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Correlation of fragility and Poisson's ratio: Difference between metallic and nonmetallic glass formers

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It is shown that fragility of supercooled metallic liquids correlates with the Poisson's ratio of the respective metallic glasses. However, the correlation differs from that found previously for simple nonmetallic glass formers [V. N. Novikov and A. P. Sokolov, Nature **431**, 961 (2004)]. The observed difference is assigned to the contribution of the free electron gas to the bulk modulus in metallic glasses.

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INTRODUCTION

The structural relaxation in liquids at high temperatures occurs via local processes that include one or a few atoms and, respectively, the structural relaxation time τ and viscosity η have Arrhenius temperature dependence. With decreasing temperature, especially in a supercooled state, deviation from the Arrhenius behavior occurs. This deviation reflects a property of liquids that is called fragility. Fragility proved to be one of the important parameters characterizing relaxation in glass forming liquids and it correlates with many other properties of materials in liquid and glassy state.[1–9] To quantify fragility, various parameters were suggested. The most commonly used definition of fragility was introduced by Angell.[10] It is defined as the slope of the logarithm of viscosity in the fragility plot (i.e., log η versus T_g/T) at T_g

$$m = \left.\frac{\partial \log \eta}{\partial(T_g/T)}\right|_{T=Tg}. \tag{1}$$

Recently a correlation between fragility of a liquid and the Poisson's ratio of the respective glass has been demonstrated for a number of simple nonmetallic glass formers.[7,8] It was shown that the fragility parameter m of a glass forming liquid is an increasing linear function of the ratio of instantaneous bulk to shear moduli, K_∞/G_∞, of the respective glass. Rationalization of this correlation was given on the basis of the connection between high and low-temperature behavior of viscosity in the Angell plot.[7,8] However, exceptions from this correlation have been reported for glass alloys,[8,9] high—molecular weight fragile polymers[8] and metallic glasses.[9]

The present paper focuses on the analysis of metallic liquids and glasses. We show that the correlation between the Poisson's ratio and fragility persist also in metallic glass formers, however it is different from that for nonmetallic materials. The reason for this difference is rationalized.

RESULTS

The correlation between the fragility parameter m of various supercooled metallic liquids and the ratio of adiabatic bulk to shear moduli, K/G, of respective bulk metallic glasses (BMG) is shown in Fig. 1. For comparison, the same correlation observed for nonmetallic glass formers (data from Ref. 7) is also shown in this figure. BMG have larger scattering of literature data for the elastic constants than the nonmetallic materials, probably, because a relatively high cooling rate is essential in the formation of BMG. Nevertheless, still a weak correlation between m and K/G in BMG is seen in Fig. 1. The best linear fit is

$$m = (7 \pm 2)K/G + (24 \pm 10) \quad (\text{BMG}). \tag{2}$$

In the case of the nonmetallic glass formers this correlation is described by[7]

$$m = (29 \pm 2)K/G - (12 \pm 5) \quad (\text{nonmetals}). \tag{3}$$

The Poisson's ratio is directly related to the ratio K/G: $\sigma = (3K/2G-1)/(3K/G+1)$. It also correlates with fragility, although in more complicated nonlinear form.

The slope of m vs K/G dependence is lower in BMG than in nonmetallic materials by a factor ~4, i.e., fragility of supercooled metallic liquids varies less with K/G or Poisson's ratio of respective glasses than fragility of nonmetallic liquids. A possible rationalization of the different dependence of m vs K/G in BMG and nonmetallic glasses is given below.

Let us note that in some papers cited in Table I the fragility index is given in terms of the parameter D, defined by the equation $\eta = \eta_0 \exp[DT_0/(T-T_0)]$. In these cases we esti-

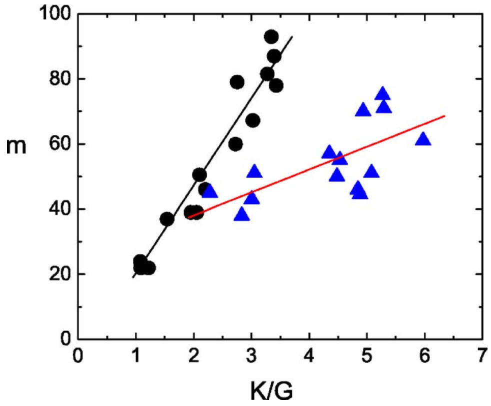

FIG. 1. (Color online) Correlation between fragility of liquids m and the ratio of instantaneous bulk to shear modulus K/G of respective glasses. Circles—data from Ref. 7 for nonmetallic glass formers, triangles—data for metallic glass formers from Table I. Solid lines—linear fits, Eqs. (2) and (3).

TABLE I. Fragility, m, the average value of fragility m_{ave}, the ratio of the bulk to shear modulus, K/G, and the Poisson's ratio, σ, of bulk metallic glasses in Fig. 1.

	m	m_{ave}	K/G	σ
$Mg_{65}Cu_{25}Tb_{10}$	45 (Ref. 19), 49 (Ref. 20)	47	2.28 (Ref. 11)	0.309
$La_{55}Al_{25}Ni_{5}Cu_{10}Co_{5}$	37 (Ref. 21)	37	2.83 (Ref. 22)	0.342
$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$	44 (Refs. 19 and 23) 42 (Ref. 21)	43	3.01 (Ref. 24)	0.350
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (VIT1)	50 (Ref. 25)	50	3.05 (Ref. 24)	0.352
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	55 (Ref. 26), 59 (Ref. 27)	57	4.35 (Ref. 28)	0.393
$Ni_{64}Pd_{16}P_{20}$	50 (Ref. 29)	50	4.48 (Ref. 29)	0.396
$Pd_{39}Ni_{10}Cu_{30}P_{21}$	55 (Ref. 26)	55	4.53 (Ref. 24)	0.397
$Pd_{40}Ni_{40}P_{20}$	41 (Ref. 30), 46 (Ref. 31), 51 (Ref. 25), 55 (Ref. 32)	46	4.84 (Ref. 28)	0.403
$Pd_{48}Ni_{32}P_{20}$	41 (Refs. 26 and 12), 48 (Ref. 19)	44	4.88 (Ref. 33)	0.404
$Ni_{60}Nb_{35}Sn_{5}$	70 (Ref. 34)	70	4.93 (Ref. 22)	0.405
$Pd_{64}Ni_{16}P_{20}$	51 (Ref. 27)	51	5.08 (Ref. 22)	0.408
$Pd_{77.5}Cu_{6}Si_{16.5}$	73 (Ref. 27)	75	5.27 (Ref. 28)	0.411
$Pd_{77}Cu_{6.5}Si_{16.5}$	75 (Ref. 27)	75	5.29 (Ref. 35)	0.411
$Pt_{60}Ni_{15}P_{25}$	54 (Ref. 26), 68 (Ref. 27)	61	5.97 (Ref. 22)	0.421

mated the respective index m using the expression from Ref. 1

$$m = 17(1 + 17/D \log e) = 17(1 + 39.2/D). \tag{4}$$

We note also that we did not include the data for $Ce_{60}Al_{10}Cu_{20}Ni_{10}$ (m=21) from Ref. 11. The reason is that m in Ref. 11 is found not from viscosity or relaxation time data, but from the parameter $T_g/\Delta T_g$ and the values of D and m in the paper are inconsistent with Eq. (4). We also did not use the data for fragility from the earlier work[12] because these data are inconsistent with the results of later measurements on the same materials.

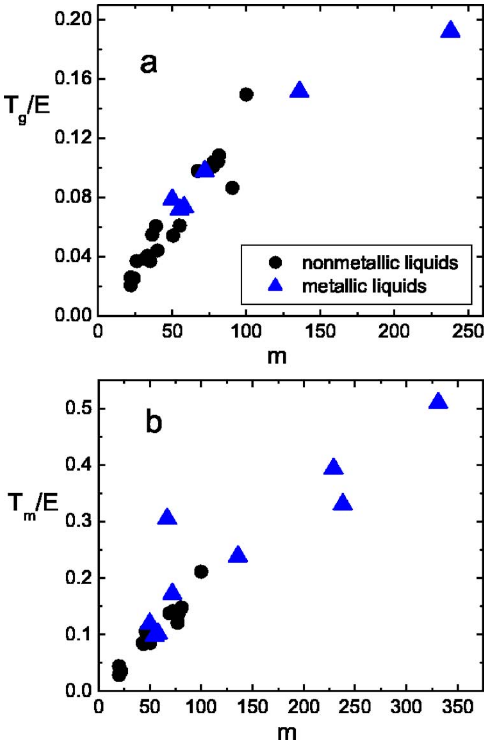

FIG. 2. (Color online) Correlation of fragility m with (a) T_g/E. Materials are listed in ascending fragility order. Nonmetallic liquids: BeF_2, SiO_2, NBS715, NBS711, DGG1, BSC, propanol, B_2O_3, glycerol, ethanol, salol, propylene carbonate, OTP, TNB, toluene, ZBLAN20. Metallic liquids: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (VIT1), $Pd_{40}Cu_{30}Ni_{10}P_{20}$, $Pd_{43}Ni_{10}Cu_{27}P_{20}$, $Zr_{55}Al_{22.5}Co_{22.5}$ (ZAC), $Ni_{59.5}Nb_{40.5}$, $Al_{85}Ni_{10}Ce_{5}$ (data from Table II). (b) T_m/E. Materials are listed in ascending fragility order. Nonmetallic liquids: BeF_2, SiO_2, B_2O_3, glycerol, ethanol, salol, propylene carbonate, OTP, TNB, toluene. Metallic liquids: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (VIT1), $Pd_{40}Cu_{30}Ni_{10}P_{20}$, $Pd_{43}Ni_{10}Cu_{27}P_{20}$, $Al_{80}Ni_{15}Ce_{5}$, $Zr_{55}Al_{22.5}Co_{22.5}$ (ZAC), $Ni_{59.5}Nb_{40.5}$, $Al_{90}Ni_{5}Ce_{5}$, $Al_{85}Ni_{10}Ce_{5}$, $Al_{84}Ni_{10}La_{3}Ce_{3}$ (data from Table II). Circles—nonmetallic liquids (data from Ref. 7), triangles—metallic liquids.

The correlation of m with K/G in nonmetallic glass formers was derived in Refs. 7 and 8 on the basis of high-temperature behavior of viscosity. At high temperatures, say 2–3 times higher than the glass transition temperature T_g, viscosity exhibits Arrhenius temperature dependence with an activation energy E. In Refs. 7 and 8 it was argued that the higher slope of $\log \eta$ at $T=T_g$ (i.e., m) corresponds to the lower slope in the limit of high temperatures in the Angell plot. The high temperature slope is equal to E/T_g. Thus the ratio T_g/E should correlate with fragility index m. Comparison of available experimental data for T_g/E and m in nonmetallic liquids indeed revealed that $T_g/E \approx 1.2 \times 10^{-3}$ m. The correlation of fragility with the K/G ratio than follows from the observations that T_g is proportional to an elastic constant and E is proportional to the instantaneous shear modulus.[13–15] Does the correlation between m and T_g/E hold also for metallic liquids, or, such as in the case of m vs K/G correlation, does it differ? In Fig. 2(a) a few points available in the literature for metallic liquids are shown together with the previously published data for nonmetallic liquids. Basically, there is no difference between the metallic and nonmetallic case with regard to this correlation. This is natural because this correlation is just the property of the Angell plot (with an additional assumption that the viscosity curves for different glass formers do not intersect on this plot between the points $T_g/T=0$ and 1).

The last point in Fig. 2(a) with $m=240$ presents $Al_{85}Ni_{10}Ce_5$ and may signal that a saturation appears in the dependence between T_g/E and m at high values of fragility.

We note that fragility also correlates well with the ratio T_m/E where T_m is a melting temperature [Fig. 2(b)]. It means that a forecast of m can be obtained on the basis of high-temperature viscosity data in normal liquid state of metals, above T_m. This observation might have a significant implication for analysis of bulk metallic glasses.

DISCUSSION

What is special in metallic glass formers that makes the correlation between m and the ratio K/G (Fig. 1) different from the case of simple nonmetallic glass formers? Existence of a free electron gas differentiates metals from other materials. The free electron gas gives additional contribution to the bulk modulus of BMG. This contribution by definition is absent in nonmetallic glass formers. The energy E_{el} of the free electron gas in BMG depends only on its density[16] and thus basically is not sensitive to structure rearrangements in the course of structure relaxation at a fixed volume V. Respectively, the same is valid for the free electron gas contribution to the bulk modulus, $K_{el}=V\partial^2E_{el}/\partial V^2$. The shear modulus is insensitive to the free electron gas because, in the

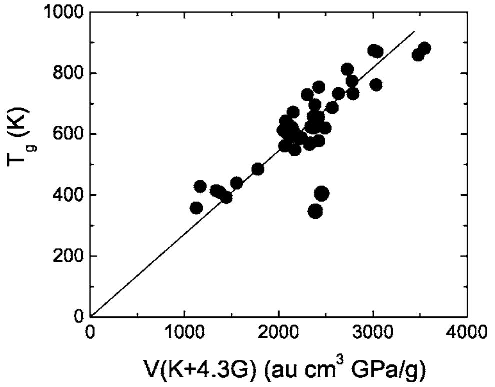

FIG. 3. Correlation between T_g and $V(K+3.4G)$ that follows from Eq. (8). Respective BMG and the values of the parameters are given in Table III. Solid line—a guide for an eye.

TABLE II. Fragility, m, the average value of fragility m_{ave}, high-temperature activation energy of viscous flow, E (in temperature units), glass transition temperature T_g, melting temperature T_m, and the ratios E/T_g and E/T_m of metallic glass formers in Fig. 2.

	m	m_{ave}	E (K)	T_g (K)	T_m (K)	E/T_g	E/T_m
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (VIT1)	50 (Ref. 25)	50	7874	615 (Ref. 37) 623 (Ref. 11)	932 (Ref. 11), 941 (Ref. 38)	12.7 (Ref. 36)	8.4
$Zr_{55}Al_{22.5}Co_{22.5}$	72 (Ref. 36)	72	7681	753 (Ref. 36)	1323 (Ref. 36)	10.2 (Ref. 36)	5.8
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	55 (Ref. 26), 59 (Ref. 27)	57	7686	561 (Ref. 40) 575 (Ref. 11)	758 (Ref. 39), 804 (Ref. 11)	13.7 (Ref. 41)	10.1
$Pd_{43}Ni_{10}Cu_{27}P_{20}$	51 (Ref. 30), 65 (Ref. 25)	58	7752	582 (Ref. 42)	790 (Ref. 43), 802 (Ref. 27)	13.6 (Ref. 42)	9.8
$Ni_{59.5}Nb_{40.5}$	136 (Ref. 36)	136	6072	920 (Ref. 44)	1448 (Ref. 44)	6.6 (Ref. 36)	4.2
$Al_{80}Ni_{15}Ce_5$	67 (Ref. 45)	67	2908 (Ref. 45)		887 (Ref. 45)		3.8
$Al_{84}Ni_{10}La_3Ce_3$	331 (Ref. 45)	331	1744 (Ref. 45)		889 (Ref. 45)		2.0
$Al_{85}Ni_{10}Ce_5$	238 (Ref. 19), 265 (Ref. 45)	252	2691 (Ref. 45)	519 (Ref. 45)	889 (Ref. 45)	5.2	3.0
$Al_{90}Ni_5Ce_5$	229 (Ref. 45)	229	2261 (Ref. 45)		890 (Ref. 45)		2.5

TABLE III. Adiabatic bulk and shear moduli, K and G, mass density, ρ, average atomic volume, V (atomic units × cm^3/g), and glass transition temperature T_g of bulk metallic glasses in Fig. 3.

	K (GPa)	G (GPa)	ρ (g/cm^3)	V (au cm^3/g)	T_g (K)
$Au_{49.5}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ (Ref. 22)	132.3	26.5	11.6	11.0	405
$Au_{55}Cu_{25}Si_{20}$ (Ref. 22)	139.8	24.6	12.2	10.6	348
$Ce_{70}Al_{10}Ni_{10}Cu_{10}$	27 (Ref. 22)	11.5 (Ref. 22)	6.67 (Ref. 22)	16.9	359 (Ref. 46)
$Cu_{46}Zr_{42}Al_7Y_5$	104.1 (Ref. 22)	31 (Ref. 22)	7.23 (Ref. 22)	10.2	672 (Ref. 50), 713 (Ref. 22)
$Cu_{46}Zr_{54}$ (Ref. 22)	128.5	30	7.62	10.3	696
$Cu_{50}Hf_{43}Al_7$ (Ref. 22)	132.8	42	11	10.0	774
$Cu_{57.5}Hf_{27.5}Ti_{15}$ (Ref. 22)	117.5	37.3		9.4	729
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	128.2 (Ref. 24)	36.9 (Ref. 24)	8.3 (Ref. 47)	9.5	754 (Refs. 24 and 28)
$Fe_{53}Cr_{15}Mo_{14}Er_1C_{15}B_6$ (Ref. 22)	180	75	6.92	7.9	860
$Fe_{55}Mn_{10}Mo_{12}Er_2C_{15}B_6$ (Ref. 48)	145	75	7.9	6.8	813
$Fe_{61}Mn_{10}Cr_4Mo_6Er_1C_{15}B_6$ (Ref. 22)	146	75	6.89	7.5	870
$La_{55}Al_{25}Ni_5Cu_{10}Co_5$	44.2 (Ref. 22)	15.6 (Ref. 22)	6.0 (Ref. 22)	15.9	439 (Ref. 21) 4652 (Ref. 44)
$Mg_{65}Cu_{25}Tb_{10}$ (Ref. 11)	44.7	19.6	3.98	11.9	414
$Mg_{65}Cu_{25}Gd_{10}$ (Ref. 22)	46.3	18.6	4.04	10.6	428
$Mg_{70}Zn_{25}Ca_5$ (Ref. 49)	48.2	17.8	2.65	13.2	393
$Nd_{60}Al_{10}Fe_{20}Co_{10}$ (Ref. 28)	46.5	20.7	7.0	15.1	493
$Ni_{40}Cu_5Ti_{17}Zr_{28}Al_{10}$	140.7 (Ref. 22)	49.7 (Ref. 22)	6.48 (Ref. 22)	9.7	762 (Ref. 51) 862 (Ref. 22)
$Ni_{45}Ti_{20}Zr_{25}Al_{10}$	129.6 (Ref. 22)	42 (Ref. 22)	6.4 (Ref. 22)	9.6	773 (Ref. 51) 733 (Ref. 28) 791 (Ref. 22)
$Ni_{48}Pd_{32}P_{20}$ (Ref. 35)	173.5	37.2	9.19	7.4	588
$Ni_{60}Nb_{35}Sn_5$	267 (Ref. 22)	66 (Ref. 22)	8.64 (Ref. 22)	8.6	882 (Ref. 43)
$Ni_{60}Nb_{20.4}Ta_{13.6}Sn_6$ (Ref. 22)	197.6	60.1	9.8	8.8	882
$Ni_{60}Nb_{27.2}Ta_{6.8}Sn_6$ (Ref. 22)	189	59.41	9.24	7.7	875
$Ni_{64}Pd_{16}P_{20}$ (Ref. 35)	169.8	37.9	8.75	7.0	602
$Pd_{35}Cu_{30}Ni_{10}Fe_5P_{20}$ (Ref. 39)	173.5	37.5	9.12	7.75	571
$Pd_{39}Ni_{10}Cu_{30}P_{21}$	159.1 (Ref. 24)	35.1 (Ref. 24)	9.15 (Ref. 24)	7.96	586 (Ref. 35)
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	145.3 (Ref. 39)	33.4 (Ref. 39)	9.19 (Ref. 39)	7.93	561 (Ref. 40) 575 (Ref. 11)

TABLE III. (*Continued.*)

	K (GPa)	G (GPa)	ρ (g/cm^3)	V (au cm^3/g)	T_g (K)
$Pd_{40}Ni_{40}P_{20}$	185 (Ref. 28)	38.2 (Ref. 28)	9.4 (Ref. 52)	7.68	578 (Ref. 53) 583 (Ref. 28) 570 (Ref. 32)
$Pd_{40}Cu_{40}P_{20}$	158 (Ref. 22)	33.2 (Ref. 22)	9.3 (Ref. 22)	7.98	473 (Ref. 37) 548 (Ref. 22)
$Pd_{48}Ni_{32}P_{20}$ (Ref. 35)	176.7	36.2	9.83	7.73	585
$Pd_{56}Fe_{24}P_{20}$ (Ref. 35)	161.2	34.2	9.9	7.35	612
$Pd_{60}Cu_{20}P_{20}$ (Ref. 22)	167	32.3	9.78	7.81	604
$Pd_{60}Fe_{20}P_{20}$ (Ref. 35)	164.5	33.7	9.98	7.49	617
$Pd_{64}Fe_{16}P_{20}$	161.9 (Refs. 33 and 54)	33.1 (Refs. 33 and 54)	10.0 (Refs. 33 and 54)	7.65	630 (Ref. 35)
$Pd_{64}Ni_{16}P_{20}$ (Ref. 35)	172	32.9	10.1	7.65	590
$Pd_{68}Fe_{12}P_{20}$ (Ref. 35)	158.1	31.4	10.1	7.80	643
$Pd_{77.5}Cu_6Si_{16.5}$	174.6 (Ref. 35)	33 (Ref. 35)	10.4 (Ref. 35)	8.66	630 (Refs. 39 and 37) 550 (Ref. 22)
$Pr_{60}Cu_{20}Ni_{10}Al_{10}$	45.2 (Ref. 24)	13.6 (Ref. 24)	6.9 (Ref. 24)	14.97	409 (Ref. 55)
$Pt_{57.5}Cu_{14.7}Ni_5P_{22.8}$ (Ref. 22)	243.2	33.4	15.2	8.66	490
$Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ (Ref. 56)	198.7	33.3	15.02	8.79	508
$Pt_{60}Ni_{15}P_{25}$ (Ref. 22)	201.9	33.8	15.7	8.50	488
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (VIT1)	114.1 (Refs. 22 and 24)	34.1 (Ref. 22), 37.4 (Ref. 24)	5.9 (Ref. 22) 6.13 (Ref. 24)	9.79	623 (Refs. 11 and 24) 618 (Ref. 22)
$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Ref. 24)	111.9	37.2	6.0	8.94	622
$Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$ (Ref. 24)	113.6	35.2	6.43	10.10	658
$Zr_{48}Nb_8Cu_{14}Ni_{12}Be_{18}$ (Refs. 22 and 38)	118.3	34.3	6.7	10.27	620
$Zr_{55}Al_{19}Co_{19}Cu_7$ (Ref. 22)	114.9	37.6	6.2	11.44	733
$Zr_{55}Ti_5Cu_{20}Ni_{10}Al_{10}$ (Refs. 22 and 38)	118	31	6.62	10.74	625
$Zr_{57.5}Cu_{15.4}Ni_{12}Al_{10}Nb_5$ (Refs. 22 and 38)	117.6	30.8	6.5	11.51	663

first approximation, the shear strain does not alter the volume. Let us assume that the bulk modulus in a BMG can be represented as a sum of the free electron gas contribution, K_{el}, and the lattice contribution, K_{lat}, so that $K=K_{el}+K_{lat}$. In the case of nonmetallic glass formers $K=K_{lat}$ and the correlation between fragility and elastic constants can be written in the form[7]

$$m = 29K_{lat}/G - 12. \tag{5}$$

We assume that in terms of the lattice elastic constants the correlation between fragility and the elastic constants in metallic glass formers is basically the same as in nonmetals. In other words, we assume that for metallic glass formers the relation (5) also holds. Introducing to Eq. (5) the full bulk modulus of BMG, K, one has

$$m=(29K_{lat}/K)K/G-12. \tag{6}$$

Equation (6) shows that the linear correlation between m and K/G in metallic glass formers has the slope that is lower than in nonmetals by a factor $K_{lat}/(K_{lat}+K_{el})$, in agreement with experimental data [Eqs. (2) and (3)]. Quantitatively, Eqs. (2) and (6) are equivalent if $K_{lat}/K\sim 0.24+1.24G/K$. The ratio G/K varies from $\sim$0.15 for fragile BMG to $\sim$0.4 for strong BMG (Fig. 1). Thus, the model requires that the lattice contribution to the bulk modulus of BMG, K_{lat}/K, lies in the interval 0.4–0.7. Respectively, the free electron gas should give 0.3–0.6 of the total bulk modulus and within the frames of the model its contribution has a tendency to be relatively smaller in strong BMG and larger in fragile BMG.

An estimate of K_{el} in the free electron gas model[16] gives

$$K_{el}=\frac{\hbar^2(3\pi^2)^{2/3}}{3m_e}n^{5/3}, \tag{7}$$

where m_e is the mass of electron and n is the density of the free electron gas. Of course, the free electron theory cannot explain the elastic properties of metals. However, it can give an order of magnitude estimate of the electron gas contribution to the bulk modulus. One finds that K_{el} in Eq. (7) has the same order of magnitude as the experimental values for the total bulk modulus K.[16] In particular, it can be in the interval 0.3–0.6 of the total K or even broader.[16] This contribution can be different for different BMG. As a result, a strong scattering of the points in Fig. 1 for BMG is expected.

Thus, the difference between nonmetallic and metallic glass formers in Fig. 1 is rationalized as follows. The free electron gas gives significant structure independent contribution to the bulk modulus in BMG. As a result, the measured values of the ratio K/G in BMG are very high, e.g., K/G reaches $\sim$4–6, the values that are not reached even for most fragile nonmetallic glass formers in Fig. 1. This electron contribution, however, does not influence fragility (or at least this influence is much weaker than that for the bulk modulus). So, a metallic and a nonmetallic glass formers with the same fragility will have different K/G ratio. The latter will be always higher for BMG than for a nonmetallic glass former. Qualitatively, this explains why the dependence of m on K/G in metallic glass formers is weaker than in nonmetals. Detailed analysis of electron contribution to the bulk elastic modulus of, at least, a few BMG will provide a good test for the proposed here explanation.

The correlation between T_g/E and m [Fig. 2(a)] together with Eq. (2) predicts that

$$T_g \propto E(K_\infty/G_\infty+3.4). \tag{8}$$

In Refs. 13–15 it is shown that the activation energy E might be related to the instantaneous (infinite frequency) shear modulus, $E=G_\infty V_a$, where V_a is an activation volume that at high temperatures is on the order of the average atomic volume V. It is interesting to check the consistency of this relation with Eq. (8). The latter can be rewritten as $T_g \propto V_a(K_\infty+3.4G_\infty)$. In Fig. 3 the correlation between T_g and $V(K+3.4G)$ for BMG is shown. The average atomic volume of a BMG is defined as $V=M/\rho$, where M is the average atomic mass and ρ is density. Basically, the correlation confirms that the high temperature activation energy of viscous flow in metallic liquids is proportional to the instantaneous shear modulus. Two points that deviate from the correlation correspond to $Au_{49.5}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ and $Au_{55}Cu_{25}Si_{20}$.

CONCLUSION

The correlation between fragility and the Poisson's ratio discussed in Ref. 7 was found for chemically simple glass formers, where the elastic constants are determined by interatomic forces. It has been shown[8,9,17,18] that glass alloys with complex chemical composition may deviate from this correlation. The reason can be fluctuations of local chemical composition and complex topology of their structure. Polymeric glasses with long chains also deviate from the correlation,[8] probably, because of the specific intramolecular features of relaxation in long molecules. Metallic glasses is another class of systems that do not follow the correlation observed for simple nonmetallic materials.[9,17] Presented here the analysis shows that fragility correlates with the ratio of instantaneous bulk to shear modulus K/G of glassy state even in metallic glass formers. However, the slope of m vs K/G correlation in the case of metallic glasses is $\sim$4 times lower than in the case of nonmetallic glasses. We ascribe this difference to the free electron gas contribution to the bulk modulus of metallic glasses. At the same time, the ratio of T_g or T_m to the activation energy of viscous flow in normal metallic liquid correlates with fragility just as in nonmetallic liquids.

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