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Softening of phonon spectra in metallic glasses

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The vibrational spectra of a series of MgZnCa amorphous alloys were computed using density functional theory and implementing the small displacement method. The atomic structures of the alloys were obtained by *ab initio* molecular dynamics simulations. The vibrational thermodynamic properties were calculated as a function of temperature and, in particular, the specific heat at low temperature was approximated by temperature cubed based on the Debye model. We computed the contribution of Mg vibrations to the specific heat and investigated the softening of Mg phonon spectra, where the maximum allowed vibrational frequency is lowered and highly collective diffusion processes are promoted. The statistical correlation between the reported critical casting thickness of the alloys and softening of Mg phonons was obtained. Similar calculations were performed for two distinctively different amorphous ZrTiCuAl alloys with large and small reported critical casting thickness, respectively. The findings were consistent with those of the MgZnCa alloys.

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INTRODUCTION

There has been increasing attention devoted to the effect of vibrational thermodynamics on the formation of different alloy phases and their associated phase transformations due to the improved accessibility of instruments capable of measuring and calculating the phonon frequencies.¹ Various thermodynamic properties such as specific heat and vibrational entropy can be derived through the vibrational density of states (VDOSs). The VDOS obtained by molecular dynamics (MD) simulations has provided useful insight into how phonon spectra are affected by both the size and surface properties of silicon nanoparticles; this is of major significance in the design of nanodevices with better heat transport properties. It was found that, as the Si particles become smaller, the density of vibrational states increases at low frequencies, and modes are transferred from the high-frequency end to the intermediate range and transverse optical modes peak are shifted to higher frequencies.²

In metallic glasses, vibrational characteristics have also been used for explaining mechanical properties. For example, recent MD simulations of a Cu₆₄Zr₃₆ metallic glass showed that the strongest participation in the modes with lowest vibrational frequency and, hence, weakest spring constants (i.e., soft modes) originate predominantly from meagrely populated polyhedra. These soft spots provide fertile sites for accommodating shear transformations.³

The softening of long wavelength acoustic phonons in PdSiCu, ZrTiCuNiBe, CeAlNiCu and ZrNbCuNiBe amorphous alloys relative to their crystalline phases have been observed experimentally using ultrasound measurements.^{4–6} Such observations are consistent with the low-temperature measurements of their specific heat, whereby an increase in temperature causes a steeper increase in specific heat in the amorphous alloys compared with their crystalline counterparts.

Specific heat is believed to be a fundamental property of materials and, in particular, glass-forming alloys. In undercooled metallic alloy liquids, the change in specific heat with temperature

is experimentally⁷ and theoretically⁸ shown to correlate to the fragility of the liquid and glass-forming ability.

The VDOSs of amorphous systems obtained from atomistic simulations can be computed from the Fourier transform of the temporal autocorrelation of velocity,⁹ the linear response and small displacement methods. To calculate phonon spectra based on velocity autocorrelation by *ab initio* MD simulation methods may not be practical, as the simulation time is either impractically long to equilibrate the system at low temperatures or to achieve a frequency resolution.¹⁰

Although increasing attention has been devoted to the study of vibrational modes in amorphous systems, *ab initio* simulations have been lagging behind due to the complexity and resource-intensive nature of such calculations. In this work, density functional theory was used to implement the small displacement method for computing the phonon spectra of a series of MgZnCa amorphous alloys, of which the atomic configurations were also obtained by *ab initio* MD simulations. We have examined the effect of composition on the VDOS and calculated the vibrational thermodynamic properties, particularly the contribution of the various constituent atom species to the specific heat, as a function of temperature. To broaden our study, a distinctly different system of ZrTiCuAl amorphous alloys was chosen and the calculations were repeated.

RESULTS AND DISCUSSION

Figure 1 gives the total VDOS for two of the alloys investigated (Mg₆₈Zn₂₈Ca₄ and Mg₇₂Zn₂₄Ca₄); the critical casting thickness (Z_c , below which a fully amorphous structure is generated, Table 1) of these alloys are largest and smallest respectively. Further, the reduced VDOS, defined as $g(\omega)/\omega^2$ is depicted in the inset of Figure 1, where at low frequencies an enhancement in VDOS relative to the Debye squared-frequency law (the Boson Peak) is seen.¹¹

Figure 2 shows the partial VDOS for the constituent atom species of these alloys with the inset showing a blow up of the Mg

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partials. It is pertinent to note that for all alloys, the total and partial VDOS are asymmetric and positively skewed, where the distribution is concentrated on lower frequencies. However, specific heat is commonly used as an elaborate quantitative illustration of this shift to lower energies in the density of states.⁴

Further examination of partial VDOS indicates that the distribution of states depends markedly on atomic concentration. The peak of the partial VDOS is found to be inversely correlated to concentration of the respective species, as shown in Figure 3a,b for Mg and Zn, respectively. In addition, the area under the partial VDOS representing total available vibrational states per atom are shown as a function of Mg and Zn concentration in Figure 3c,d, respectively. It is seen that, as the concentration of each species increases, there is a decrease in the total available states. As such, Ca has the smallest concentration in each alloy, has the highest vibrational states per atom followed by Zn and Mg.

The temperature dependence of specific heat at low temperatures is of particular importance in the analysis of physical properties of solids, as it reveals ionic and electronic contributions to the thermal energy. Figure 4a illustrates the contribution of Mg to the specific heat of the $\text{Mg}_{72}\text{Zn}_{24}\text{Ca}_4$ and $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ alloys over the temperature range ~ 0 –30 K. According to the Debye approximation, the contribution of phonons to the specific heat is proportional to the cube of temperature (T) at low absolute temperatures¹² such that the specific heat can be expressed as $C_V \approx \beta T^3$, where $\beta = 12\pi^4 R / 5\theta_D^3$, and R and θ_D are the gas constant and Debye temperature, respectively.¹³ The Debye approximation

was suggested to evaluate analytically the specific heat based on the quantum theory of harmonic crystal and predicted the temperature cube law for C_V , which agreed very well with the observation at very low temperatures. The approximation was based on the fact that, at very low temperatures, the contribution to C_V of modes with $\hbar\omega \gg k_B T$ is negligible, whereas for acoustic modes with sufficiently long wavelength, the contribution to C_V is appreciable and the corresponding vibrations can be regarded as linearly dispersed.¹² At very low temperatures, not only are such simplifications valid for amorphous solids but also the measurements of specific heat of glassy solids agree well with the Debye temperature cube law.^{4,5,13}

The energy at θ_D is related to the Debye frequency ω_D by $k_B\theta_D = \hbar\omega_D$ and ω_D represents the maximum allowed vibrational frequency in the structure. Both θ_D and ω_D may also be regarded as a measure of the stiffness of a material,¹² as they are related to the curvature of the energy landscape at the local minimum of a basin (stiffness).¹⁴ Assuming that the contribution of electrons to the specific heat in an electrical conductor is proportional to T , then it can be shown that $C_V/T = \beta T^2 + \gamma$, where β and γ are the gradient and intercept of C_V/T as a function of T^2 . Table 1 provides β and γ as obtained from the contributions of Mg and Zn to the specific heat at low temperatures. The selected temperature range was in the range 5–20 K to avoid pronounced temperature dependence of β and hence θ_D . The values of β show that some alloys are softer than the others and further investigation of the calculated and experimentally measured properties reveals that there is a statistical correlation between β_{Mg} and the critical

Figure 1. Total VDOS of $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ and $\text{Mg}_{72}\text{Zn}_{24}\text{Ca}_4$ alloys. The inset shows the reduced VDOS of these two alloys.

Figure 2. Partial VDOS of $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ (solid line) and $\text{Mg}_{72}\text{Zn}_{24}\text{Ca}_4$ (broken-dotted line) alloys. The inset shows the contribution of Mg atoms to VDOS.

Table 1. Table of simulation data

Alloys	Mg					Zn					Z_c
	f_{mode}	VDOS_{max}	I	β	γ	f_{mode}	VDOS_{max}	I	β	γ	
$\text{Mg}_{72}\text{Zn}_{24}\text{Ca}_4$	1.92E+01	3.53E-04	6.94E-03	1.43E-05	7.060E-04	1.05E+01	1.82E-03	2.08E-02	5.68E-05	2.430E-03	1.1
$\text{Mg}_{70}\text{Zn}_{26}\text{Ca}_4$	2.38E+01	3.48E-04	7.14E-03	1.43E-05	8.394E-04	1.05E+01	1.61E-03	1.92E-02	5.86E-05	2.483E-03	2.8
$\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$	1.67E+01	3.78E-04	7.35E-03	1.66E-05	8.393E-04	8.48E+00	1.52E-03	1.79E-02	6.14E-05	4.034E-03	4.0
$\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$	2.30E+01	3.85E-04	7.58E-03	1.43E-05	9.887E-04	8.89E+00	1.36E-03	1.67E-02	5.70E-05	3.001E-03	3.5
$\text{Mg}_{64}\text{Zn}_{32}\text{Ca}_4$	2.25E+01	4.08E-04	7.81E-03	1.19E-05	1.297E-03	9.31E+00	1.45E-03	1.56E-02	5.18E-05	3.540E-03	0.7
$\text{Mg}_{70}\text{Zn}_{24}\text{Ca}_6$	2.01E+01	3.46E-04	7.14E-03	1.47E-05	6.165E-04	7.65E+00	1.80E-03	2.08E-02	5.76E-05	2.286E-03	3.0
$\text{Mg}_{68}\text{Zn}_{26}\text{Ca}_6$	2.30E+01	3.58E-04	7.35E-03	1.52E-05	8.411E-04	8.89E+00	1.74E-03	1.92E-02	5.55E-05	1.548E-03	3.3
$\text{Mg}_{66}\text{Zn}_{28}\text{Ca}_6$	2.21E+01	3.75E-04	7.58E-03	1.51E-05	1.423E-03	9.72E+00	1.64E-03	1.79E-02	6.00E-05	4.253E-03	2.8
$\text{Mg}_{64}\text{Zn}_{30}\text{Ca}_6$	2.34E+01	3.84E-04	7.81E-03	1.39E-05	1.193E-03	1.01E+01	1.46E-03	1.67E-02	5.50E-05	2.404E-03	2.7
$\text{Mg}_{62}\text{Zn}_{32}\text{Ca}_6$	2.38E+01	4.12E-04	8.06E-03	1.32E-05	6.733E-04	1.01E+01	1.26E-03	1.56E-02	5.27E-05	2.293E-03	1.5

Abbreviations: VDOS, vibrational density of state.

Units are meV for the frequency of maximum VDOS f_{mode} . Number/meV/atom for the maximum of partial vibrational density of states VDOS_{max} . Number/atom for the partial VDOS integral I . k_B/K^3 /atom for the gradient of C_V/T as a function of T^2 , β . k_B/K /atom for the intercept of C_V/T as a function of T^2 , γ . mm for critical casting thickness Z_c .

Figure 3. (a, b) Maximum number of partial vibrational states and (c, d) the integral of the partial VDOS per atom over all frequencies as a function of Mg and Zn concentration, respectively.

Figure 4. (a) Contribution of Mg vibrations to the specific heat for $\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$ and $\text{Mg}_{72}\text{Zn}_{24}\text{Ca}_4$ alloys. (b) β_{Mg} versus critical casting thickness (Z_c). The coefficient of determination for the linear fit is 0.68.

casting thickness (Z_c),¹⁵ as depicted in Figure 4b. In other words, as the temperature is raised, the contribution of Mg phonons to the specific heat tends to show a steeper increase in those alloys with greater Z_c . As β is inversely proportional to both θ_D and ω_D , a greater Z_c concurs with a lower Debye frequency of Mg atoms vibrating in the vicinity of a local minimum in a shallow megabasin of the energy landscape.

The energy landscape paradigm articulates that, for a material system comprising a certain number of particles in a given volume, the energy landscape is fixed, whereas the process by which the landscape is sampled depends on temperature.^{16,17} In the supercooled liquid at temperatures higher than the glass transition (T_g), configurational sampling of neighbouring megabasins occurs¹⁷ and megabasins with smaller curvature at their local minimum implying softened phonon spectra may notably promote a highly cooperative diffusion process where a large number of atoms (typically above 10 (ref. 18)) take part in a

collective hopping over energy barriers. The collective diffusion in supercooled liquids has been observed both experimentally¹⁹ and theoretically in MD simulations.²⁰ At lower temperatures, hopping over barriers in the energy landscape requires large atomic amplitudes that can be provided by localised soft vibrations.¹⁸ At higher temperatures, there is an increase in both the atomic displacements and the number of atoms participating in the jumps.²¹

It is pertinent to note that, although crystallisation is universally known to be a first-order thermodynamic transformation,^{22,23} glass transition has been prevalently considered as a largely dynamical phenomenon²⁴ and soft phonons are known to be related to the dynamics of amorphous alloys.^{18,25}

Although the energy landscape curvature and mean-squared atomic displacements (MSD) are two different quantities, they are inter-connected often in complicated relations. The calculated MSD of Mg atoms in the vicinity of glass transition temperature¹⁵

(400 K) for the alloys with the largest ($\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$) and smallest Z_c ($\text{Mg}_{64}\text{Zn}_{32}\text{Ca}_4$) are depicted in Figure 5. It is seen that the dynamic slows down for alloy the Z_c of which is larger. To minimise the fluctuations in the MSD plots and to provide a clearer perspective, the alloys have been categorised by their reported Z_c as small Z_c (with $Z_c \leq 2$ mm), medium (with $2 \text{ mm} < Z_c \leq 3 \text{ mm}$) and large Z_c (with $Z_c > 3 \text{ mm}$), respectively. The mean MSD of Mg for each group at 400 K has been calculated and provided in the inset to Figure 5. It is observed that the dynamic slowdown is most prominent for the category with large Z_c followed by alloys with medium and small Z_c . It should be noted that $\text{Mg}_{70}\text{Zn}_{26}\text{Ca}_4$ was excluded from the medium Z_c and considered as an outlier.

To broaden the variety of samples and strengthen the validity of the correlation, we have opted for a distinctively different family of alloys and applied the same method to compute the vibrational properties of amorphous $\text{Zr}_{61}\text{Ti}_2\text{Cu}_{25}\text{Al}_{12}$ and $\text{Zr}_{63.5}\text{Ti}_{4.5}\text{Cu}_{23}\text{Al}_9$ structures.

Figure 5. The mean-squared displacement (MSD) of Mg atoms in the vicinity of glass transition temperature with the largest ($\text{Mg}_{68}\text{Zn}_{28}\text{Ca}_4$) and smallest Z_c ($\text{Mg}_{64}\text{Zn}_{32}\text{Ca}_4$). The inset shows the averaged MSD of Mg for alloys with small, medium and large Z_c , respectively.

Figure 6. (a) Partial VDOS of $\text{Zr}_{61}\text{Ti}_2\text{Cu}_{25}\text{Al}_{12}$ (solid line) and $\text{Zr}_{63.5}\text{Ti}_{4.5}\text{Cu}_{23}\text{Al}_9$ (broken-dotted line) representing the contribution of Cu atoms to VDOS. (b) Contribution of Cu vibrations to the specific heat and (c) the mean mobility of atom species (broken-dotted lines are drawn as guides to the eye), as a function of temperature for $\text{Zr}_{61}\text{Ti}_2\text{Cu}_{25}\text{Al}_{12}$ and $\text{Zr}_{63.5}\text{Ti}_{4.5}\text{Cu}_{23}\text{Al}_9$ alloys, respectively.

The reported critical casting thickness for these alloys is 10 and 3 mm, respectively.^{26,27} The partial VDOS of these alloys representing Cu vibrational spectra are shown in Figure 6a. Figure 6b depicts the contribution of Cu vibrations to the specific heat of these Zr-based alloys as a function of temperature. Having fitted the linear regression line to C_v/T as a function of T^2 , we find β_{Cu} to be 0.02195 and 0.02063 $\text{k}_B/\text{K}^3/\text{atom}$ for $\text{Zr}_{61}\text{Ti}_2\text{Cu}_{25}\text{Al}_{12}$ and $\text{Zr}_{63.5}\text{Ti}_{4.5}\text{Cu}_{23}\text{Al}_9$, respectively. As for the contribution of Al vibrations to the specific heat, β_{Al} was computed to be 0.00606 and 0.00586 $\text{k}_B/\text{K}^3/\text{atom}$ for the former and the latter alloy, respectively. It is also seen that here a higher Z_c concurs with a greater β_{Cu} and β_{Al} . Indeed, the analysis of specific heat in MgZnCa amorphous alloys appears to be consistent to that of these widely dissimilar ZrTiCuAl metallic glasses. Although Cu concentration is less than half of Zr, the mobility of Cu was calculated and found to be the highest, as shown in Figure 6c.

MATERIALS AND METHODS

First-principles MD was used to simulate the melting and quenching processes of the alloys given in Table 1.²⁸ We considered 200 atoms in a cell with dimensions of the order of ~ 18 Å. The software of choice was VASP²⁹ implementing the projector augmented wave method to represent core electrons.³⁰ Generalised gradient functional was used to approximate the exchange and correlation energies.³¹ To sample the Brillouin zone, Γ point only was considered due to the large cell size. The systems were equilibrated well above the liquidus temperature and then quenched to room temperature with a cooling rate of 0.66×10^{13} K/s at 3,000 time steps per 100 K.³² The simulated pair distribution functions were found to be in close agreement with the results of high-energy X-ray scattering experiments.²⁸

To calculate the vibrational properties, the k-point sampling was increased to $2 \times 2 \times 2$, a full grid was adopted for Fourier transformation, the energy cut off was raised to 30% above the default values and the equilibrated configuration at room temperature was relaxed using the conjugate gradient method until the force on each atom was below 0.01 eV/Å and the total drift in forces were minimal. At this stage, the system is located at a local minimum and the energy can be regarded as the equilibrium potential energy. To find the Taylor expansion of the energy, the small displacement method was implemented³³ on the relaxed structure, displacing each configurational degree of freedom by 0.02 Å. Six hundred different configurations thus created were subject to static calculations based on density functional theory and the force field for each displacement was used to calculate the dynamical matrix and its eigenvalues, the square roots of which constitute the vibrational frequencies.¹ The total free energy of the system can be approximated

by the sum of the configurational energy of the relaxed structure and the total energy of the harmonic oscillators.³³ The latter is expressed as¹³ $F_{\text{harm}} = \int g(\omega) \langle n(T) \rangle d\omega$, where ω , T , $\langle n(T) \rangle$ and $g(\omega)$ are the vibrational frequency, temperature, Plank distribution and VDOS, respectively, which can be obtained from the square roots of the eigenvalues of the dynamical matrix. Once the vibrational free energy is known, the vibrational entropy and internal energy can also be calculated. In particular, the specific heat at constant volume can be obtained from $C_V = \partial F_{\text{harm}} / \partial T$.

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CONTRIBUTIONS

RM carried out the *ab initio* MD and density functional theory calculations for MgZnCa alloys. NH carried out the *ab initio* MD and density functional theory calculations for ZrTiCuAl alloys. KL designed the experimental programme and MF coordinated the overall project. All authors contributed to the interpretation of the results and to the writing of the paper.

COMPETING INTERESTS

The authors declare no conflict of interest.

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