determining the relaxation strength. It is suggested that electronic effects may be more significant.

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September 15, 1962

Metallurgy Branch (Code 423)
Office of Naval Research
Department of the Navy
Washington 25, D. C.

Gentlemen:

This technical report entitled "On the Zener Effect in Alloys" was prepared under contract Nonr 710(29) and represents the sixth report in a series dealing with the general subjects of the effects of clustering and short-range order in alloys. This report is to be submitted in final form for publication.

We thank you for your support of our work in this area.

Yours truly,

John M. Sivertsen
Associate Professor

JMS:JM

On the Zener Effect in Alloys

I. The Size Factor

Introduction.

Ordinarily, an externally induced change in state of a crystalline solid such as an elastic deformation, magnetization or electric polarization is reversible. However, when such reversible processes are coupled with diffusion-type mechanisms the atoms of the crystal, assisted by thermal fluctuations, will exceed activation energy barriers and migrate to neighboring lattice sites. The previously reversible phenomena are now retarded and damped; for example, the strain lags behind the stress field, etc., vibrational energy of an oscillating system is transformed irreversibly to thermal energy at a finite rate. Such phenomena are called relaxations. Systems which show a specific capacity for dissipating energy internally are said by Zener to exhibit internal friction(1).

Now there are a number of micromechanisms which can contribute to the internal friction of a crystalline solid. The one we shall consider in this paper is that of stress-induced ordering of solute atoms in solid solutions. In particular, we shall consider the effect of the so-called Size Factor of the solid solution.

If we assume that we have a system undergoing periodic mechanical vibrations (e.g., a torsional pendulum), which were initiated with a certain amplitude and allowed to decay freely, the amplitudes of the oscillations will die out exponentially in time. The internal friction is then usually expressed quantitatively in terms of the logarithmic decrement δ of the oscillations which we define by

$$\delta = \log_e(A_n/A_{n+1}) \tag{1}$$

If instead the system is driven at constant amplitude then

$$\delta = \tfrac{1}{2}(\Delta E/E) \tag{2}$$

where ΔE is the energy lost to heat per cycle and E is the maximum amount of energy stored in the specimen during one cycle of oscillation.

In 1948 Zener proposed the following dynamical equation in giving a general phenomonological description of anelastic behavior,

$$\sigma + \tau_\epsilon \dot{\sigma} = M_r(\epsilon + \tau_\sigma \dot{\epsilon}) \tag{3}$$

τ_ϵ = the relaxation time of stress at constant strain,

τ_σ = the relaxation time of strain at constant stress, and

M_r = the relaxed modulus

For those processes characterized by a single relaxation time $\bar{\tau}$ Zener obtained the result

$$\frac{\delta}{\pi} = \tan\varphi = \frac{M_u - M_r}{M_r} \quad \frac{\omega\bar{\tau}}{1 - (\omega\bar{\tau})^2} = Q^{-1} \tag{4}$$

$\bar{\tau} = (\tau_\epsilon \tau_\sigma)^{\frac{1}{2}}$, $\bar{M} = (M_u M_r)^{\frac{1}{2}}$, φ = the phase angle by which the strain lags the stress, and M_u = the unrelaxed modulus. Q^{-1} is called by Zener the internal friction. If we plot Q^{-1} versus the frequency, ω, we obtain a bell-shaped curve whose maximum occurs at a frequency given by $\omega\bar{\tau} = 1$, see Figure 1.

In general, the internal friction has been observed to be quite frequency dependent, usually showing successive regions of high and low damping. The peaks in the damping behavior, i.e, of high energy loss, are called relaxation peaks and are the resultant effect of the coupling of some irreversible process in the material with the applied stress. In our case, that of the Zener effect, the internal friction peak arises from the coupling of the stress with the diffusional motions of atoms in substitutional alloys as they become preferrentially ordered in the stressed crystal.

In situations where the relaxation processes are thermally activated we have

$$\bar{\tau} = \bar{\tau}_0 \exp(\Delta H/RT); \quad \Delta H = \text{the activation energy of the relaxation} \qquad (5)$$

so that we may conveniently vary the relaxation time instead of the frequency in order to observe a peak. Figure 2 shows a typical Zener relaxation peak as a function of temperature obtained by Nowick for a Ag-30% Zn alloy.

There are two parameters which characterize a relaxation peak

i) the relaxation strength Δ_M

ii) the relaxation time $\bar{\tau}$

Δ_M is a measure of the peak height and is a thermodynamic quantity, depending only upon the initial and final states of the crystal. Following Zener's treatment we define Δ_M by

$$\Delta_M = (M_u - M_r)/M_r \qquad (6)$$

$\bar{\tau}$ is a kinetic quantity and cannot be treated by equilibrium methods; in our range of interest $\Delta H \cong$ the activation energies for diffusion in the alloy.

Zener has described the internal friction peak bearing his name as follows: Under the action of an externally applied stress the internal stresses tend to be relieved if the distribution of atoms (local order) is altered, thus the term stress-induced ordering. In particular, the relaxation is due to the reorientation of pairs of adjacent solute atoms into preferrential positions under the influence of an applied shear stress. Such a relaxation is possible because the size difference between solute and solvent atoms results in a tetragonal distortion of the lattice when like pairs of atoms are similarly oriented. The number of solute atom pairs was assumed by Zener to remain constant throughout the process. This model seems to be in general agreement with the result that relaxations are difficult to observe in systems which show a small size factor.

However, as pointed out by LeClaire and Lomer,(2) and Nowick and his co-workers(3)(4)(5), the problem is of considerably greater complexity than indicated by the simple pair model. The configurational arrangement of atoms in the crystal is much more complex at high concentrations (15-50%) than can be described by a simple distribution of solute atom pairs. No account is taken of the possibility of short range order or clustering being present in the alloy. Higher order neighbor interactions are ignored and in general the number of pairs of solute atoms is not constant.

Now it is known that alloys while in the stress-free state show isotropic short-range order parameters. On the other hand, it can be shown that the local order in a stressed solid is directional. In fact, the short-range order is a symmetric second rank tensor. We are then required to specify a number of directional ordering parameters α_j which are consistent with the crystal neighbor relations. These α_j may then be used to form a short-range order tensor which is related to the anelastic strain. To do this we shall follow the model proposed by Chikazumi(6) and others(7) in treating the magnetic annealing behavior of ferromagnetic alloys. In making this calculation only the atomic size difference is taken into account. After doing this we will then calculate Δ_M and its behavior as a function of orientation, temperature, etc.

Given a crystal of A and B type atoms having N sites there are ½ZN nearest neighbor pairs of all types. We write this as

$$[AA] + [AB] + [BA] + [BB] = \tfrac{1}{2}ZN = nN \qquad (7)$$

where $[AA]$ = the number of AA pairs, etc.; $n = \tfrac{1}{2}ZN$ = the number of independent orientations possible for each pair. Considering the total number of nearest neighbor pairs aligned the j^{th} direction we have

$$[AA]_j + [AB]_j + [BA]_j + [BB]_j = N \qquad (8)$$

Also $2\,[AA]_j + [AB]_j + [BA]_j = 2\,[A]$

and $2\,[BB]_j + [BA]_j + [AB]_j = 2\,[B]$

If one further defines a concentration parameter C to be

$$C = ([A] - [B])/N \tag{9}$$

and a directional order parameter, α_j, for nearest neighbor pairs along the j^{th} direction to be

$$\alpha_j = \frac{1}{N}\left\{ [AB]_j + [BA]_j - [AA]_j - [BB]_j \right\} \tag{10}$$

one obtains

$$[AA]_j = \frac{N}{4}(1 + 2C - \alpha_j)$$

and

$$[BB]_j = \frac{N}{4}(1 - 2C - \alpha_j)$$

From this result one can then write down the average atom spacing along the j^{th} direction of the stressed crystal as

$$d_j = \frac{1}{N}\Big\{(r_{\circ} + \delta r_{AA})\,[AA]_j + (r_{\circ} + \delta r_{AB})(\,[AB]_j + [BA]_j) - (r_{\circ} + \delta r_{BB})\,[BB]_j\Big\} \tag{11}$$

where $r_{\circ}$ = the average atom diameter determined from the lattice parameter. By substitution this result reduces to

$$d_j = r_{\circ} - \tfrac{1}{4}(1+2C-\alpha_j)\delta r_{AA} + \tfrac{1}{2}(1-\alpha_j)\delta r_{AB} + \tfrac{1}{4}(1-2C-\alpha_j)\delta r_{BB}$$

The average spacing $\overline{d}_j$ along the j^{th} direction of the stress-free crystal is given simply by substituting the isotropic value,

$\bar{\alpha}$, for the short range order parameter α_j. The linear dilatation along the j^{th} direction due to the stress-induced ordering of atoms is then given by

$$(d_j - \bar{d}_j)/\bar{d}_j = -\Theta(\alpha_j - \bar{\alpha})/2r_o \qquad (12)$$

where $\Theta = \frac{1}{2}(\delta r_{AA} + \delta r_{BB}) - \delta r_{AB}$ and is related to deviations from Vegard's law for lattice parameters. When $\Theta = 0$, Vegard's rule is obeyed. To first order we may also assume that the linear dilatations along directions normal to the j^{th} direction due to ordering along direction j are zero.

We now write the total contribution to the strain $\vec{\vec{e}}_j$ due to ordering along the j^{th} direction as

$$\vec{\vec{e}}_j = \frac{du_\sigma}{d\sigma}\hat{\sigma}\hat{\sigma} \qquad (13)$$

where $du_\sigma/d\sigma = \frac{-\Theta}{2r_o}(\alpha_j - \bar{\alpha})$ and σ is a cartesian coordinate along direction j; $\hat{\sigma}$ is a unit vector along the j^{th} direction which we may write as $\hat{\sigma} = \lambda_{jx}\hat{i} + \lambda_{jy}\hat{j} + \lambda_{jz}\hat{k}$. The λ_{ji} are the direction cosines of $\hat{\sigma}$ relative to the i^{th} crystal axis.

Taking account of the contributions to the strain due to ordering along all of the j directions we have

$$\vec{\vec{e}} = \sum_{j=1}^{n} \vec{\vec{e}}_j = \frac{-\Theta}{2r_o}\vec{\vec{\gamma}} \qquad (14)$$

$\vec{\vec{\gamma}}$ is a short-range order tensor which we define by

$$\psi_{ik} = \sum_{j=1}^{n} (\alpha_j - \overline{\alpha}) \lambda_{ji}\lambda_{jk} \qquad (15)$$

In the case of the body-centered cubic and face-centered cubic structures the $\lambda_{ji} = \pm(3)^{-\frac{1}{2}}$, and 0 and $\pm(2)^{-\frac{1}{2}}$ respectively. In terms of this result we should note that when Vegard's Law holds ($\theta = 0$) there will be no anelastic strain associated with stress-induced changes in order which arise from the size factor of the alloy. This is in agreement with the conclusions of LeClaire and Lomer(2) based on their earlier theory of directional ordering effects in internal friction.

Calculation of Δ_M.

Now to calculate Δ_M we must determine the Helmholtz free energy F as a function of (σ, ϵ, T, x_i, α_j). Then, by the thermodynamic theory of relaxation processes, we calculate Δ_M as a function of orientation, temperature, etc.

Following DeDonder, Meixner and others(8) we have for the case of isothermal relaxations.

$$\sum_j \frac{d\alpha}{dt}j = \sum_j \left[(\partial\alpha_j/\partial\sigma)_{\epsilon,T}\dot{\sigma} + (\partial\alpha_j/\partial\epsilon)_{\sigma,T}\dot{\epsilon}\right]$$

$$= -<R>\sum_j A_j \qquad (16)^{**}$$

$$= -<R>\sum_j \left[(\partial A_j/\partial\sigma)_{\epsilon,T}\sigma + (\partial A_j/\partial\epsilon)_{\sigma,T}\epsilon\right]$$

where both α_j and A_j are linear functions of σ, ϵ and T. A_j is the Chemical Affinity corresponding to α_j and is defined by

$$-A_j = \partial F/\partial\alpha_j; \quad A_j = 0 \text{ at equilibrium.}$$

Dividing each j-term on both sides of the equation by $<R>$ $(\partial A_j/\partial\sigma)_{\epsilon,T}$ we obtain on re-arranging terms

$$\sigma + \frac{\dot{\sigma}}{n}\sum_j \frac{1}{<R>}(\partial\alpha_j/\partial A_j)_{\epsilon,T} = M_r\left\{\epsilon + \frac{\dot{\epsilon}}{n}\sum_j \frac{1}{<R>}(\partial\alpha_j/\partial A_j)_{\sigma,T}\right\} \qquad (17)$$

Comparing this result with Zener's equation (3) we may write that

$$\bar{\tau}_\sigma = \frac{1}{n<R>}\sum_j (\partial\alpha_j/\partial A_j)_{\sigma,T}$$

and

$$\bar{\tau}_\epsilon = \frac{1}{n<R>}\sum_j (\partial\alpha_j/\partial A_j)_{\epsilon,T}$$

And from this

$$\Delta_M = (M_u - M_r)/M_r = (\bar{\tau}_\sigma - \bar{\tau}_\epsilon)/\bar{\tau}_\epsilon$$

[**] $<R>$ represents an appropriate Arrhenius rate factor.

since $M_u = M_r \dfrac{\tau_\sigma}{\tau_\varepsilon}$.

From the thermodynamic relation

$$(\partial A_j/\partial \alpha_j)_{\sigma,T} = (\partial A_j/\partial \alpha_j)_{\varepsilon,T} - M_u(\partial \varepsilon/\partial \alpha_j)^2_{\sigma,T} \qquad (16)$$

we may then show that

$$\Delta_M = \sum_j \left\{ \frac{M_u(\partial \varepsilon/\partial \alpha_j)^2_{\sigma,T}}{(\partial A_j/\partial \alpha_j)_{\varepsilon,T} - M_u(\partial \varepsilon/\partial \alpha_j)^2_{\sigma,T}} \right\} \qquad (17)$$

which is a result similar to that of Zener.

In general we can break the Free Energy up into three terms

(1) Internal energy including chemical interactions and electronic effects, U.

(2) Strain energy contributions, W.

(3) Configurational entropy terms, S_{conf}.

Following Iwata(7) we consider that the Quasi-Chemical Approximation applies and we then write

$$U = \sum_j \left\{ V_{AA}[AA]_j + V_{BB}[BB]_j + V_{AB}([AB]_j + [BA]_j) \right\} \qquad (18)$$

$$= \text{Constant} - \tfrac{1}{2}N\varphi \sum_j \alpha_j$$

where $\varphi = \tfrac{1}{2}(V_{AA} + V_{BB}) - V_{AB}$. When $\varphi > 0$ then we tend to get ordering; if $\varphi < 0$ we tend to get clustering.

Linear elasticity theory gives the strain energy to be

$$W = -\tfrac{1}{2}\sum_{i,k} \sigma_{ik}\epsilon_{ik} = \frac{\theta}{4r_{\circ}}\sum_{i,k}\sigma_{ik}\gamma_{ik} \qquad (19)$$

Iwata(7) has also calculated the configurational entropy for nearest neighbors by the self-consistent method of Takagi(9) which is obtained from

$$S_{conf} = k \log_e W$$

where $W = (nN)!\, P_I P_{II} / [AA]_j!\, [AB]_j!\, [BA]_j!\, [BB]_j! =$ the thermodynamic probability.

for the case of a body-centered cubic lattice. P_I and P_{II} are the probabilities for all consistent occupations of the sub-lattices I and II. A similar result is obtained for the face-centered cubic lattice, which has four sub-lattices. (The equilibrium values of the α_j may be obtained from the condition $A_j = 0$). The result then gives the configurational entropy as

$S_{conf} = f(\alpha_j, x_i, \mathcal{S})$ where $\mathcal{S}$ is a long range order parameter.

If we consider the case where $\mathcal{S} = 0$, and with the Free Energy we have calculated, $F(\sigma, \epsilon, T, x_i, \alpha_j) = U - W - TS_{conf}$, we may then evaluate A_j and hence Δ_M. We obtain the result that

$$-A_j = \frac{\partial F}{\partial \alpha_j} = -\tfrac{1}{2}N\varphi + \frac{\theta}{4r_{\circ}}\sum_{i,k}\sigma_{ik}\lambda_{ji}\lambda_{jk} - \frac{kTN}{4}\, Q(\alpha_j, x_n) \qquad (20)$$

$Q(\alpha_j, x_n)$ is a function of the directional ordering parameters α_j, and the atom fractions of the constituents, x_n. By substitution into equation (17) we may then calculate the relaxation strengths of BCC alloys associated with the various components of the anelastic strain. We give the results for tensile and shear relaxations along the < 100 > and < 111 > directions respectively.

$$\Delta_{E,100} = \frac{4E_{100}\theta^2/9Nk\bar{\gamma}r_\circ^2}{T - E_{100}\theta^2/9Nk\bar{\gamma}r_\circ^2}, \ \bar{\gamma} \cong 1$$

$$\Delta_{E,111} = \frac{4E_{111}}{Nk\bar{\gamma}} \left\{ \frac{(\theta/2r_\circ)^2}{T - 4E_{111}\theta^2/4Nk\bar{\gamma}r_\circ^2} + \frac{3(\theta/18r_\circ)^2}{T-4E_{111}\theta^2 Nk\bar{\gamma}18r_\circ^2} \right\} \tag{21}$$

are the relaxation strengths along the < 100 > and < 111 > directions associated with the Young's Modulus.

$\bar{\gamma}$ is a function of the ordering parameters, α_j, and the concentrations, x_n. E_{100} and E_{111} are the unrelaxed Young's moduli for the < 100 > and < 111 > directions respectively.

$$\Delta_{G,100} = \frac{4G_{100}\theta^2/Nk\bar{\gamma}9r_\circ^2}{T - 2G_{100}\theta^2/Nk\bar{\gamma}9r_\circ^2}$$

and

$$\Delta_{G,111} = \frac{4G_{111}\theta^2/Nk\bar{\gamma}27r_\circ^2}{T - 4G_{111}\theta^2/Nk\bar{\gamma}54r_\circ^2} \tag{22}$$

are the relaxation strengths in the < 100 > and < 111 > directions associated with the shear modulus G. G_{100} and G_{111} are the unrelaxed shear moduli for the < 100 > and < 111 > directions respectively. A similar set of relations may be obtained for the analogous relaxation strengths in FCC alloys.

Discussion.

If we consider the results of the calculation certain conclusions may be drawn. (1) equation (17) gives a general expression for an anisotropic Δ_M which is independent of a specific model for the relaxation. (2) the Size Factor contributions to the relaxation, given by (21) and (22), predict results which contradict the directional dependence that is observed experimentally; see Figures 3 and 4. (3) a relaxation of a pure hydrostatic pressure is predicted by equations (17) and (19) This agrees with the predictions of LeClaire and Lomer(2). (4) the temperature dependence predicted by equations (17) and (20) for Δ_M is that which was first predicted by Zener(1) and observed experimentally by Li and Nowick(3).

The anisotropy ratios $\Delta_{E,100}/\Delta_{E,111}$ and $\Delta_{G,111}/\Delta_{G,100}$, calculated from equations (21) and (22), give the wrong directional dependence when compared with experimental results for BCC(4). A similar calculation made for FCC systems is likewise in error in the same sense. The anisotropy in Δ_M is the same for FCC as for BCC alloys(4)(5). Our conclusion is, therefore, that the <u>atomic size difference cannot account</u> for these relaxations. Furthermore, if we substitute the appropriate values of E,G, Θ, $\bar{\gamma}$ and r_0, into equations (21) and (22) the calculated values obtained for Δ_E and Δ_G are $\approx 10^{-4}$ and are at least an order of magnitude smaller than the observed relaxation strengths given in Figures 3 and 4. The composition dependence of Δ_M enters through the dimensionless number $\bar{\gamma}$, which is approximately proportional to the square of the solute concentration in the dilute case.

The lack of agreement between experiment and predictions based on nearest neighbor pair-reorientation theories was explained by Nowick et al.(4)(5) as being due to neglect of next neighbor pair terms. To check this possibility our calculation was modified to consider next neighbor ordering directions also. Our results did not show any change in the character of the directional dependence and hence no improvment in agreement with experiment. It does not appear that any further generalization of the atomic size factor contribution will lead to any improvement. Attempts to include chemical interactions with the size effect contribution have also met with little success(2). In our view, the reason for this is that the relaxation is closely related with perturbations of the electronic structure of the alloy. This is because of the known dependence of the electronic structure on the degree of short-range order in the alloy. The most likely contributions are those involving interactions between the Fermi surface of the alloys and their average Brillouin zone boundaries. We are investigating this problem at the present time and will discuss it in a later report.

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References

1. C. Zener, Elasticity and Anelasticity of Metals, University of Chicago Press, (1948).
2. A. D. LeClaire and W. M. Lomer, Acta Met., 2, p.731, (1954).
3. C. Y. Li and A. S. Nowick, Acta Met., 9, p. 49, (1961).
4. A. S. Nowick and D. P. Seraphim, Acta Met., 9, p. 40, (1961); D. P. Seraphim and A. S. Nowick, Acta Met., 9, p. 85, (1961).
5. B. S. Berry, Acta Met., 9, p. 98, (1961).
6. S. Chikazumi, J. Phys. Soc. Japan, 5, p. 327 and 333, (1950).
7. L. Nëel, Compt. Rend., 237, p. 1613, (1953); T. Iwata, Sci. Rep. RITU, A10, p. 34, (1958).
8. L. DeDonder, Affinity, Stanford University Press, (1936); W. Meixner, Naturforsch., 4a, p. 594, (1949).
9. Y. Takagi, Proc. Phys. Math. Soc. Japan, 23, p. 44, (1941).

Figure Captions

Figure 1. Schematic representation of a relaxation peak (1) in the internal friction. The S-shaped curve gives the frequency dependence of the associated elastic modulus.

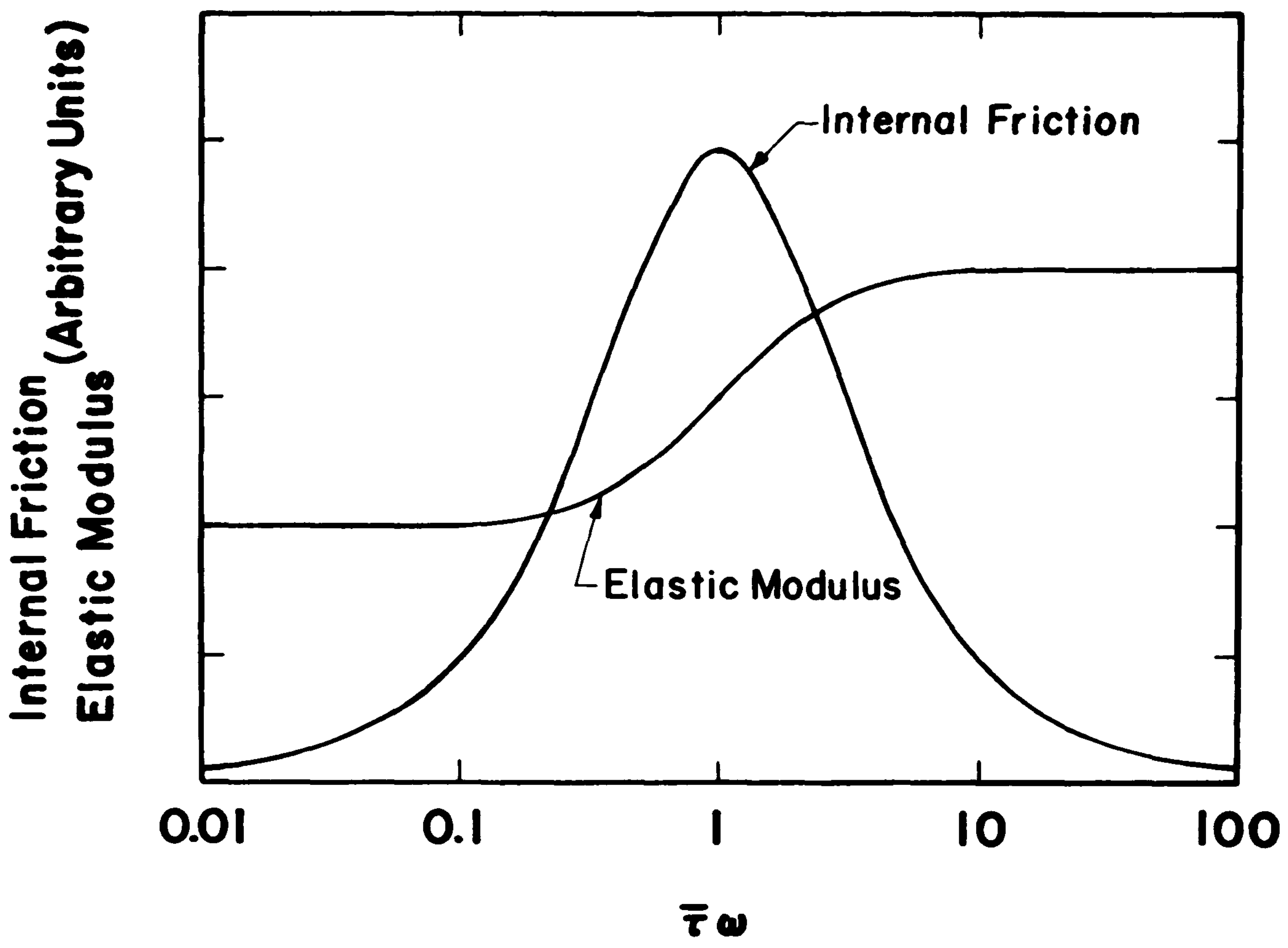
Figure 2. The internal friction peak for two Ag-Zn alloys of 30.25% and 16.5% Zn composition according to Nowick et al.(4)

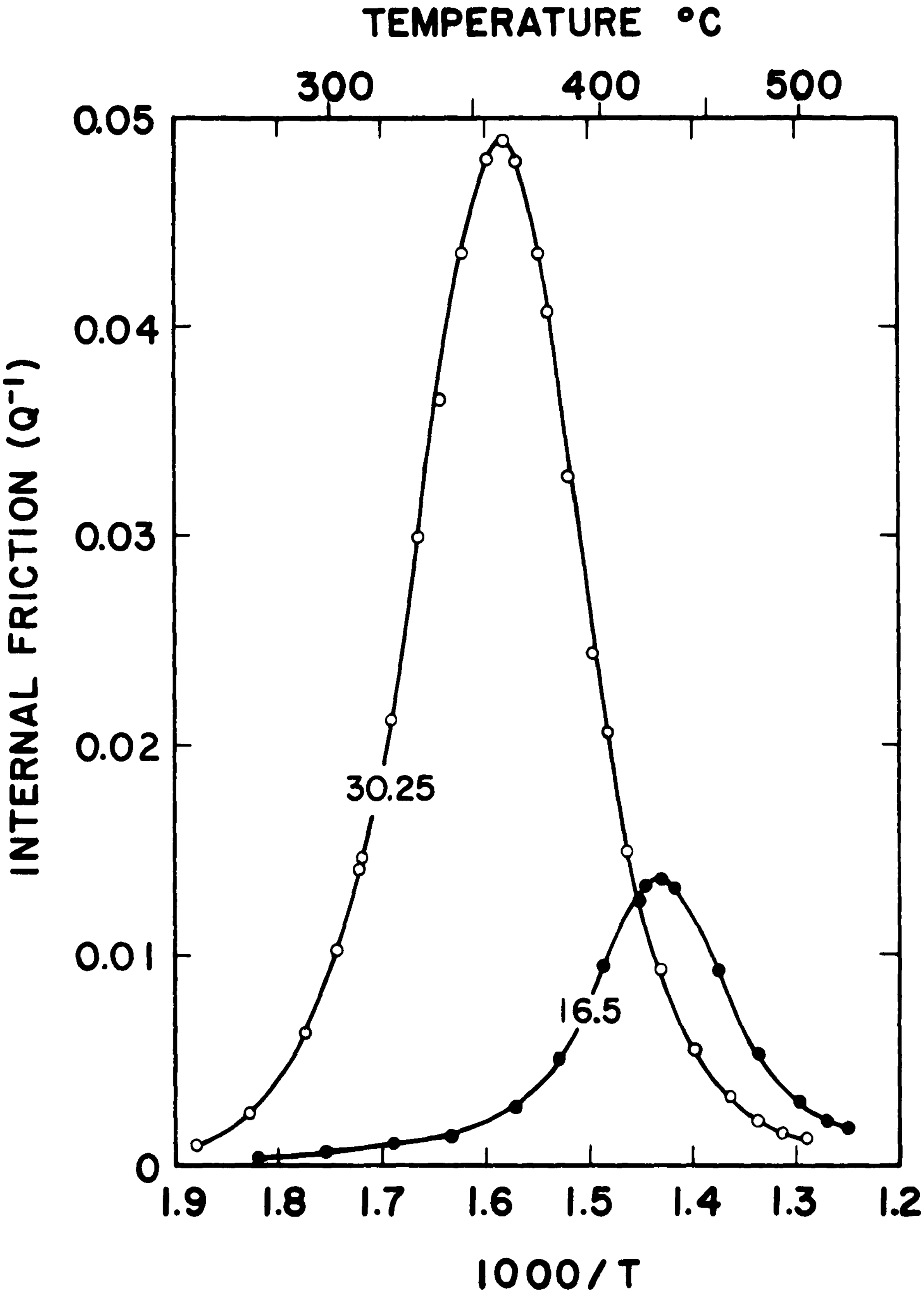
Figure 3. The relaxation strengths Δ_E and Δ_G for FCC single crystal wires (4) of different orientations. The alloys were Ag-26 at .% Zn by composition. The function Γ defines the orientation of the wire axis where

$$\Gamma = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2$$

λ_1, λ_2, and λ_3 are the direction cosines of the axial direction relative to the <100> directions of the crystals. A similar behavior is observed for BCC Li-Mg alloys.

Figure 4. Orientation dependence of Δ_E for Ag-Zn alloys (4) of various compositions.


Internal Friction
Elastic Modulus (Arbitrary Units)
Internal Friction
Elastic Modulus
0.01
0.1
1
10
100
$\bar{\tau}\omega$


TEMPERATURE °C
300
400
500
INTERNAL FRICTION (Q^{-1})
0.05
0.04
0.03
0.02
0.01
0
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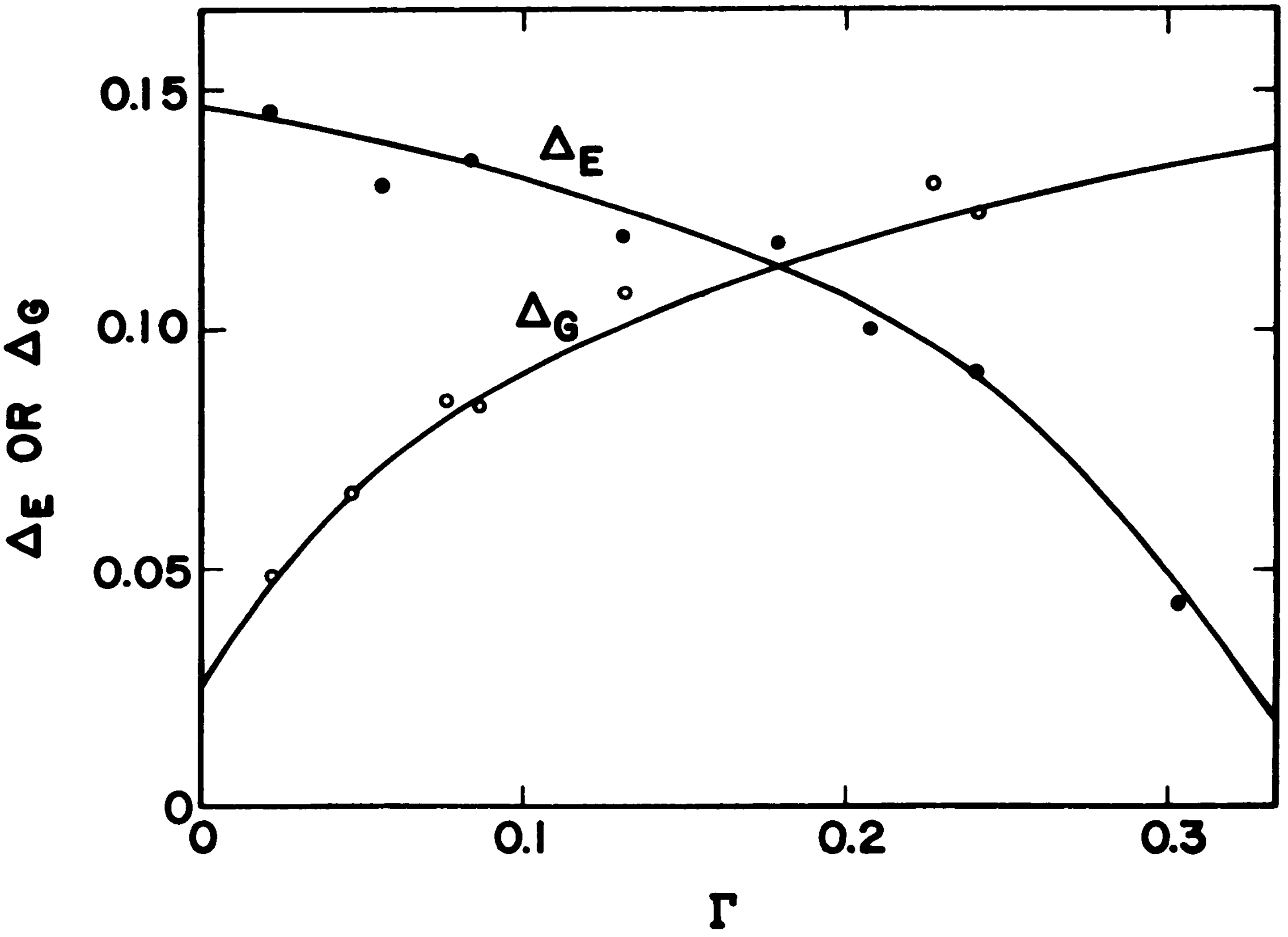
16.5
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1000/T


Δ_E OR Δ_G
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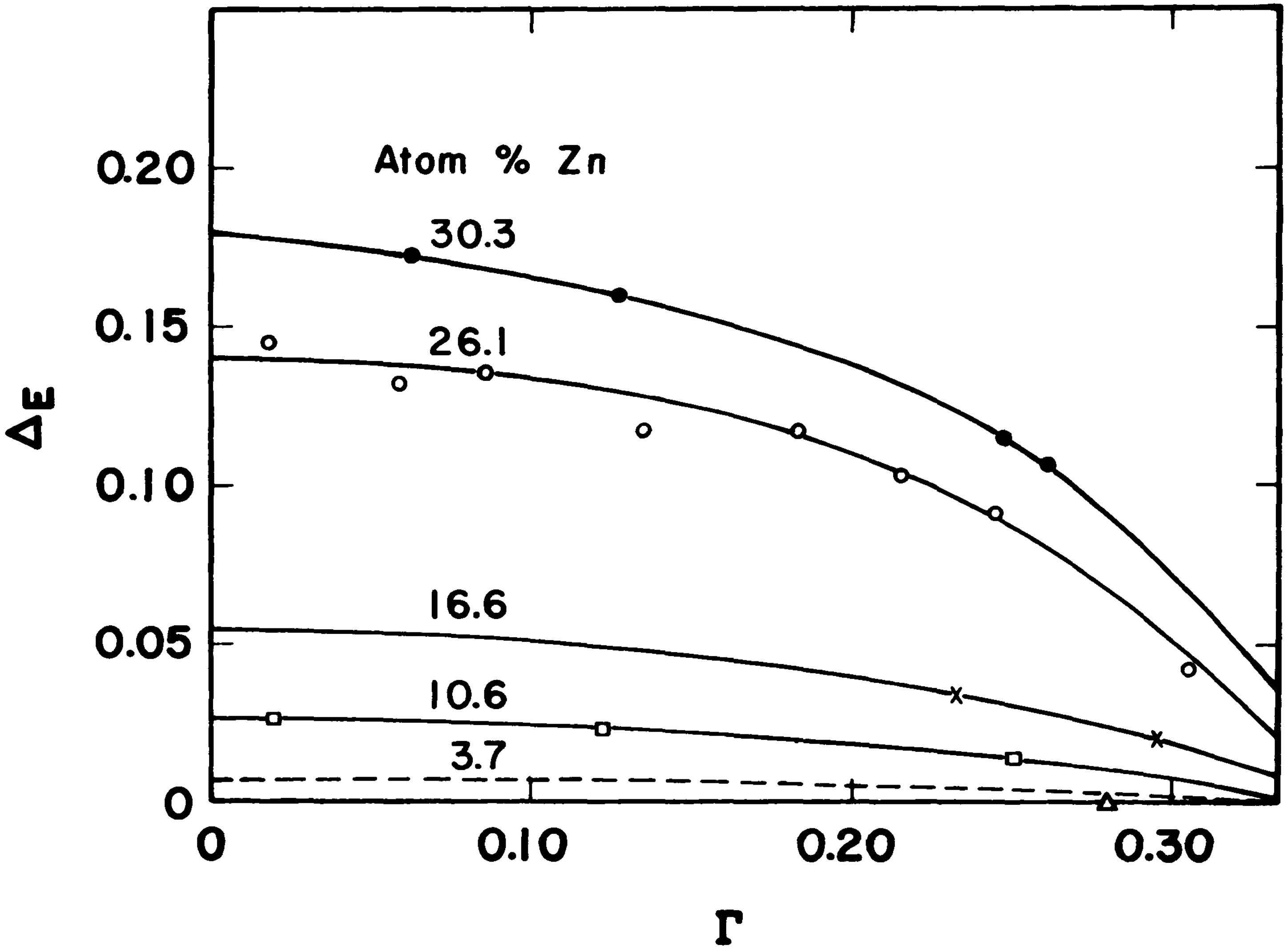
0.10
0.05
0
0
0.1
0.2
0.3
Γ
Δ_E
Δ_G


Atom % Zn
30.3
26.1
16.6
10.6
3.7
Δ_E
0.20
0.15
0.10
0.05
0
0
0.10
0.20
0.30
Γ