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Elastic properties of a metallic glass relative to the crystal

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The elastic properties of a metallic glass have been calculated in a tight-binding model for the attractive part of the energy and a Born-Mayer-type potential for the repulsive one, and have been compared to those of the crystalline phase. The bulk modulus at 0 K is shown to be similar in both phases, but decreases more rapidly with temperature in the glassy state. The Debye frequency is reduced by a factor of 10 to 20% in the glassy state due to the disorder, i.e., the occurrence of soft modes. This also induces a large decrease in the shear modulus. Both effects are in agreement with the existing experimental results.

I. INTRODUCTION

Very few experiments exist on the elastic properties of amorphous transition metals. However, interest in them is rapidly growing due to their properties. We are interested in setting up a theoretical model in order to explain or predict some trends in their properties.

As we have not discussed the effect of magnetism on the elastic constant, the materials of most interest for us will be Pd-rich Pd-based alloys Pd-Si or Pd-Si-Au, Pd-Si-Cu which have been rather well studied and reported in the literature. We sum up here the main experimental results.[1,2]

It is observed that the extrapolated bulk modulus at $T = 0$ is a little smaller, or the same as in the crystalline state in these compounds, the decrease with temperature being probably a little more pronounced for the amorphous state. However, results are very scarce. There are many more data as far as the shear modulus or the Young modulus are concerned. At zero temperature, the shear modulus is 30% smaller in the amorphous state and the decrease with temperature is more pronounced. However, there is a large discrepancy for the slope between different experiments. The most reliable measurement seems to be through acoustic measurement of Golding *et al.*[2] For the Pd-Si-Cu glass, they also measured a decrease of 15% of the Debye temperature. For all those materials, we notice that the change of density is very small, a few percent.

Little theoretical work exists on the subject because the main effort up to now has been put on modeling the structure and working out the electronic properties. However, Weaire *et al.*[3] have done a numerical calculation of the elastic constants of amorphous metal using the approximation of pairwise central interatomic potentials and models for the structure of the amorphous state. Their main results are that while the bulk modulus is not changed very much, the shear modulus is considerably lower than that of the crystal, on the order of 30%. However, pairwise forces cannot describe bonding in transition metals since the Cauchy relations are not obeyed; but this result is valid in a more general model, which we will show in this paper.

The crystalline transition metals have been explained in a satisfactory way by using a tight-binding approximation.[4-7] Cohesive properties,[5] crystalline structure,[5] elastic properties,[6] and surface properties[7] have been semiquantitatively obtained in this simple model. This framework has been also used to calculate the electronic density of states, resistivity data, and heat of fusion of amorphous and liquid transition metals, such as Ni and Co.[8] The aim of this paper is to show that such a method can explain or predict elastic properties of amorphous transition-metal-rich alloys with P, Si, etc. We will successively discuss the mean interatomic distance, the cohesive energy, the elastic-constant bulk and shear modulus, the Debye and Einstein frequencies, and the behavior of the elastic constant with temperature. Our main result is that there is little difference between the crystalline and the amorphous material except for the Debye frequency and the shear modulus which are much smaller in the amorphous state.

II. MODEL

Many physical properties of transition metals and alloys have been explained through a tight-binding approximation, giving an attractive band energy.[4-8] Equilibrium is maintained by the addition of a repulsive-energy contribution due to the repulsion between internal shells and the compression of valence states due to orthogonalization. Using this model, Ducastelle[6] has explained the behavior of the elastic constants of crystalline transition metals. The energy is thus written as the sum of two terms:

$$E = E_B + E_R . \tag{1}$$

E_R is the repulsive part represented by a Born-Mayer potential

$$E_R = C \exp(-pR) . \tag{2}$$

E_B is the d-band contribution to the cohesive energy given by

$$E_B = \int^{E_F} En(E)dE , \tag{3}$$

where $n(E)$ is the electronic density of states.

In the tight-binding approximation, the one-electron Hamiltonian has the form $H = T + \sum V_i$, where V_i is the atomic potential centered at site i. The site diagonal Green's function G_{ii} may be developed as a continued fraction[9]

$$G_{ii} = \frac{1}{E - a_{i0} - b_{i0}F_i} ,$$

with

$$F_i = \cfrac{1}{E - a_{i1} - \cfrac{b_{i1}}{E - a_{i2} - \cfrac{b_{i2}}{\cdots}}} ,$$

where the a_{in}, b_{in} are related to the moments of the density of states on the site i,

$$\mu_{in} = \int_{-\infty}^{\infty} E^n n_i(E) dE .$$

These moments can be evaluated by a simple walk-counting technique[5,7,8] for any type of lattice, crystalline or disordered (liquid, amorphous). Numerical calculations of these coefficients a and b show that they converge to a limiting value much more rapidly than the moments, the convergence being quicker for an amorphous material.[8] A good approximation is thus to consider that at a certain level, all the coefficients are identical, i.e., $a_{in} = a$ and $b_{in} = b$ for $n > p$ for all i. This permits us to sum the continued fraction and obtain

$$G_{ii}(E) = 1/(E - a_{i0} - b_{i0}F) ,$$

where

$$F = 1/(E - a - bF) .$$

In order to have purely analytical calculations, we will consider that $p = 1$, and thus we will take

$$a = \mu_1$$

and (4)

$$b = \mu_2 - (\mu_1)^2 .$$

Defining the zero of the energy such that $a = 0$, we then have

$$E_B = -\frac{8}{3\pi}\sqrt{b}\left(1 - \frac{E_F^2}{4b}\right)^{3/2} , \tag{5}$$

where E_F is given by the number of electrons per atom

$$n = 1 + \frac{2}{\pi}\left[\sin^{-1}\frac{E_F}{2\sqrt{b}} + \frac{E_F}{2\sqrt{b}}\left(1 - \frac{E_F}{2\sqrt{b}}\right)^{1/2}\right] . \tag{6}$$

The second moment can be easily expressed in terms of the two-center nearest-neighbor hopping integrals $\beta_{\lambda\mu}^{ij}$,

$$\mu_2 = \frac{1}{5N}\sum_{ij} \beta_{\lambda\mu}^{ij} ,$$

N being the number of atoms and $\beta_{\lambda\mu}^{ij} = \langle i\lambda | V_i | j\mu \rangle = \beta_{\lambda\mu}(\vec{R}i - \vec{R}_j)$, λ and μ specifying the atomic degeneracy and $|i\lambda\rangle$ a set of atomic orbitals centered on the site i. As shown by Slater and Koster[10] these hopping integrals can be expressed in terms of the direction cosines of $(\vec{R}_i - \vec{R}_j)$. Moreover, one can assume that their logarithmic derivatives for the equilibrium-lattice distance R_0 are roughly equal to minus three[6] so that we can write

$$\mu^2 = \frac{1}{N}\sum_{ij} t^2 e^{-2qR_{ij}} , \tag{7}$$

with $qR_0 = 3$ when t is an averaged overlap integral.

III. TOTAL ENERGY

The total energy is

$$E = \frac{1}{N}\sum_{ij} Ce^{-pR_{ij}} - \frac{8}{3\pi}\left(1 - \frac{E_F^2}{4b}\right)^{3/2}\sqrt{b} \tag{8}$$

with b given by Eqs. (4) and (7) and E_F^2/b being a constant independent of the distance R_{ij} fixed by the number of electrons in the band [Eq. (6)].

For a crystal with a coordination number of Z, the equilibrium condition which gives the interatomic distance R_0 is

$$\left.\frac{\partial E}{\partial R}\right|_{R=R_0} = 0 = -pZCe^{-pR_0} + \frac{8}{3\pi}q\left(1 - \frac{E_F^2}{4b}\right)^{3/2}\sqrt{Z}te^{-qR_0} . \tag{9}$$

For an amorphous state, one has to average over all the possible configurations, through the radial distribution function $g(R)$. The repulsive part thus is written

$$E_R = \frac{1}{N}\sum_{ij} Ce^{-pR_{ij}} = C\int e^{-pR} g(R) dR .$$

$g(R)$ being isotropic is a function of the average interatomic distance R_{0a}, and we can approximate E_R as

$$E_R = Z_a e^{-pR_{0a}} ,$$

where Z_a is the coordination number in the amorphous state. Using the same approximation for

E_B, we obtain a similar equilibrium condition as for the crystal where Z and R_0 are replaced, respectively, by Z_A and R_{0a}. The change in the mean equilibrium distance for the amorphous state is thus given by

$$(p-q)\delta R_0=\frac{1}{2}\frac{\delta Z}{Z}\,. \tag{10}$$

This leads with the usual values of $pR_0=9$ and $qR_0=3$ (Ref. 6) to a very slight change of the average interatomic distance

$$\frac{\delta R_0}{R_0}=\frac{1}{12}\frac{\delta Z}{Z}\sim-7\times10^{-3}$$

with $\delta Z/Z\sim-\frac{1}{12}$ when going from the crystalline to the amorphous state.

The variation of the total energy can also be calculated in this model and we have

$$\frac{\delta E}{E}=\frac{1}{2}\frac{\delta Z}{Z}-qR_0\frac{\delta R_0}{R}\,, \tag{11}$$

i.e.,

$$\frac{\delta E}{E}\sim-2\times10^{-2}\,.$$

As expected δE is >0 and the amorphous state is metastable. Let us also remark that the value obtained here is in agreement with that obtained for Co using a more sophisticated model.[8]

IV. ELASTIC CONSTANTS

Using the method of the preceding sections, the energy of the distorted glass can be calculated as a function of strain and leads to the elastic constants. The bulk modulus K is given by

$$K=\frac{1}{9R_0}\frac{\partial^2E}{\partial R^2}=-\tfrac{1}{9}pq\frac{E}{R_0}\,. \tag{12}$$

The change in bulk modulus between an amorphous material and a crystal is thus

$$\frac{\delta K}{K}=\frac{\delta E}{E}-3\frac{\delta R_0}{R_0}\simeq0\,.$$

With the set of parameters we have used, the bulk modulus at zero temperature is not changed when going to the amorphous state.

In order to calculate the shear modulus, we consider the change in the radial distribution function under an orthorhombic distortion. If we do not permit any rearrangement of atoms, this function no longer has a spherical symmetry but now possesses an elliptical one. If the distance in the x direction is increased as $R(1+\epsilon)$, in the y and z direction it is decreased as $R(1-\frac{1}{2}\epsilon)$. To second order in the distortion, the energy is given as an average over sites of the quantity

$$\delta=\sum_j\frac{\vec{R}_j\cdot\delta\vec{R}_j}{R_j^2}\,,$$

where j are the nearest neighbors of one given site. In a glassy metal, we have to perform a configuration average. For that, we consider that the structural random network is made of an assembly of icosahedral and cubo-octahedral units. The shear modulus would thus be

$$\mu_a=-\frac{\delta}{12}\frac{1}{Z_a}\frac{pq}{p-q}(p-2q)\frac{E_a}{R_{0a}}\,, \tag{13}$$

with $\delta\simeq1$. For an fcc lattice we calculate the shear modulus

$$\mu=\tfrac{1}{2}(C_{11}-C_{12})=-\tfrac{1}{24}[pq/(p-q)](p-2q)E/R_0\,. \tag{14}$$

However, if the assumption of no internal rearrangement is justified for the bulk modulus, it is likely to be entirely wrong for the shear modulus. Indeed for the bulk modulus, we make a uniform change of scale of the configuration and the atoms remain in equilibrium. In a shear stress, this is not true and atoms can relax towards a new position of equilibrium.[3] It is well known that in amorphous materials there exist soft points and low-energy phonons. This is seen for instance in the specific-heat results. It means that under a shear stress, some atoms will relax and partially anneal the stress. Thus the energy needed for the distortion will be reduced compared to the one previous calculated. We show, after having calculated the Debye and Einstein frequencies, how to estimate this effect.

The Einstein frequency is obtained from the energy required to displace an atom from equilibrium with no movement of neighboring atoms.

The second-order change in energy when moving one atom's position by δR_0 its first-nearest neighbor j being fixed, is

$$\delta E=\sum_j Ce^{-pR_j}\left[-\tfrac{1}{2}pR_j\frac{\delta R_0^2}{R_j^2}+\tfrac{1}{2}pR_j(1+pR_j)\left(\frac{\vec{R}_j\cdot\delta\vec{R}_0}{R_j^2}\right)^2\right]$$
$$-\frac{8\sqrt{b}}{3\pi}\left\{\tfrac{1}{2}\sum_j\frac{t^2e^{-2qR_j}}{b}\left[-qR_j\frac{\delta R_0^2}{R_j^2}+qR_j(1+qR_j)\left(\frac{\vec{R}_j\cdot\delta\vec{R}_0}{R_j^2}\right)^2\right]-\frac{1}{8}\frac{t^4}{b^2}\left(\sum_j e^{-2qR_j}qR_j\frac{\vec{R}_j\cdot\delta\vec{R}_0}{R_j^2}\right)^2\right\}.$$

Setting θ_j the angle between $\vec{R}_j$ and $\delta\vec{R}_0$ and averaging over the radial distribution function to get an average of the Einstein frequency, we have

$$\omega_E = (1/m^{1/2})[ZCe^{-pR}\alpha p(p-2q)]^{1/2}, \tag{15}$$

where α is the average of $\cos^2\theta_j$.

In an fcc crystal, this value does not depend on the direction of vibration of the considered atoms and $\alpha = \frac{1}{3}$. In an amorphous metal, we get also a value of $\frac{1}{3}$ by averaging over a sphere. The change of the average Einstein frequency between an amorphous and a crystalline state is then only due to the corresponding change in Z and R, calculated in Sec. II, and is thus very small.

However, contrary to the crystalline fcc case, the Einstein frequency will depend on the directions of vibration and this will affect the Debye frequency. If we distort from the cubic environment of a given atom, we can decrease the value of α for a particular direction. More precisely, if around an atom there is distortion giving a local charge of the interatomic distance of ΔR, we have a decrease of $\Delta\alpha$ such that

$$\Delta\alpha/\alpha \simeq -2\Delta R/R\,.$$

A reasonable estimation of the possible local distortion is $\Delta R/R \sim 0.05$ to 0.1, so that the minimum Einstein frequency for a site can be lowered by a factor of 5% compared to the average one.

Let us now emphasize that this effect will lower the measured Debye frequency ω_D. Indeed, if $s_\lambda(\vec{q})$ is the sound velocity in the $\vec{q}$ direction with polarization λ, we have the classical equation

$$\frac{9}{\omega_D^3} = \frac{1}{(2\pi)^3}\,\frac{1}{\rho}\sum_\lambda \int \frac{d\Omega}{|s_\lambda(\vec{q})|^3}\,, \tag{16}$$

where ρ is the density. ω_D will thus be dominated by the values of the minima of the sound velocity. The order of magnitude of the sound velocity is given by the Einstein frequency, as we have roughly

$$\omega_E = s\pi/R_0\,.$$

In a glass, we can first assume that when vibrations polarized along the x direction propagate, all the atoms will oscillate along the x direction. We could therefore use the average Einstein frequency, in Eq. (16), and this is the equivalent of our assumptions made above in the calculation of the shear modulus. But this is not true, as they will oscillate in the directions of easiest oscillation even if on a macroscopic scale the oscillation is along the x direction. We have thus to use in Eq. (16) not the average Einstein frequency but an average of the minimum values of ω_E. The Debye frequency will then be smaller in the amorphous state than in the crystal, and we have

$$\frac{\delta\omega_D}{\omega_D} \sim \frac{\Delta\alpha}{\alpha} \sim -\frac{2\Delta R}{R}\,. \tag{17}$$

The Debye frequency will be lowered by a factor of 10% in the amorphous state. This conclusion is in agreement with results of Golding *et al.*[2] on a $Pd_{77}Si_{17}Cu_6$ glass which shows a decrease of 15% in the Debye temperature and results on $Fe_cNi_{80-c}P_{14}B_6$.[11]

Coming back to the value of the shear modulus in the amorphous state, we notice that the Debye frequency is

$$\frac{1}{\omega_D^3} \sim \frac{1}{\rho}\left(\frac{1}{s_L^3} + \frac{2}{s_T^3}\right),$$

where L and T mean longitudinal and transverse. The longitudinal sound velocity does not change very much when passing from the amorphous state to the crystal[2] and this is related to the negligible variation of the bulk modulus. The change of ω_D is thus mainly due to the change in the velocity of the transverse sound, so that

$$\frac{\delta\omega_D}{\omega_D} \sim \frac{\delta s_T}{s_T}\,.$$

The shear modulus is directly related to the velocity of the transverse sound, as

$$s_T = \sqrt{\mu/\rho}$$

and (18)

$$\frac{\delta\omega_D}{\omega} \simeq \frac{1}{2}\,\frac{\delta\mu}{\mu}\,.$$

The decrease in the Debye frequency we have obtained in the glassy state will thus lead to a large decrease in the shear modulus of the order of 20 to 40%, in agreement with all the experimental results.[1,2]

Finally, let us calculate the variation of the bulk modulus with temperature. If we approximate the thermal part of the free energy which is due to the phonons by

$$F = 3kT\log(\hbar\omega_E/kT)\,,$$

the change of the bulk modulus with temperature is given by

$$K(T) = K(0) + \frac{kT}{3R_0}\,\frac{\partial^2}{\partial R^2}\,(\log\hbar\omega_E)_{R_0}\,.$$

We get

$$S = \frac{1}{K(0)}\,\frac{dK}{dT} = -\frac{1}{3R_0}\,qp\left(\frac{p-q}{p-2q}\right)^2\frac{k}{K(0)}\,.$$

The change in the slope S is given by

$$\frac{\delta S}{S} = -\frac{3\,\delta R}{R} \sim 2\times10^{-2}\,.$$

It is larger for the amorphous state than for the crystalline state, i.e., the bulk modulus of the glass decreases more rapidly than for the crystal. This explains the fact that the change is very small at $T = 0$, whereas at the crystallization point, the fraction change can be important.[1]

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