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Comment on "Thermal expansion measurements by X-ray scattering and breakdown of Ehrenfest's relation in alloy liquids" [Appl. Phys. Lett. 104, 191907 (2014)]

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Gangopadhyay et al.[1] recently reported for glass-forming liquid alloys on the relationship between the position of the first diffraction maximum q_1 in reciprocal space and the atomic volume v in real space. As mentioned in the abstract, for crystalline materials a direct relationship exists between diffraction peak positions q_{hkl} and lattice plane distances d_{hkl}, which is well known as Bragg's law: $q_{hkl} = 2\pi/d_{hkl}$. The so-called Ehrenfest equation derived 100 years ago for the diffraction intensity of a di-atomic gas[2] is valid only for that particular case of a molecule having only one interatomic distance d between atoms. The scattered intensity then is determined by the function sinx/x ($x = q_1*d$). The first maximum for $q > 0$ is at x = 1.23*2π and $q_1 = \frac{1.23°2\pi}{d}$. It is well known that Ehrenfest's equation cannot be used to calculate the exact distance (or atomic volume) of two scattering centers in a liquid or glass, because the assumption of the scattering occurring by independent pairs of atoms is not met. For multi-component alloys, the diffraction maximum of glasses and liquids is a sum of weighted partial functions, which may result in different values of q_1 for X-ray and neutron diffraction. The analysis of experimental data show indeed a general tendency $q_1 \sim 1/d$ (or $q_1{}^3 \sim 1/v$) for many liquids and glasses; however, the product q_1*d ($q_1{}^3*v$) for elemental liquids[3] exhibits a scatter of about ±5%, which is not only caused by experimental errors in densities and peak positions.

In the last 10 years, a modified Ehrenfest equation ($q_1^3 = \frac{const}{v}$) was used by several authors for calculation of thermal expansion coefficients of metallic glasses and liquids,[4–6] for the determination of free volume in metallic glasses[4,7] and even more, a fractal character of the atomic structure of metallic glasses was concluded[8] from the analysis of the exponent of q_1 versus v.

Gangopadhyay et al.[1] compared experimentally determined data of q_1 and v for different multicomponent liquids. By comparing the measured macroscopic volume expansion with the shift of q_1 upon heating, they show that is not possible to determine exact values of thermal expansion coefficients from the diffraction data. The reason (not discussed in the paper) is the change of local atomic arrangements of glasses and liquids with temperature, which has an additional influence on the diffraction maxima positions.[9] As a second conclusion, Gangopadhyay et al.[1] proposed a "simple relationship" between q_1 and v by a power law or $q_1^{2.28} \sim 1/v$, which is not justified if one notice the rather small q, v range, and the scatter of the data presented in a double-logarithmic scale (Fig. 3 of Ref. 1).

Figure 1(a) shows results of the fit the atomic volume of elemental liquids v according to power laws q^{-3} and $q^{-2.28}$

using the data reported by Waseda.[3] These data, represented by the diamonds, cover a much larger range in q_1 and v compared to those reported in Ref. 1 also presented in Figure 1(a) by the circles. The deviation between experimental data and fit is much smaller for the q^{-3} dependence. A similar analysis is shown in Figure 1(b) using the data, as given in Table I of Ref. 1. The "best" fit of the data results in an exponent of −2.48. However, the scatter is relatively large in the limited q-range as can be seen in Fig. 1(b). The error bar of ±0.11 for the exponent is obviously underestimated.

In summary, due to the lack of translation symmetry, there is no direct relationship between diffraction maxima and interatomic distances for glassy and liquid alloys. The use of Ehrenfest's equation for liquids and glasses delivers only approximated values. Different local arrangement in different liquid and glassy alloys may lead to different q_1-values even for identical atomic volume. Cheng and Ma[10] have shown that the exponent of an assumed power law becomes altered using different data sets of metallic glasses. Real space interpretation of q_1 overestimates the information
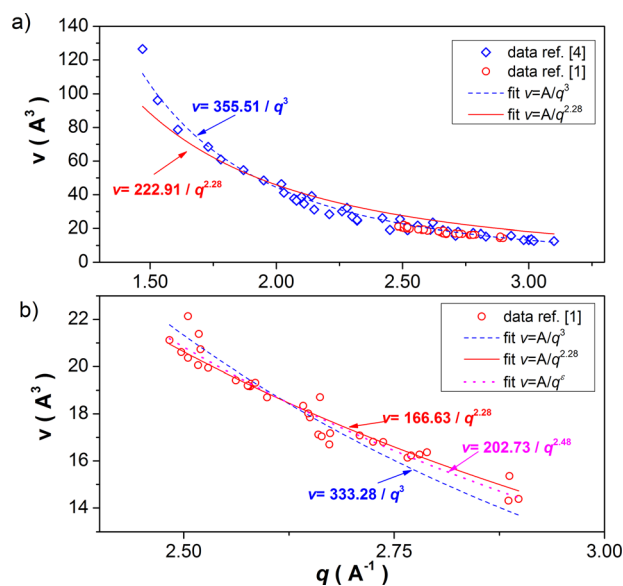

FIG. 1. Atomic volume v versus maximum position q_1. (a) Experimental data for elemental liquids[3] marked by (blue) diamonds. The lines are the results of the fit for different power laws. The data from Ref. 1 are shown by the (red) circles for comparison. (b) Experimental data according to Table I of Ref. 1. Lines are the results of fits according to power laws q^{-3} (dashed line) and $q^{-2.28}$ (solid line). The fit with variable exponent results in $\varepsilon = -2.48$ (dotted line).

content of one point in reciprocal space for liquids and underestimates or neglects systematic deviations related to the local structure. The average atomic volume follows roughly a power law $v \sim q^{-3}$. The thermal expansion coefficient as calculated from the shift of q_1 with temperature can vary up to a factor of three compared to those values of macroscopic volume measurements.[9,11] The calculation of free volume from the shift of q_1 as proposed in Ref. [5] is not possible. The exponent of the power law discussed in Refs. [1] and [8] has probably no physical meaning.

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