RESEARCH ARTICLE | DECEMBER 19 2007

A simple model to predict the temperature dependence of elastic moduli of bulk metallic glasses

Zhiying Zhang; Veerle Keppens; Takeshi Egami

J. Appl. Phys. 102, 123508 (2007)
https://doi.org/10.1063/1.2818046

A simple model to predict the temperature dependence of elastic moduli of bulk metallic glasses

Zhiying Zhang
Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee 37996, USA

Veerle Keppens[a]
Department of Materials Science and Engineering and Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA

Takeshi Egami
Department of Materials Science and Engineering and Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA and Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

(Received 10 July 2007; accepted 4 October 2007; published online 19 December 2007)

We report a simple model to predict the temperature dependence of elastic moduli of bulk metallic glasses from room temperature measurements, using the Varshni equation and the basic assumption that between absolute zero and the melting point, the shear and bulk moduli change, respectively, by 45% and 22%. This model has been tested using experimental data obtained on a large variety of bulk metallic glasses, and the predicted values are found to be in very good agreement with the experimental results. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2818046]

I. INTRODUCTION

The elastic properties of a solid describe how the material responds to stress and are of considerable interest to both science and technology. Not only do they contain fundamental information about the nature of the interatomic bonding in the material, but they also determine the mechanical behavior of solids and are, therefore, essential parameters to determine potential failure of an object in a given application. In the past few years, significant research efforts have been devoted to the study of the elastic moduli of bulk metallic glasses (BMGs).[1–3] These studies are partially triggered by the reported correlation between the energy of fracture and the Poisson ratio for bulk metallic glasses, with brittle glasses displaying a low Poisson ratio.[4] The importance of the Poisson ratio in the behavior of liquids was also pointed out by Novikov and Sokolov,[5] who showed that the ratio of instantaneous shear to bulk modulus G/B in glasses or, alternatively, the Poisson ratio ν is linked to the fragility of the glass-forming liquid, an important parameter used to evaluate the glass-forming ability of glasses. Even though the latter is still controversial,[6] the above references suggest that a systematic study of the elastic properties and, thus, the Poisson ratio of metallic glasses is expected to yield important information about their mechanical properties. However, reliable measurements as a function of temperature on high-quality materials are often time consuming. In this work, a simple model has been developed to predict the temperature dependence of the elastic moduli for BMGs based on room temperature measurements. Our own database of experimental data obtained on a large variety of bulk metallic glasses was used to test the validity of the model.

[a]Author to whom correspondence should be addressed: Tel.: +1 865 974 3494. FAX: +1 865 974 4115. Electronic mail: vkeppens@utk.edu.

II. MODELING

In 1970, Varshni[7] examined the temperature dependence of 57 elastic constants for 22 substances, which led to the so-called Varshni equation,

$$C(T) = C_0 - \frac{s}{e^{t/T} - 1}, \tag{1}$$

describing the temperature dependence of elastically "normal" solids. In the equation, $C(T)$ is the elastic constant at temperature T, C_0 represents the elastic constant at 0 K, and s and t are the fitting parameters. Even though this equation has only marginal theoretical justification, it has been shown to adequately model the temperature dependence of the elastic moduli of a large variety of solids. In the present paper, we report on our attempts to take this Varshni model one step further and eliminate the fitting parameters by making some basic assumptions with the goal of developing a model that can be used to extrapolate/calculate elastic moduli measured at room temperature to lower and/or higher temperatures. Our first assumption is based on Varshni's remark that in the case of metals, melting takes place when the shear modulus G is reduced to 55% of the modulus at 0 K, i.e., $G(T_m) = (1-n_G)G_0$, with $n_G=0.45$, T_m the melting temperature, and G_0 the shear modulus at 0 K. The second assumption is to take $t=\theta_D$, the Debye temperature of the solid, which can be obtained from the room temperature elastic moduli,

$$t = \theta_D = \frac{h}{k_B}\left(\frac{9N_A\rho}{4\pi M}\right)^{1/3}\left[\left(\frac{\rho}{B+4G/3}\right)^{3/2} + 2\left(\frac{\rho}{G}\right)^{3/2}\right]^{-1/3}, \tag{2}$$

with G and B the shear and bulk moduli at room temperature, M the molecular mass, ρ the physical density, h the Planck constant, k_B the Boltzmann constant, and N_A the Avogadro

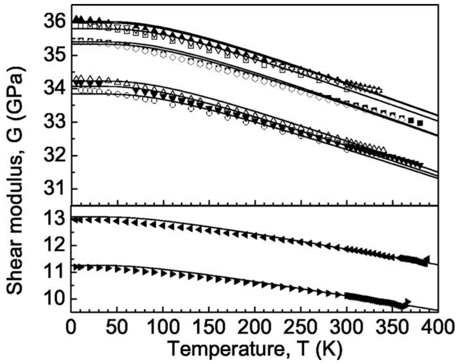

FIG. 1. Temperature dependence of shear modulus for Zr-based BMGs $Zr_{50}Cu_{30}Ni_{10}Al_{10}$ (□), $Zr_{50}Cu_{40}Al_{10}$ (■), $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (○), $Zr_{50}Cu_{35}Al_{10}Pd_5$ (▲), $Zr_{50}Cu_{33}Al_{10}Pd_7$ (◇), and $Zr_{50}Cu_{31}Al_{10}Pd_9$ (▽), Cu-based BMGs [$Cu_{47.5}Zr_{47.5}Al_5$ (△) and $Cu_{47.5}Zr_{38}Hf_{9.5}Al_5$ (▼)], and Ca-based BMGs [$Ca_{55}Mg_{18}Zn_{11}Cu_{16}$ (◀) and $Ca_{65}Mg_{15}Zn_{20}$ (▶)]. The solid line is the model calculation.

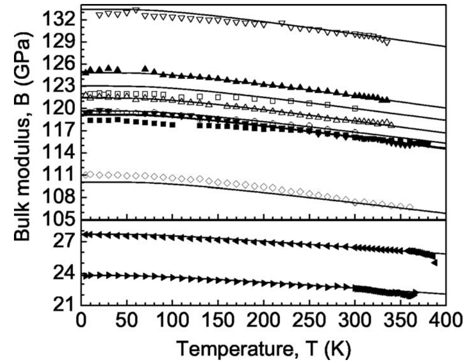

FIG. 2. Temperature dependence of bulk modulus for Zr-based BMGs [$Zr_{50}Cu_{30}Ni_{10}Al_{10}$ (□), $Zr_{50}Cu_{40}Al_{10}$ (■), $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (○), $Zr_{50}Cu_{35}Al_{10}Pd_5$ (▲), $Zr_{50}Cu_{33}Al_{10}Pd_7$ (◇), and $Zr_{50}Cu_{31}Al_{10}Pd_9$ (▽)], Cu-based BMGs [$Cu_{47.5}Zr_{47.5}Al_5$ (△) and $Cu_{47.5}Zr_{38}Hf_{9.5}Al_5$ (▼)], and Ca-based BMGs [$Ca_{55}Mg_{18}Zn_{11}Cu_{16}$ (◀) and $Ca_{65}Mg_{15}Zn_{20}$ (▶)]. The solid line is the model calculation.

number.[8,9] Using the above assumptions, the Varshni parameter s can be obtained from

$$\frac{s}{e^{\theta_D/T_{\mathrm{RT}}}-1}-\frac{s}{n_G(e^{\theta_D/T_m}-1)}+G(T_{\mathrm{RT}})=0, \tag{3}$$

with T_{RT} room temperature. Consequently, the entire temperature dependence of the shear modulus can be determined using

$$G(T)=G(T_{\mathrm{RT}})+\frac{s}{e^{\theta_D/T_{\mathrm{RT}}}-1}-\frac{s}{n_G(e^{\theta_D/T}-1)}. \tag{4}$$

III. RESULTS AND DISCUSSION

Figure 1 compares this model calculation with recently obtained measurements of the temperature dependence of the shear modulus for a variety of bulk metallic glasses.[10,11] The solid lines in the figure were obtained from Eq. (4), using the "average" melting temperature of the compound listed in Table I together with the values for the parameters used in our calculation. The average melting temperature was obtained using $T_m=\Sigma_i x_i T_{m,i}$ with x_i the atomic fraction of component i and $T_{m,i}$ its melting temperature. The average melting temperature represents the lattice elastic energy of a multicomponent system better than the real melting temperature, which is affected by subtle balance in free energy against liquid and is lowered, for instance, in the eutectic alloy system. The average melting temperature provides a good zeroth-order estimate of the relative magnitude of $\nu_0 B$, with ν_0 the atomic volume and B the average bulk modulus. There is good correlation[12,13] between the average melting temperature and the glass transition temperature, which is related to the elastic moduli.[14] Figure 1 shows excellent agreement between our model and the experimental data for the shear modulus.

The next step is to test the validity of this model to calculate/predict other moduli as well. Since BMGs are isotropic materials, there are only two independent elastic moduli. If, for instance, the shear and bulk modulus are known, the other moduli (longitudinal modulus L, Young's modulus E, and Poisson ratio ν) can easily be obtained using one of the following relations:

$$L=B+\frac{4}{3}G, \tag{5}$$

$$E=\frac{9GB}{3B+G}, \tag{6}$$

TABLE I. Averaged melting temperature T_m, density ρ, shear modulus at room temperature $G(T_{\mathrm{RT}})$, bulk modulus at room temperature $B(T_{\mathrm{RT}})$, Debye temperature θ_D, s_G, and s_B for Zr-based, Cu-based, and Ca-based BMGs.

Composition	T_m (K)	ρ (g/cm^3)	$G(T_{\mathrm{RT}})$ (GPa)	$B(T_{\mathrm{RT}})$ (GPa)	θ_D (K)	s_G (GPa)	s_B (GPa)
$Zr_{50}Cu_{30}Ni_{10}Al_{10}$	1737.5	6.862	33.98	120.0	285.28	2.8738	4.8302
$Zr_{50}Cu_{40}Al_{10}$	1700.5	6.714	33.56	116.1	283.83	2.8934	4.7605
$Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$	1802.9	6.632	32.18	116.8	279.73	2.5558	4.4187
$Zr_{50}Cu_{35}Al_{10}Pd_5$	1724.0	6.890	34.17	121.7	282.58	2.8866	4.8912
$Zr_{50}Cu_{33}Al_{10}Pd_7$	1733.4	6.771	33.52	107.3	279.15	2.7780	4.2308
$Zr_{50}Cu_{31}Al_{10}Pd_9$	1742.8	7.067	34.14	130.1	279.47	2.8153	5.1053
$Cu_{47.5}Zr_{47.5}Al_5$	1702.4	7.058	32.43	118.3	275.52	2.7058	4.6926
$Cu_{47.5}Zr_{38}Hf_{9.5}Al_5$	1738.3	7.006	32.29	116.2	265.73	2.5321	4.3329
$Ca_{55}Mg_{18}Zn_{11}Cu_{16}$	1072.8	2.404	11.87	26.45	236.33	1.4505	1.5019
$Ca_{65}Mg_{15}Zn_{20}$	1001.7	2.040	10.12	22.64	226.03	1.2827	1.3264

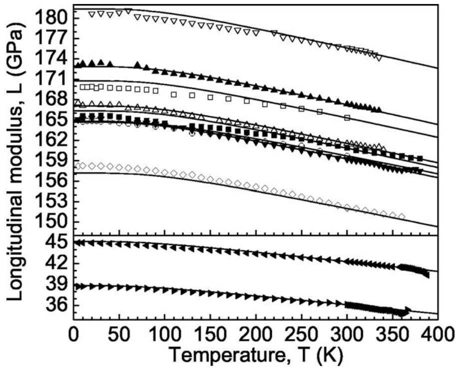

FIG. 3. Temperature dependence of longitudinal modulus for Zr-based BMGs [$Zr_{50}Cu_{30}Ni_{10}Al_{10}$ (□), $Zr_{50}Cu_{40}Al_{10}$ (■), $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (○), $Zr_{50}Cu_{35}Al_{10}Pd_5$ (▲), $Zr_{50}Cu_{33}Al_{10}Pd_7$ (◇), and $Zr_{50}Cu_{31}Al_{10}Pd_9$ (▽)], Cu-based BMGs [$Cu_{47.5}Zr_{47.5}Al_5$ (△) and $Cu_{47.5}Zr_{38}Hf_{9.5}Al_5$ (▼)], and Ca-based BMGs [$Ca_{55}Mg_{18}Zn_{11}Cu_{16}$ (◀) and $Ca_{65}Mg_{15}Zn_{20}$ (▶)]. The solid line is the model calculation.

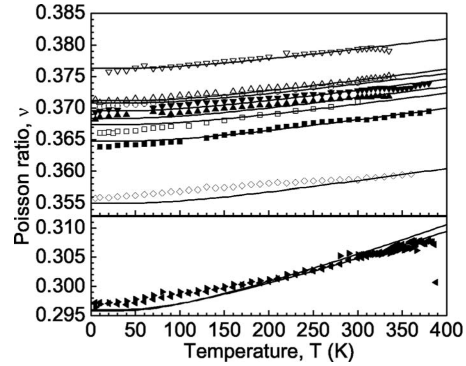

FIG. 5. Temperature dependence of Poisson ratio for Zr-based BMGs [$Zr_{50}Cu_{30}Ni_{10}Al_{10}$ (□), $Zr_{50}Cu_{40}Al_{10}$ (■), $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (○), $Zr_{50}Cu_{35}Al_{10}Pd_5$ (▲), $Zr_{50}Cu_{33}Al_{10}Pd_7$ (◇), and $Zr_{50}Cu_{31}Al_{10}Pd_9$ (▽)], Cu-based BMGs [$Cu_{47.5}Zr_{47.5}Al_5$ (△) and $Cu_{47.5}Zr_{38}Hf_{9.5}Al_5$ (▼)], and Ca-based BMGs [$Ca_{55}Mg_{18}Zn_{11}Cu_{16}$ (◀) and $Ca_{65}Mg_{15}Zn_{20}$ (▶)]. The solid line is the model calculation.

$$\nu = \frac{1}{2} - \frac{1}{2(B/G + 1/3)}. \tag{7}$$

As discussed above, the shear modulus in metals is known to decrease about 45% between 0 K and melting temperature. The bulk modulus, however, is not expected to change as much. It has been shown that the topology of the dense random packing structure is unstable against shear deformation, leading to apparent softening of the shear modulus of the glassy state compared to the crystalline state.[15] On the other hand, the bulk modulus of the glassy state is about the same as that of the crystalline state.[12] The distribution of the local atomic level shear modulus indicates that there are some atomic sites with vanishingly small values of shear modulus. This is not the case for bulk modulus, leading to less softening of the bulk modulus.[12] A careful evaluation of the available data for the bulk modulus B shows that a typical variation in B is of the order of 20%–25% in metals. We, therefore, took our above model with $n_B = 1 - B(T_m)/B_0 = 0.22$, and compared the calculated temperature dependence to our experimental data for the bulk modulus, shown in Fig. 2. Very good agreement is reached for the various alloys.

In a final test, we calculated the temperature dependence of the longitudinal modulus, Young's modulus, and Poisson ratio using relations (5)–(7) and the parameters obtained from the calculated shear and bulk moduli (Table I). Results are shown in Figs. 3–5. Adequate agreement is reached for all moduli for this large variety of alloys. The differences between the predicted values and the experimental results are less than 1%.

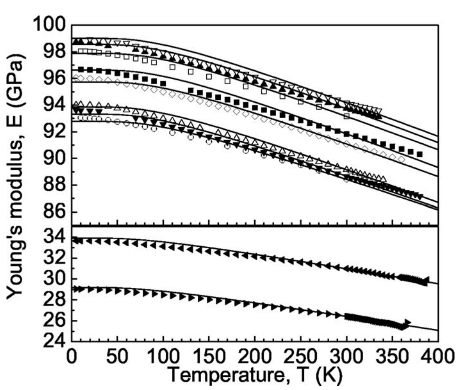

FIG. 4. Temperature dependence of Young's modulus for Zr-based BMGs [$Zr_{50}Cu_{30}Ni_{10}Al_{10}$ (□), $Zr_{50}Cu_{40}Al_{10}$ (■), $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (○), $Zr_{50}Cu_{35}Al_{10}Pd_5$ (▲), $Zr_{50}Cu_{33}Al_{10}Pd_7$ (◇), and $Zr_{50}Cu_{31}Al_{10}Pd_9$ (▽)], Cu-based BMGs [$Cu_{47.5}Zr_{47.5}Al_5$ (△) and $Cu_{47.5}Zr_{38}Hf_{9.5}Al_5$ (▼)], and Ca-based BMGs [$Ca_{55}Mg_{18}Zn_{11}Cu_{16}$ (◀) and $Ca_{65}Mg_{15}Zn_{20}$ (▶)]. The solid line is the model calculation.

IV. CONCLUSIONS

The excellent agreement between the model calculation and the experimental data indicates that our attempt to eliminate the arbitrary Varshni parameters using two basic assumptions is quite successful. Our simple model will enable a quick estimate of the temperature dependence of elastic moduli for a variety of metallic glasses when experimental data beyond room temperature are not available. However, it needs to be pointed out that using the model for BMGs with various compositions may require slight modification of n_B for bulk modulus. The dependence of n_B on Poisson ratio will be investigated further.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation Grant No. DMR-0506292 and the Department of Energy under Contract No. DE-AC05-00OR-22725.

[1]M. L. Lind, G. Duan, and W. L. Johnson, Phys. Rev. Lett. **97**, 015501 (2006).
[2]W. H. Wang, J. Appl. Phys. **99**, 093506 (2006).
[3]K. Tanaka, T. Ichitsubo, and E. Matsubara, Mater. Sci. Eng., A **442**, 278 (2006).
[4]J. J. Lewandowski, W. H. Wang, and A. L. Greer, Philos. Mag. Lett. **85**, 77 (2005).
[5]V. N. Novikov and A. P. Sokolov, Nature (London) **431**, 961 (2004).
[6]L. Battezzati, Mater. Trans., JIM **46**, 2915 (2005).
[7]Y. P. Varshni, Phys. Rev. B **2**, 3592 (1970).
[8]C. Kittel, *Introduction to Solid State Physics*, 6th ed. (New York, Wiley, 1986).
[9]W. H. Wang, P. Wen, D. Q. Zhao, M. X. Pan, and R. J. Wang, J. Mater.

Res. **18**, 2747 (2003).
[10]Z. Zhang, V. Keppens, P. K. Liaw, Y. Yokoyama, and A. Inoue, J. Mater. Res. **22**, 364 (2007).
[11]Z. Zhang, V. Keppens, O. N. Senkov, and D. B. Miracle, Mater. Sci. Eng., A **471**, 151 (2007).
[12]T. Egami and D. Srolovitz, J. Phys. F: Met. Phys. **12**, 2141 (1982).
[13]T. Egami, Rep. Prog. Phys. **47**, 1601 (1984).
[14]T. Egami, S. J. Poon, Z. Zhang, and V. Keppens, Phys. Rev. B **76**, 024203 (2007).
[15]Y. Suzuki and T. Egami, J. Non-Cryst. Solids **75**, 361 (1985).