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Thermal expansion measurements by x-ray scattering and breakdown of Ehrenfest's relation in alloy liquids

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Measurements of sharp diffraction peaks as a function of temperature are routinely used to obtain precise linear expansion coefficients of crystalline solids. In this case, the relation between temperature dependent changes in peak position in momentum transfer (q_1) and volume expansion is straightforward (Ehrenfest's relation: $q_1 = K(2\pi/d)$, where K is a constant and d is the interatomic spacing) and the data obtained are usually in close agreement with more direct measurements. With high intensity synchrotron x-ray and spallation neutron sources, it is also possible to accurately measure the positions of the much broader peaks for liquids and glasses. This has led to a debate on whether linear expansion coefficients derived from these data are an accurate representation of the volume expansion coefficients. We present here volume thermal expansion and x-ray diffraction data for a large number of glass-forming alloy liquids acquired in a containerless environment using the beamline electrostatic levitation technique. The data show a large difference in the values obtained from the two different techniques. Moreover, the position of the first peak (q_1) in the scattered intensity in the structure factor ($S(q)$) and the atomic volume v for all liquids follow a simple relationship, $v \propto (q_1)^{-\varepsilon}$. The exponent, $\varepsilon = 2.28 (\pm 0.11)$, is much different from the expected value of 3 from Ehrenfest's relation and shows no temperature dependence over the temperature range of the data collected. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4876125>]

Various diffraction techniques, such as x-ray, neutron, and electron, are routinely used to study the structure of materials. For crystalline materials, the sharp Bragg peaks allow accurate determination of the atomic positions in the crystal lattice. The temperature dependence of lattice parameters provides accurate data for the volume (α) and linear (β) expansion coefficients, which are usually in close agreement with direct measurements of bulk materials. Only at sufficiently high temperatures, when the concentration of lattice vacancies and other defects is significant, do direct volume measurements give slightly higher values than those obtained from diffraction measurements.¹ In stark contrast to crystalline materials, liquids, and amorphous materials lack long-range order, which results in a broad distribution in atomic neighbor distances and broadening of the diffraction peaks. However, they still maintain short- and medium-range order over several nearest neighbor distances. Since diffraction data provide information in the reciprocal space, an important question was raised by Ehrenfest² almost a century ago of whether real space structural information (atomic distances) can be obtained from the diffraction patterns of liquids and glasses. He argued that if the atomic scattering factor is a slowly varying function of q , the position (q_1) of the first maximum in $S(q)$ can be related to the nearest neighbor distance in real space (d), by $q_1 = K(2\pi/d)$, where K is a constant. Therefore, it should be possible to determine the linear expansion coefficients of liquids and glasses from the temperature dependence of q_1 in a similar manner as used for crystalline solids. Accurate determination of the $S(q)$

maxima for liquids and amorphous materials became possible only recently with the use of high intensity synchrotron x-ray and spallation neutron sources. Based on Ehrenfest's relation, the temperature dependence of the position of the first peak maximum in $S(q)$ has been used by several groups^{3–7} to determine the linear thermal expansion coefficients (β) of metallic glasses.

Good agreement has been reported between α and β for a marginal glass, $\text{Cu}_{55}\text{Hf}_{25}\text{Ti}_{15}\text{Pd}_5$,⁵ and for two bulk metallic glasses (BMGs), $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$,^{3,4} and $\text{La}_{62}\text{Al}_{14}\text{Cu}_{11.7}\text{Ag}_{2.3}\text{Ni}_5\text{Co}_5$.⁶ However, a more recent investigation⁷ found a lower value for β from direct measurements compared to that from the x-ray diffraction measurements for the same $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ glass and liquid. Further, the general validity of Ehrenfest's relation for amorphous and liquid metals has been questioned.^{7,8} Since very few such studies exist of supercooled (metastable liquid below the liquidus temperature, T_l) liquids,⁷ a broader validity of Ehrenfest's relation calls for more comprehensive investigation of many different equilibrium and supercooled alloy liquids. We present here such data for a large number of glass forming alloy liquids, including a few bulk metallic glasses, using the electrostatic levitation (ESL) and beamline ESL (BESL) techniques. The main result is that the *expansion coefficients obtained from these two different experimental techniques are usually in disagreement for liquids*. The main reason for this disagreement is a deviation from the expected relation between the atomic volume, v , and the atomic separation, d , ($v \propto d^3$), which is equivalent to $v \propto (q_1)^{-3}$, if Ehrenfest's relationship is valid. What is found instead is that $v \propto (q_1)^{-2.28(\pm 0.11)}$, with a *temperature independent* exponent within the precisions of measurements. Since it has been suggested⁸ that the exponent is a measure of

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the fractal dimension of the medium-range order (MRO) in liquids, which decreases with increasing temperature, a temperature independent exponent is surprising.

Master alloy ingots (about 1 g) of desired compositions were prepared by repeated (at least 3 times) arc-melting of stoichiometric amounts of high purity (higher than 3 N) elements on a water-cooled copper hearth under a Ti-Zr-gettered Ar (99.999%) atmosphere. For the levitation studies, smaller ingots (45–80 mg) were prepared from portions of the master ingots by arc melting. Mass losses during melting and ESL processing were negligible, leading to no significant change in sample composition during processing.

All measurements were performed on levitated samples in a high vacuum ($\approx 10^{-7}$ Torr) chamber, using the ESL or BESL techniques.^{9,10} The samples were heated and melted with a 50 W diode laser and the corresponding temperatures were measured with a two color pyrometer. The volumes of the levitated samples as a function of temperature were determined from an analysis of recorded video images of the profile of the spherical liquid droplets using a well-established method.^{11,12} The highest measurement temperatures were typically 200–300 K above the liquidus temperature; heating to such a high temperature was necessary to achieve the maximum supercooling before crystallization. The lowest measurement temperatures were limited by crystallization from the metastable supercooled liquids, marked by a sudden rise in temperature (recalescence) and significant deformation of the spherical droplets. The data collected from a number of cooling cycles were binned together to improve statistics. The volume expansion coefficient, $\alpha = 1/V(dV/dT)$, was obtained from the slopes of $V(T)$. The atomic volume, $v(T)$, was calculated from the molar volume obtained from the measured $V(T)$.

X-ray scattering data from the levitated droplets were obtained in a transmission geometry using high-energy X-rays (129 keV, 0.0958(6) Å) on the 6ID-D beamline of the Advanced Photon Source located within Argonne National Laboratory. The diffraction patterns were recorded over a scattering range of $0.8 \leq q \leq 14 \text{ Å}^{-1}$ using a GE Revolution 41-RT area detector (details can be found in Ref. 13). The sample-to-detector distance and its orientation relative to the beam normal were determined using a levitated silicon sphere. The temperature-dependent structure factor, $S(q)$, was determined using in-house software,¹⁴ which corrected for absorption from the spherical samples, background contributions from air between the vacuum chamber and the area detector, and Compton and multiple scattering.

As a typical example, Fig. 1(a) shows the measured $S(q)$ at various temperatures for one representative alloy liquid in the equilibrium and supercooled states; Fig. 1(b) focuses on the first peak of $S(q)$. The position of the first peak in $S(q)$, q_1 , was determined by a cubic spline fit to the experimental data. Figure 2 shows $q_1(T)$ for a few representative alloy liquids. An approximately linear temperature dependence of q_1 was observed. Table I lists T_b , α , the atomic volume v and q_1 at T_b , and $\beta = 1/q_1(dq_1/dT)$ for a large number of glass-forming liquids. For isotropic expansion, the relation $\beta = \alpha/3$ is expected, if q_1 is a true measure of the average interatomic distances. Neglecting anisotropy, this relationship is generally valid for crystalline solids.¹ In contrast, we find (Table I) that

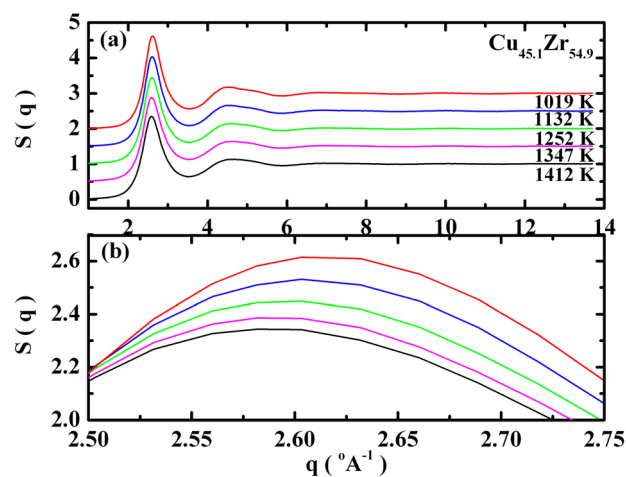


FIG. 1. (a) Temperature dependence of the structure factor, $S(q)$, of a representative alloy liquid. (b) Magnified first peak showing the shifts to larger q with decreasing temperature.

the volume expansivities are much smaller than 3β for the alloy liquids. The absence of a clear correlation between α and β raises the question of whether any common relationship exists between $v(T)$ and q_1 at a specific temperature for all alloy liquids, as is suggested by Ehrenfest's relationship. Recently,⁸ from x-ray and neutron scattering measurements of q_1 as well as mass density measurements of a series of amorphous alloys at room temperature, a relationship $v \propto (q_1)^{-2.31}$ was found. To check whether a similar relationship also holds for the liquids, a double logarithmic plot of v as a function of q_1 is shown in Fig. 3. To facilitate a comparison between the different alloy liquids with very different T_g and T_l values, a common temperature of $2T_g$ was chosen instead of T_b , since the relevant temperature for glass formation is T_g , and T_l is only a measure of the relative stability of the liquid with respect to the underlying crystal phases. The data fall in a straight line with an average slope of $-2.28 (\pm 0.12)$, confirming a relationship: $v \propto (q_1)^{-2.28 \pm 0.11}$. The exponent for the liquids is in agreement with that obtained for the glasses at room temperature,⁸ but much smaller than the expected value of 3 from Ehrenfest's relation.

Since experimental data for both v and q_1 exist over a large temperature range (300–600 K), and since $v(T)$ and $q_1(T)$ change linearly with temperature, it was possible to examine the temperature dependence of the exponent. Calculated values for $v(T)$ and $q_1(T)$, instead of experimentally determined ones, were used for this analyses since it was not possible to obtain data for all liquids over an equally large temperature range. Moreover, the use of the experimentally determined slopes for $v(T)$ and $q_1(T)$ gave less scatter than if the individual data points were used. Naturally, the temperature range under consideration was limited by the experimental data and the reliability of the linear extrapolation procedures for $q_1(T)$ and $v(T)$. For a number of these alloys, a linear relationship for $v(T)$ has been found to hold good in the deeply supercooled liquids.¹⁵ Our ongoing studies¹⁶ of the present alloys indicate that irrespective of whether they are strong or fragile according to the Angell classification scheme,¹⁷ q_1 changes linearly with temperature, even close to T_g . However, the temperature dependence

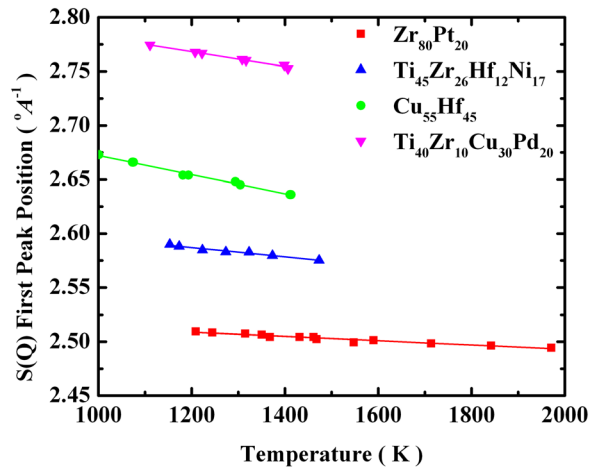


FIG. 2. Temperature dependence of the first peak position in $S(q)$ for a few representative alloy liquids. The lines are fits to the data.

of height of $S(q_1)$ and v become non-linear near T_g . Such non-linearities have been speculated¹⁸ and observed recently in the volume measurements for two strong glasses (Vitreloy 106 and 106a) from measurements far above T_l to well below T_g .¹⁹ In contrast, deviations from linearity are expected to be much smaller in the peak positions and that too at temperatures close to T_g . These considerations restricted our analysis to temperatures above $1.2 T_g$.

Similar to the results shown in Fig. 3, double logarithmic plots of v and q_1 at the select temperatures (scaled to T_g) gave reasonable straight-line fits. The derived exponents (ε in the relation: $v \propto (q_1)^{-\varepsilon}$) are shown as a function of scaled temperatures in Fig. 4. Within experimental error (about $\pm 6\%$ from 1σ fit of the data to the relation), the exponent does not show any detectable change over such a large temperature range. The authors of Ref. 8 suggest that ε is the fractal dimension of the MRO in glasses. If so, the present result is surprising. This would suggest that the fractal dimension of MRO does not change between $2.5 T_g$ and 1.2

TABLE I. Measured volume expansion coefficient α , first peak position in $S(q)$, q_1 , and the atomic volume v at the liquidus temperature, T_l , and the linear expansion coefficient β for the alloy liquids studied. The numbers in the parenthesis are the errors (1σ) in linear fits to the data. The T_g values are taken from the literature as cited; T_l of the binary alloys are taken from the binary phase diagrams.³⁸

Composition (at. %)	T_g (K)	T_l (K)	Atomic volume (v) at T_l (\AA^3)	Volume expansion coefficient, α (10^{-5})	First peak position in $S(q)$ at T_l (\AA^{-1})	Linear expansion coefficient from $S(q)$, β (10^{-5})
Cu _{63.4} Zr _{36.6}	730 ^a	1200	16.80	8.3 (0.2)	2.737	3.8 (0.2)
Cu ₆₀ Zr ₂₀ Ti ₂₀	700 ²⁵	1125	16.37	7.9 (0.2)	2.789	2.7 (0.22)
Cu _{60.8} Hf _{39.3}	773 ²⁶	1535	16.70	8.1 (0.3)	2.673	3.8 (0.1)
Cu _{59.7} Zr _{40.3}	710 ^a	1226	17.08	7.5 (0.15)	2.709	3.1 (0.19)
Cu _{58.1} Zr _{35.9} Al ₆	700 ²⁷	1140	16.81	7.1 (0.19)	2.725	2.8 (0.22)
Cu ₅₅ Hf ₄₅	771 ²⁶	1295	17.12	7.5 (0.3)	2.660	3.8 (0.9)
Cu ₅₅ Hf ₂₀ Ti ₂₅	715 ²⁸	1180	16.14	8.2 (0.2)	2.766	3.9 (0.3)
Cu ₅₃ Zr ₄₇	675 ^a	1215	17.85	6.9 (0.15)	2.650	3.4 (0.28)
Cu _{51.6} Zr _{48.4}	681 ^a	1222	18.02	6.5 (0.2)	2.648	2.7 (0.12)
Cu ₅₀ Zr ₄₅ Al ₅	676 ²⁷	1178	17.04	7.1 (0.2)	2.664	3.0 (0.30)
Cu ₅₀ Zr _{42.5} Ti _{7.5}	677 ²⁹	1152	18.71	6.5 (0.15)	2.662	2.5 (0.49)
Cu ₅₀ Zr ₄₀ Ti ₁₀	680 ²⁹	1168	17.18	6.2 (0.1)	2.674	3.1 (0.10)
Cu _{49.4} Zr _{50.6}	667 ^a	1213	18.34	6.6 (0.15)	2.642	2.6 (0.14)
Cu _{45.1} Zr _{54.9}	648 ^a	1263	18.70	6.0 (0.1)	2.599	2.6 (0.17)
Cu _{26.8} Zr _{73.2}	590 ^a	1389	20.61	5.5(0.2)	2.497	1.03(0.20)
Ni _{59.5} Nb _{40.5}	891 ^{15,30}	1448	14.31	6.1 (0.1)	2.886	1.96 (0.32)
Ni ₆₂ Nb ₃₈	892 ^{15,30}	1483	14.38	6.6 (0.4)	2.898	2.2 (0.12)
Ni ₆₀ Nb ₃₀ Ta ₁₀	934 ^{15,31}	1559	15.36	6.6 (0.10)	2.887	1.89 (0.18)
Ti ₄₅ Zr ₃₈ Ni ₁₇	^b	1333	19.28	5.2 (0.1)	2.580	1.59(0.18)
Ti ₄₅ Zr ₂₆ Hf ₁₂ Ni ₁₇	639 ³²	1364	19.17	5.0 (0.1)	2.579	1.94 (0.09)
Ti ₄₅ Zr ₂₀ Hf ₁₈ Ni ₁₇	647 ³²	1448	19.18	4.9 (0.1)	2.577	1.74 (0.09)
Ti ₄₅ Zr ₁₇ Hf ₂₁ Ni ₁₇	652 ³²	1490	19.20	4.7 (0.1)	2.576	1.53 (0.08)
Ti ₄₅ Hf ₃₈ Ni ₁₇	675 ³²	1560	19.32	5.8 (0.05)	2.585	1.62 (0.17)
Ti ₄₀ Zr ₁₀ Cu ₃₀ Pd ₂₀	687 ³³	1279	16.23	7.2 (0.2)	2.770	2.07 (0.16)
Ti ₄₀ Zr ₁₀ Cu ₃₆ Pd ₁₄	669 ³³	1191	16.27	7.8 (0.12)	2.780	2.8 (0.24)
Zr ₈₀ Ni ₂₀	572 ³⁴	1450	21.12	4.6 (0.4)	2.483	0.84(0.06)
Zr ₇₆ Ni ₂₄	600 ³⁴	1233	20.37	4.2 (0.2)	2.505	1.45(0.30)
Zr ₇₀ Ni ₃₀	645 ³⁴	1335	19.95	4.3 (0.15)	2.529	1.21 (0.11)
Zr ₇₀ Ni ₂₀ Al ₁₀	636 ³⁵	1205	20.06	4.5 (0.2)	2.517	1.41 (0.66)
Zr ₆₀ Ni ₂₅ Al ₁₅	705 ³⁵	1180	19.42	4.75 (0.2)	2.562	1.05 (0.09)
Zr ₈₀ Pt ₂₀	^b	1450	22.14	4.6 (0.1)	2.505	0.96 (0.06)
Zr ₇₅ Pt ₂₅	^c	1705	21.38	4.5 (0.1)	2.518	0.58 (0.07)
Zr ₇₀ Pd ₃₀	701 ³⁷	1350	20.73	5.0 (0.2)	2.520	1.22 (0.21)

^aEstimate from Ref. 24.

^bDoes not form amorphous alloys by rapid quenching.

^cForms amorphous alloy, but T_g is not detectable (Ref. 37).

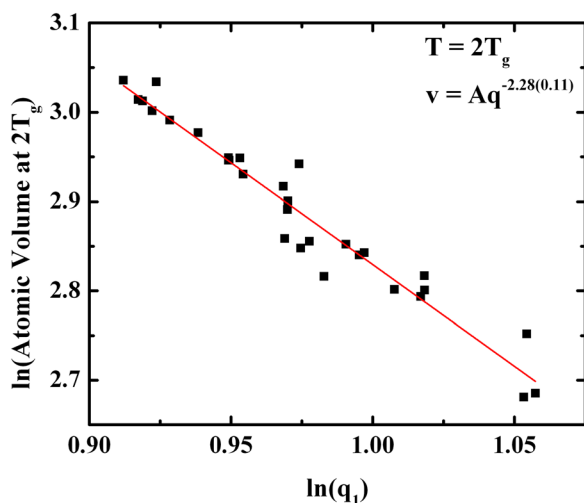


FIG. 3. A double logarithmic plot of atomic volume (v) and the position (q_1) of the first maximum in $S(q)$ at a temperature of $2T_g$ for all alloy liquids listed in Table I.

T_g and is similar to that in the glass. This is somewhat counter-intuitive. It is widely recognized that the short- and medium-range orders develop with decreasing temperature in supercooled liquids, especially near T_g . The development is more rapid for fragile liquids compared to stronger liquids close to T_g .¹⁷ The medium-range order is expected to be small at temperatures far above T_l . Considering, then, that bulk glass formers (usually stronger liquids) and more fragile marginal glass formers (binary Zr-Ni, Zr-Pt, Zr-Pd, etc.) are both included in this study, it is difficult to understand why all would show significant MRO at temperatures as high as $2.5 T_g$.

In summary, this study focused on the question of whether reliable linear thermal expansion data can be obtained from the measurements of temperature-dependent liquid structure factors, $S(q)$, from scattering experiments (x-ray, neutron, and electron). The temperature dependence of the volume and first peak position in $S(q)$ for a large number of equilibrium and supercooled alloy liquids were measured in a containerless environment. These data show that the

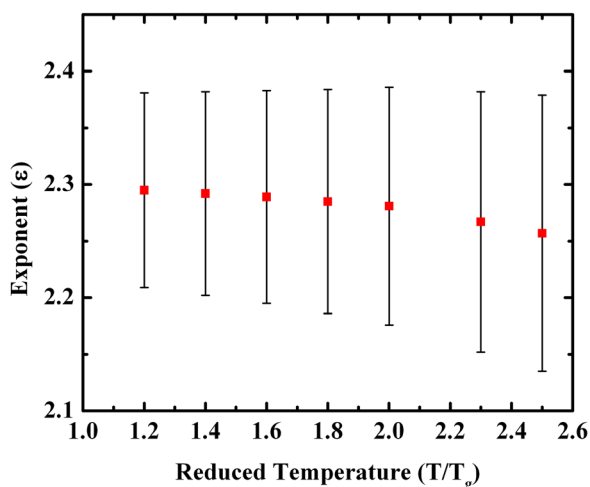


FIG. 4. Temperature dependence of the exponent ε in the relationship $v \propto (q_1)^{-\varepsilon}$ for all alloy liquids studied as a function of reduced temperatures, T/T_g .

exponent ε in the relationship, $v \propto (q_1)^{-\varepsilon}$, is much different from the expected value of 3 from Ehrenfest's relationship. Therefore, $S(q)$ data obtained from scattering experiments can only be used to estimate the thermal expansivity of liquids when the correct empirically determined exponent is used ($\varepsilon = 2.28 \pm 0.11$). Based on both the results reported here and from studies of glasses,⁸ it is difficult to understand the good agreement reported between α and β in earlier experiments for some glasses using a value of 3 for the exponent.^{3–6} It is relevant to add that the use of the first peak position in the pair distribution function, $g(r)$, in "real-space" is even less suitable for measurements of thermal expansion coefficients of liquids and glasses. A number of recent studies^{20–22} have shown that the first peak in $g(r)$ show anomalous contraction with increasing temperatures and the higher order peaks expand, but at rates much different from that expected from the volume expansion coefficient.²¹

The fundamental interpretation of the exponent, ε , is unclear, however. It has been suggested to be a measure of the fractal dimension of the medium-range order in glasses.⁸ Within that interpretation, the results presented here would argue that all of the liquids studied (both strong and fragile) have significant MRO at temperatures much higher than the liquidus temperature, and that the fractal dimension of this MRO is temperature independent. This is a very surprising conclusion and leads to a questioning of the interpretation argued for the glasses. It has also been suggested²³ that ε may be connected with the topological order in the glass and, therefore, different for different glasses. What this study provides is an average value for all alloy liquids investigated. To further investigate this point, studies of correlation between atomic volume and q_1 in the same liquid as a function of temperature from far above T_l down to T_g are necessary. Unfortunately, except for a few exceptionally good glass formers, much of this temperature range is experimentally inaccessible due to crystallization in the supercooled state. Obviously, more work is needed to find a correct interpretation of ε .

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