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The temperature-independent component of the diaelastic effect*

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Abstract

Relaxation and resonance effects are well known in the internal friction and ultrasonic attenuation literature. In recent years a new kind of response, the diaelastic effect, has become useful in the characterization of defects in solids. The diaelastic effect is analogous to the diamagnetic effect for magnetic materials, and corresponds to the stress-induced generation of dipoles in the crystal, in contrast to the stress-induced ordering of preexisting dipoles, which leads to relaxation effects. The response is temperature- and frequency-independent, but does depend on polarization. The latter feature makes it useful in characterizing the symmetry of defects. Examples for different crystal types are discussed. The known diaelastic response of crystals containing interstitials has been used to construct a model according to which liquid and amorphous metals are crystals containing a few percent of self-interstitials. The phenomenological aspects of the model do not depend, however, on the microscopic configuration, but only on the diaelastic properties known experimentally to be universal for amorphous materials.

1. Introduction

The ultrasonic response of solids is generally of two types, relaxational and resonance. Theories for these effects are well developed and readily available in many articles, reviews and books [1–3]. We review these briefly and show that they do not provide for a new kind of frequency- and temperature-independent diaelastic response which has become of importance in recent years, but that a slight modification of existing formalism can serve this purpose. When applied to crystals containing self-interstitials, this leads to a model according to which liquids and glasses are crystals containing a few percent of interstitials.

2. Relaxation and resonance

In a description of mechanical effects caused by defects in crystal lattices, Kroner [4, 5] introduced the idea of para- and diaelasticity by analogy with the para- and diaelectric phenomena of electrostatics. Paraelasticity and relaxation are the same. The defect strain results from the competition between the ordering effects produced by an external field on an existing elastic dipole and the disordering effects due to thermal fluctuations. It requires thermal activation over an energy barrier and is therefore normally strongly temperature-dependent. The defect energy is linear in the external strain. For relaxation processes, the response is given in the standard Debye form in terms of two parameters, the relaxation strength Δ_R, and the relaxation time τ. For a classical system

$$\Delta_R(T)=\alpha^2 c/CkT \text{ and } \tau(T)=\tau_0 \exp(U/kT) \qquad (1)$$

where α is the coupling constant for a dipolar defect interaction with the sound wave, τ_0 is the prefactor and U is the barrier height for the relaxing defect of concentration c. The same form holds for quantum systems, but the temperature dependence is different. The relaxation height goes to zero for a low enough temperature, and the relaxation time is often weaker than exponential. Quantum effects are generally recognized, though, by analysis of the temperature dependence of Δ and τ. It can happen that the relaxation time is Arrhenius in form, but still be quantum in nature; then the preexponential factor τ_0 is generally much smaller than a characteristic atomic period. By analysis of $\Delta_R(T)$ and $\tau(T)$, the basic parameters of the defect system are deduced.

Diaelasticity and resonance are also the same. It is the direct response corresponding to an induced elastic dipole to an applied force even when there is no thermal activation over a barrier. The defect energy is quadratic in the external strain.

2.1. Dislocations

2.1.1. Resonance

The vibrating string model [6, 7] describes a diaelastic resonant response of the induced dislocation dipole representing the forced motion of a restrained dislocation segment under an applied shear stress. For low

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stress amplitudes, the theory is analogous to dielectric theory, with dislocation displacement taking the place of charge displacement.

2.1.2. Relaxation

The Bordoni peak, in contrast, is described as a relaxation arising from the thermal activation of dislocations over a Peierls barrier. This is described in detail at this conference [8, 9] and in numerous review articles [10, 11].

2.2. Dipolar point defects

2.2.1. Classical relaxation

The theory for classical paraelastic relaxation effects is reviewed in several books [1–3]. Surrounding a point defect in a crystal is a local field of elastic distortions. If the defect has a lower symmetry than that of the crystal, then the strain field produced by the defect will have a "dipolar" character. Depending on the symmetry class of the defect and that of the crystal, there will then exist a number of equivalent possible orientations for the dipole to assume.

An externally applied strain can interact with the dipole through the strain field. For certain externally applied strains, some of the possible dipole orientations may become energetically favored over the others, and thermally activated transitions to the favored orientations will occur. When the externally applied strain is an ultrasonic wave, the reorientation process gives rise to an attenuation and a change in the sound velocity. For a crystal and a defect of given symmetry class, Nowick and Berry [1] have shown that, on the basis of symmetry arguments, certain externally applied strains can and others cannot induce transitions.

2.2.2. Quantum effects

The theory of attenuation and elastic constant changes for a quantum two-level system (TLS) in crystals is basically the same as that familiar for amorphous systems, but simpler. For amorphous systems there is not only a distribution of strains, but also a distribution of tunneling gaps, extending down to zero. For TLS in crystals, there is a minimum gap, Δ_0, and for ultrasonic measurements with $\hbar\omega < \Delta_0$ there is no direct resonant absorption. The theory was given already by Jackle and coworkers [12] in 1972, and applied immediately to amorphous systems. The results for crystalline systems are derived and reviewed by Hunklinger and Arnold [13] and Granato *et al.* [14] in other ways which facilitate a discussion of the strain dependence.

The elastic constant C is given by definition as

$$C = \partial^2 F(\epsilon)/\partial\epsilon^2 \tag{2}$$

where F is the free energy per unit volume, ϵ is an elastic strain, and C is the elastic constant belonging to that strain. The free energy is given by

$$F = -kT \ln Z \tag{3}$$

where Z is the partition function given by

$$Z = \sum_i \exp^{-(E_i/kT)} \tag{4}$$

where $E_i(\epsilon)$ are the states of the system. There are paraelastic and diaelastic effects resulting for dipolar point defects, corresponding to magnetic dipolar effects These can be illustrated with the simple two-level system shown schematically in Fig. 1. For $\epsilon = 0$, the dipole is supposed to have two equivalent orientations (A1). The ground state is tunnel-split with a gap of 2Δ. If a stress or strain ϵ is applied, one orientation becomes energetically favored (A2). If time is available, transitions will occur, bringing the system back into thermal equilibrium. For the two-level system shown, however, no relaxation takes place for small amplitude ultrasonic waves about $\epsilon = 0$ because the energy of the states is flat for small ϵ, maintaining the equilibrium population of the states.

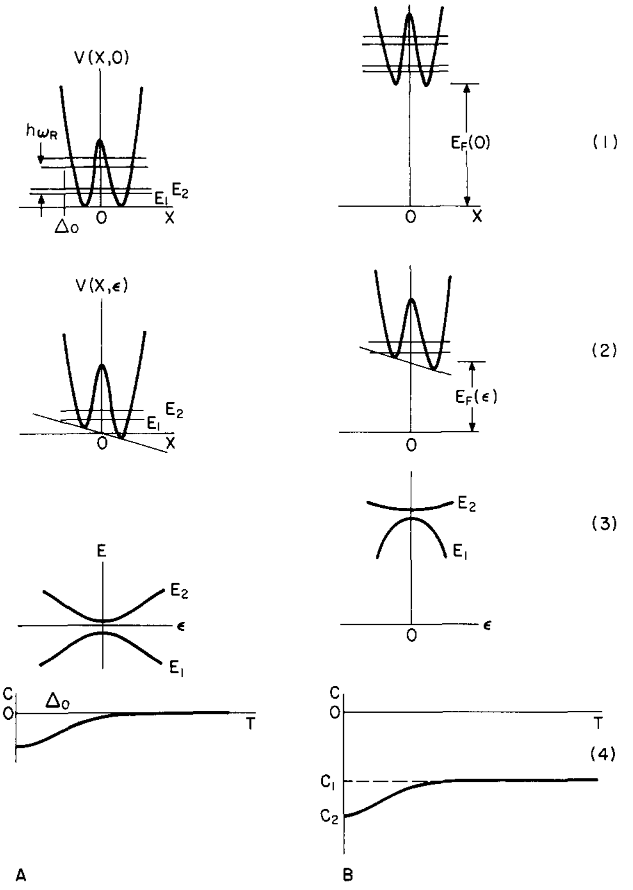

Fig. 1. Schematic depiction of two-level system (TLS) behavior; (A) Standard representation; (B) modified representation; (1) potential at zero strain; (2) potential for finite shear strain; (3) strain dependence of lower energy levels; (4) temperature dependence of diaelastic effect.

2.2.3. Resonance

For $T \ll \Delta$, only the ground state is populated. For small ultrasonic stress amplitudes, the elastic constant is given by the curvature of the ground state, according to eqn. (2), and the elastic constant change is negative. The dipole moment is induced, proportional to the strain ϵ, has a resonance-like character, and the change is called diaelastic. The resonance frequency is normally far above the megahertz range. As a result, no attenuation is seen, but only the low frequency change of an elastic constant is found. At very high temperature, the two states E_1 and E_2 are nearly equally populated, the two curvatures seen in Fig. 1(A3) are opposite, and cancel out so that this diaelastic effect goes to zero (A4). The effect is a quantum effect, whose classical high temperature limit is zero, and which is also zero if the tunneling gap at zero strain, $\Delta_0 = 0$.

The elastic constant change is given by the standard TLS formalism as

$$\frac{\Delta C}{C} = \frac{\alpha^2 c}{CkT} \frac{\Delta_0^2 kT}{(\Delta_0^2 + \alpha^2\epsilon^2)^{3/2}} \tanh \frac{(\Delta_0^2 + \alpha^2\epsilon^2)^{1/2}}{kT} \qquad (5)$$

3. Experimental results for self-interstitials

Measurements of the change in the three independent elastic constants of copper as a function of Frenkel pair concentration produced by neutron irradiation at helium temperature [15] are shown in Fig. 2. The elastic constants decrease linearly with defect concentration. For the annealing range I_D, where interstitials disappear, the changes are found to be $d(\ln C_{ij})/dc = -31$, -15 and 0 for C_{44}, $C' = (C_{11} - C_{12})/2$ and B respectively, where B is the bulk modulus. The change in C_{44} is very large. Changes of most properties, such as the volume or bulk modulus, are of unity order. The change of C_{44}, if extrapolated linearly, would imply that the lattice becomes unstable for about 3% of interstitials.

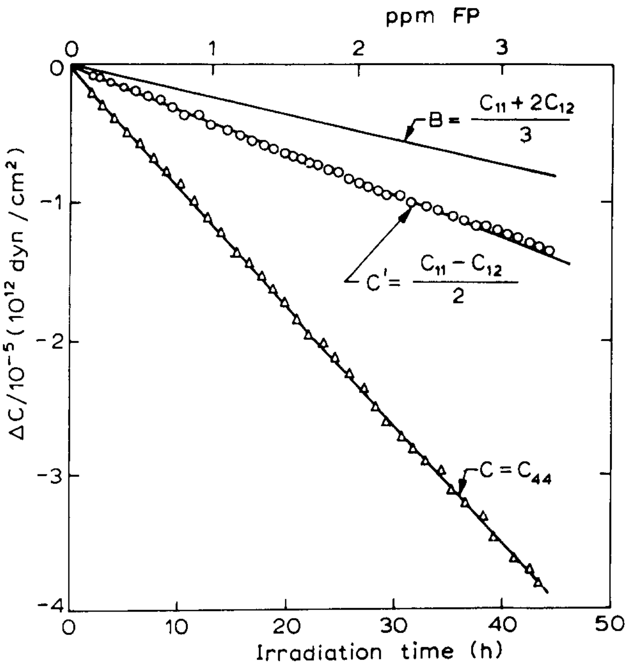

Fig. 2. Elastic constant changes in copper as a function of Frenkel pair concentration [15].

The change of the C_{44} shear modulus of iron with electron radiation [16] is shown in Fig. 3. For no radiation, the temperature dependence is that of the perfect lattice. With increasing defect density, the modulus decreases, with the change being both temperature- and frequency-independent. The polarization dependence of the shear constant change in body-centered cubic (b.c.c.) iron is opposite to that of face-centered cubic (f.c.c.) copper. The effect is linear in the defect density as shown in the inset to Fig. 3. The magnitude and anisotropy of the shear constant changes are strong evidence [15, 16, 17] for the dumb-bell interstitialcy configuration of the interstitial, shown in Fig. 4(a) for the f.c.c. lattice.

The dumb-bell displacements are aligned in ⟨100⟩ directions and are strongly coupled to atoms in the close-packed ⟨110⟩ directions, so that the configuration consists of a ⟨100⟩ dumb-bell extended with appreciable chains for several atoms along ⟨110⟩ directions. The stable and saddle-point configurations are reversed for an interstitial atom from that for a vacancy. This has far-reaching consequences. In particular, the interstitialcy configuration has a strong coupling to external shear stress, low-frequency resonance modes [18] and an extended linear string-like character which can lead to large entropy effects. It has been pointed out by Schober [19] that many features of low-temperature glass anomalies (low-frequency vibrations, relaxation processes and general TLS behavior) are also observed in crystals after irradiation at doses much less than those needed for amorphization. The vibrational frequency spectrum of f.c.c. crystals containing isolated interstitialcies has been described in detail by Dederichs *et al.* [18]. They find both low-frequency resonance modes and high-frequency local modes as shown in Fig. 4(b). The results depend a bit on the interatomic potential chosen.

This effect is clearly due to an induced dipole and therefore is diaelastic, but the observed temperature independence of the effect finds no place in the existing formalism for diaelastic effects given by eqn. (5). This deficiency can be remedied simply by recognizing that the standard formalism takes no account of the fact that the defect, a self-interstitial in this case, has a finite formation energy E_F, and also that E_F is a function of the shear strain $E_F(\epsilon)$, so that $E = E_F(\epsilon) \pm \Delta(\epsilon)$, as indicated schematically in Fig. 1(B2). This changes the

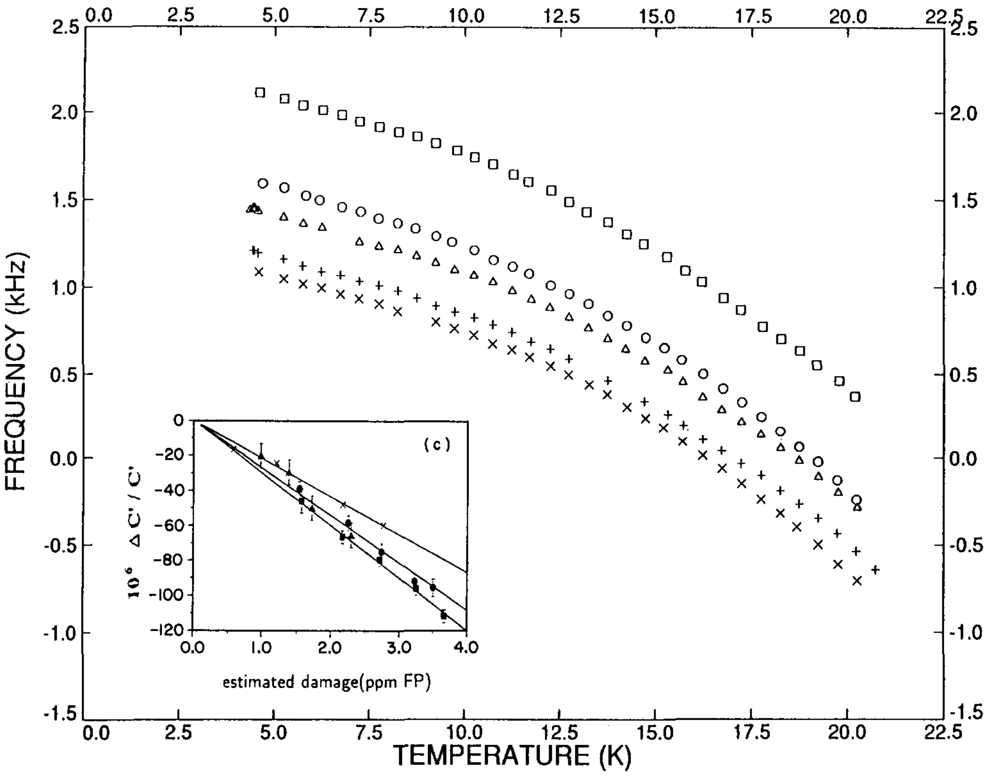

Fig. 3. Temperature dependence of C_{44} in electron irradiated Fe. The elastic constant changes are proportional in the frequency measured in an ultrasonic interferometer. The inset gives the dependence on defect density [16].

energy levels to those shown in Fig. 1(B3), and now the high temperature classical limit is not zero (B4). The diaelastic contribution to the elastic constant now has a second component C_1, derived in the next section, which is temperature-independent. Both components C_1 and the standard $\Delta C = C_2 - C_1$ are diaelastic resonant effects arising from an induced dipole whose energy is quadratic in the strain. However, we shall refer to the temperature-independent component C_1 as the "diaelastic effect", and the standard temperature-dependent component as the "resonance effect".

These two features for self-interstitials, (1) a strong softening of the shear modulus and (2) resonance modes, which lead to a large entropy for interstitials, are the essential ingredients of a quantitative model [20] for condensed matter states of simple materials.

4. A model for condensed matter states

It is supposed that the volume, V_0, bulk modulus, B_0, shear modulus, G_0, and their pressure derivatives, B' and G', evaluated for the static lattice (no thermal or zero-point vibrations) are given, and the Helmholtz free energy $\bar{F}=\bar{F}(V,\epsilon)$, where ϵ is the shear strain, can be expressed in terms of these parameters. For high temperatures, using a quasi-harmonic Einstein approximation for the vibrational free energy, one then has the free energy of the perfect crystal, F_p, given by $F_p=\bar{F}(V,\epsilon)+3NkT\ \ln[\hbar\omega_E(V)/kT]$.

For the change in free energy, δF, of the crystal containing n defects, where $c=n/N$, one must add(1) the work, F_w, necessary to create a concentration, c, of interstitialcies, (2) the change, δF_v, of the vibrational free energy resulting from the change in the frequency spectra, and (3) a configurational free energy, F_c, given by $F_c=-T\Delta Sc=-Tnk[1+\ln\ zN/n]$. The latter term differs from the usual small c expression for the configurational entropy only by the factor z, put in to take account of the fact that the interstitialcy can be oriented along any of z directions ($z=3$ f.c.c. lattices).

It is required that F_w be given in terms of the independent variables and assumed that this dependence can be expressed in the form $\delta f_w/\delta c=\alpha_1 G\Omega+\alpha_2 B\Omega$, where $f=\delta F/N$, Ω is the volume per atom, and α_1 and α_2 are constants presumed to be the same for the same crystal structure. This is the principal assumption of the model.

We further expect that $\alpha_2/\alpha_1 \ll 1$ (and find $\alpha_2/\alpha_1 \approx 0.03$ in a fitting procedure for Cu). This means that the work is mainly that of a shear deformation. For a concentration, c, of interstitials, f_w becomes

$$f_w=\int_0^c[\alpha_1 G\Omega+\alpha_2 B\Omega]\mathrm{d}c \qquad (6)$$

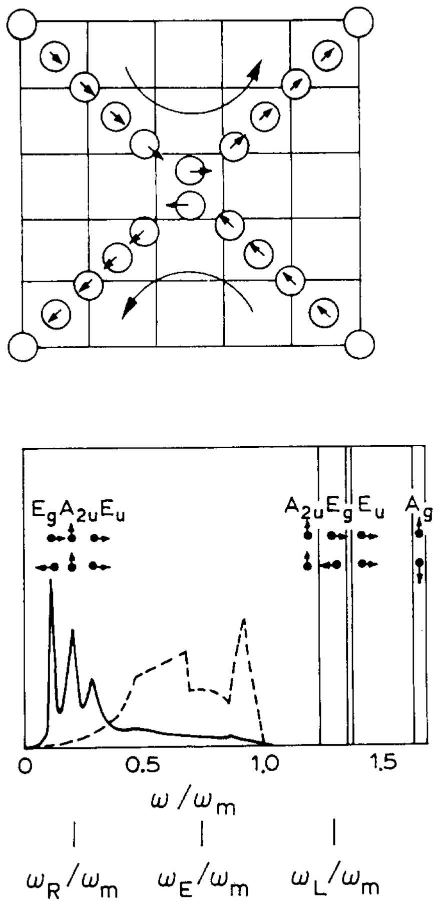

Fig. 4. (a) Dumb-bell interstitialcy configuration in f.c.c. metals. Arrows indicate displacements for an applied shear stress and the E_g resonance mode. (b) Calculated lattice phonon spectrum (– – –) resonance, ω_R, and local modes, ω_L, for copper [18]. The symmetry and displacements of the central dumb-bell atoms are indicated for the resonance and local modes. For a high-temperature approximate calculation, we replace the lattice frequencies by the single Einstein frequency ω_E, the resonance modes by a single ω_R, and the local modes by a single ω_L, as indicated at the bottom of the figure.

For a high-temperature approximation, the lattice frequencies are replaced by a single Einstein frequency, ω_E, the resonance modes by a single ω_R, and the local modes by a single ω_L as indicated in Fig. 4(b). There are five resonance and six local modes for each interstitialcy. Since the resonance and local modes come at the expense of the lattice modes, the change in the free energy per particles becomes

$$f = f_w - kTc[5 \ln \omega_E/\omega_R + 6 \ln \omega_E/\omega_L + (1 + \ln z/c)] \qquad (7)$$

A self-consistency argument using the definition of the shear modulus $G \equiv (\partial^2 F/\partial_\epsilon^2) N\Omega_0$ with eqns. (6) and (7), recognizing that the shear modulus in a crystal along planes separated by a distance d must be periodic in displacements b, which repeat the lattice structure yields the diaelastic effect. Assuming the simplest periodic even function, we take $G = G(V, c) \cos 2\pi x/b = G \cos 2\pi d\epsilon/b$, where $\epsilon = x/d$. Then $\partial^2 G/\partial\epsilon^2 = -\beta G$, where $\beta = 4\pi^2 d^2/b^2$. As a first approximation, taking $\Omega/\Omega_0 \simeq 1$, this leads to

$$G = \tilde{G}\ (V, \epsilon) \exp(-\alpha_1 \beta c) \qquad (8)$$

for the concentration dependence of the shear modulus, where $\beta \sim 4\pi^2$.

The result, eqn. (8), is basic for the model. It describes a large diaelastic softening of the shear modulus and of the free energy with defect concentration. With $\alpha_1 \sim 1$, a concentration of a few percent of interstitialcies should greatly reduce the shear modulus, in agreement with the results shown in Fig. 2.

With eqns. (8) and (6) in (7), the change in the Helmholtz free energy is determined. The Gibbs free energy, $\mathcal{G}$, is obtained from F by $\mathcal{G} = F + pV$, so that $\mathcal{G}(p, T, \tau, c)$ is given as a simple analytic function. The change in the Gibbs free energy using parameters fitted to copper at zero pressure and shear stress as a function of concentration for different temperatures is shown in Fig. 5. The normalized Gibbs free energy difference $y = \delta\mathcal{G}\ \beta/NG_0V_0[1 + (\alpha_2 B/\alpha_1 G)]$, the normalized concentration $x = \alpha_2 \beta c$, and the normalized temperature $t = T/T_m$, where T_m is the melting temperature.

Three distinct regimes are found by setting $d(\delta\mathcal{G})/dc = 0$. For low enough temperatures, only one solution, $c_1(T)$, is obtained which gives the equilibrium interstitialcy concentration in the crystal depending exponentially on temperature with the isolated interstitialcy formation enthalpy as the activation energy. This is a very shallow minimum near the origin and is not visible

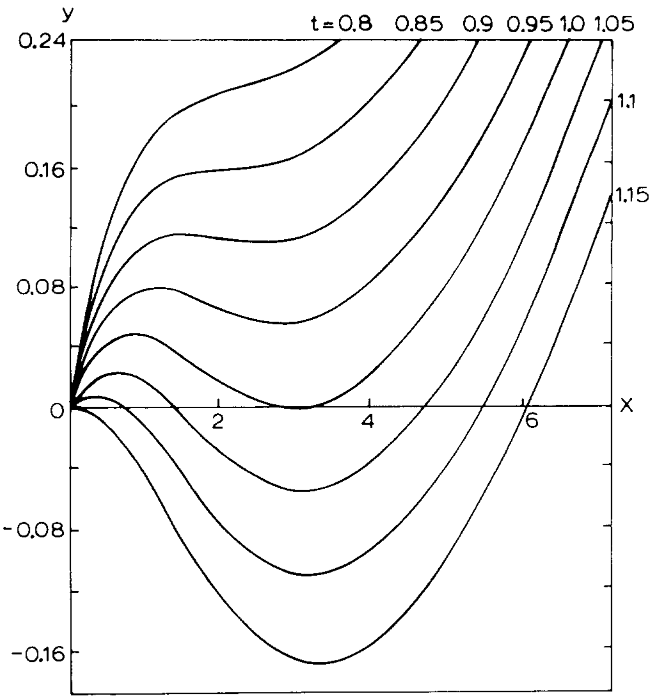

Fig. 5. Normalized Gibbs free energy, y, *vs.* normalized interstitialcy concentration, c, for different temperatures, t, normalized to the melting temperature [20].

on the scale of Fig. 5. For temperatures near the melting temperature, there are three solutions, c_1, c_2 and c_3. $c_3(T)$ is interpreted as the equilibrium liquid state, with c_2 the concentration at which $\delta\mathcal{G}$ has a maximum. For high enough temperatures, $c_3(T)$ is the only equilibrium stable state. Frozen-in concentrations, c_3^0, represent amorphous states. One sees from Fig. 5 that there is a possible super-cooling range of about 15% below T_m. Melting occurs at the temperature T_m where $\delta\mathcal{G}$ and $d\delta\mathcal{G}/dc = 0$. This gives a relation between T_m and the isolated interstitialcy formation enthalpy which is equivalent to Lindemann's melting criterion. The existence of an effective Lindemann's law gives confidence that fits may be achieved for a wide range of materials.

5. Summary

A temperature- and frequency-independent diaelastic effect is found in irradiated materials. This effect is not contained in the standard available formalism for ultrasonic resonance effects, but is easily taken into account by including a shear strain-dependent formation energy for the interstitial. A large softening of the shear elastic constant with defect concentration is derived, and used as a basis for a model of liquids and glasses, which are interpreted to be crystals containing a few percent of self-interstitials. Ultrasonic measurements provide the basic data both for the formulation and the use of the model.

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