Low-temperature acoustic properties and quasiharmonic analysis for Cu-based bulk metallic glasses

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Low-temperature elastic constant $C_{ij}(T)$ measurements for $Cu_{60}Zr_{30}Ti_{10}$ and $Cu_{60}Hf_{25}Ti_{15}$ bulk metallic glasses (BMGs) have been carried out to clarify their acoustic properties including a nonlinear interaction term. The BMGs show remarkably low shear to bulk modulus ratio C_{44}/B or equivalently high Poisson's ratio ν compared with the corresponding crystalline states. The $C_{ij}(T)$ behaviors are well described by Varshni's formula [Phys. Rev. B **2**, 3952 (1970)] and estimated Einstein temperatures suggested significant softening in the transverse-mode acoustic phonon. Mean Grüneisen parameters γ derived from dB/dT slopes become almost identical with those of crystalline Cu. Our theoretical analysis based on inhomogeneous microstructure model successively explains the elastic constants and characteristic features of the BMGs within a framework of quasiharmonic thermodynamics, suggesting that microstructural inhomogeneity plays a dominant role in the BMGs.

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I. INTRODUCTION

Elastic constants C_{ij} and their temperature behaviors are closely related to atomic configurations and potentials including anharmonic interaction terms.[1] The precise measurements on $C_{ij}(T)$ are therefore essential to understand the physical properties displayed in condensed matter. Bulk metallic glasses (BMGs) attract special interest because of their distinctive glass transition feature as well as superior mechanical properties,[2] although some of the underlying physics remain not clarified.[3,4] Recently, Johnson and co-workers reported a strong correlation between shear modulus and yield criteria and gave explanation by cooperative shear model.[5–7] Novikov and Sokolov reported a linear relation between bulk to shear modulus ratio and kinetic fragility m which is defined as an apparent activation energy for viscous flow.[8,9] While the presented experimental data show scattering, similar correlation between C_{ij} and viscosity has been suggested.[7,10–12] Also, correlations between fragility m and lattice vibration[13] and anharmonicity[14] have been reported. On the other hand, glass transition temperature T_g itself could be related to C_{ij} (Refs. 12 and 15) as it is summarized in a review article by Wang.[16] These reports clearly represent that $C_{ij}(T)$ of BMGs plays dominant role to solve the puzzling correlations and to clarify the underlying universal features in the new class of material.

Golding *et al.*[17] studied low-temperature elastic constants for a Pd-based metallic glass and revealed a remarkable softening in transverse-mode acoustic phonons. They pointed out that the softening is caused by the low density and static atomic displacement in the glassy structure. Similar elastic features have also been confirmed with Pd- and Zr-based BMGs.[18,19] Lambson *et al.*[20] and Wang *et al.*[21,22] studied the pressure-dependent elastic constants to determine zone-center-mode Grüneisen parameters γ_i and thermodynamic equation of state (EOS). Their studies suggest that simple density difference between the glassy and corresponding crystalline states fails to explain the marked softening within a framework of quasiharmonic thermodynamics. Wen *et al.* reported the changes in instantaneous bulk and shear moduli of Zr-based BMG due to structural relaxation and provided qualitative explanation from an energy landscape perspective.[23] Weaire *et al.*[24] preliminary performed computer simulation and suggested notable decrease in shear modulus. Cyrot-Lackman[25] reported essentially similar features using a tight-binding potential model. Franzblau and Tersoff[26] employed a network model and explained macroscopic elastic behaviors by incorporating zero-frequency vibration modes in the dynamical matrix. Pineda calculated Poisson's ratio for an ideal unicomponent metallic glass from radial distribution function and discussed the effect of microstructure on it.[27]

Previous experimental and theoretical studies show qualitative concurrence; metallic glasses have remarkably low shear modulus stemming from its unique random-packed structure, while descriptions on the origin are controversial and we are away from the general consensus. Recently, Ichitsubo *et al.*[28] proposed an inhomogeneous microstructure model which assumes two elastic domains (weakly and strongly bonded regions) in glassy structure and gives qualitative explanation for macroscopic elastic features and fragility. To fairly justify the model, quantitative verification is essential. In the present study, we investigate low-temperature elastic constants $C_{ij}(T)$ for Cu-based BMGs which consist only of metallic elements. From analysis of the $C_{ij}(T)$ behavior, we determined the acoustic Debye temperature Θ_D, zone-center-mode mean Grüneisen parameter γ, and the Einstein temperature Θ_E for the respective phonon modes. Based on the results, we demonstrate that the inhomogeneous microstructure model sufficiently explains the experimental results within a framework of quasiharmonic thermodynamics.

The construction of this paper is as follows. In the next section, we show details of BMG samples and an ultrasound spectroscopy technique which give us precise elastic constants and their temperature dependences. Experimental results including Θ_D, Θ_E, and γ are presented in Sec. III. In Sec. IV, we discuss about macroscopic elastic constants of the BMGs and show their possible interpretations using the inhomogeneous microstructure model. Some concluding remarks are presented in Sec. V.

II. EXPERIMENTAL PROCEDURE

A. Material

The materials used in this study are $Cu_{60}Zr_{30}Ti_{10}$ and $Cu_{60}Hf_{25}Ti_{15}$ BMGs prepared by injection molding technique.[29] These BMGs do not include any metalloid element such as phosphorous or boron so that metallic bonding should be dominant. T_g and crystallization temperature T_x are 697 and 716 K for CuZrTi and 724 and 761 K for CuHfTi determined by differential scanning calorimetry with a heating rate of 40 K/min. X-ray diffraction pattern showed typical amorphous feature; only a halo pattern has been confirmed. Specimens were mechanically sliced into a cylindrical shape with diameters of 3 or 2 mm. Mass densities were measured by the Archimedes method to be 7416 and 9460 kg/m^3 for CuZrTi and CuHfTi, respectively.

B. Ultrasound spectroscopy

Elastic constants of the BMGs are measured by electromagnetic acoustic resonance (EMAR).[30] A specimen is inserted into a solenoid coil and we mount them into a cryogenic chamber. A static magnetic field (0.2 T) is applied from outside of the chamber by pairs of permanent magnets. Then, driving burst current ($\sim$1 MHz, 80 μs) is fed to induce ultrasound vibration in the specimen through Lorentz-force mechanism. Free vibration resonance spectrum is successfully obtained by a frequency sweep of the input current. The EMAR measurements are carried out from 5 to 293 K for A_g and B_{3g} vibration modes. As shown by Demarest,[31] the stationary point of Lagrangian gives resonance frequencies (or eigenvalues) of an elastic medium. This variation is numerically solved using Rayleigh-Ritz method by approximating the displacements with Legendre polynomial functions.[32] A complete set of elastic constants C_{ij} is then obtained by minimizing the resonance-frequency differences obtained by experiment and calculation. Note that elastic constant inaccuracy is approximately 1%.

III. EXPERIMENTAL RESULTS

A. Elastic constants

Figure 1 shows A_g-group resonance spectra of the CuZrTi BMG obtained at (a) 298 K and (b) 5 K. Here, vibration modes are unambiguously identified by measuring the displacement distribution using a laser Doppler interferometer.[33] Both spectra show clear resonance peaks suggesting that the BMG has a low internal friction in this frequency range. Frequency shifts between the spectra indicate the increase in elastic constants with the decrease in temperature since C_{ij} are proportional to the second power of resonance frequencies. Similar features have been found in the CuHfTi BMG.

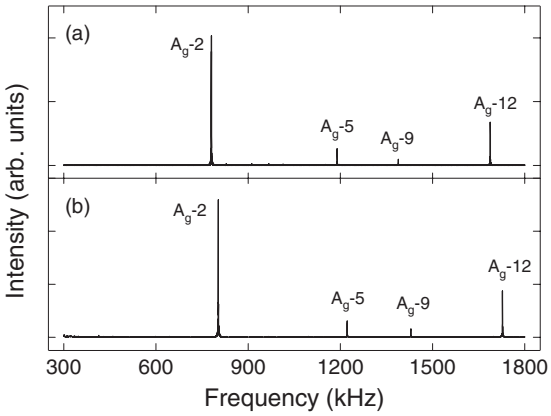

FIG. 1. A_g-group free vibration resonance spectra of CuZrTi BMG obtained at (a) 298 K and (b) 5 K. Indices in the figure represent the free resonance vibration modes identified by measuring displacement distributions using a laser Doppler interferometer.

Figure 2 shows temperature dependence of normalized elastic constants for (a) CuZrTi and (b) CuHfTi BMGs. For

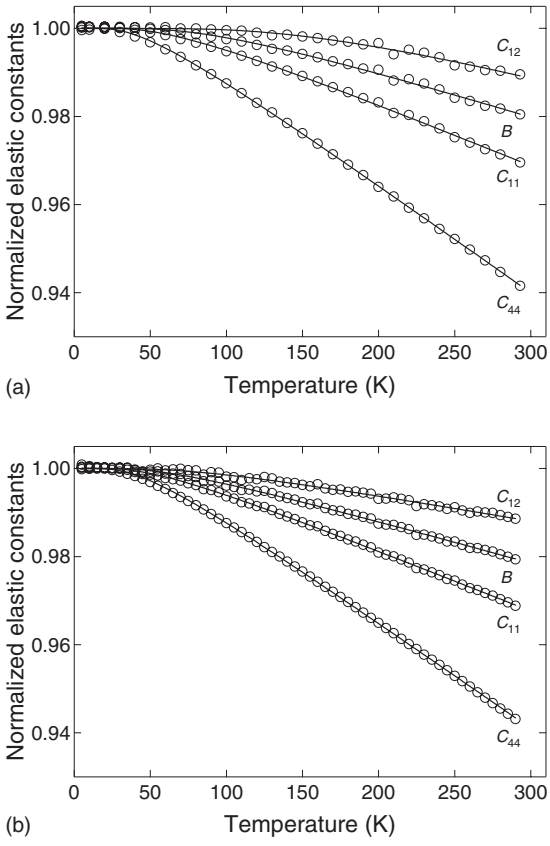

FIG. 2. Temperature dependence of elastic constants of (a) CuZrTi and (b) CuHfTi BMGs obtained by EMAR. Open circles represent measurement points normalized by those of extrapolated 0 K values. The solid lines represent least-squares fit by Eq. (1).

TABLE I. Elastic constants C_{ij} (GPa), bulk modulus B (GPa), Poisson's ratio ν, and acoustic Debye temperature Θ_D (K) of BMGs (g-CuZrTi and g-CuHfTi) and corresponding crystalline states (c-CuZrTi and c-CuHfTi). Note that the relation $C_{12}=C_{11}-2C_{44}$ holds for the all materials.

Material	T (K)	C_{11}	C_{12}	C_{44}	B	ν	C_{44}/B	Θ_D
g-CuZrTi	4.5	179.0	103.3	37.80	128.5	0.366	0.294	302.3
g-CuZrTi	298	169.7	102.1	33.80	124.6	0.376	0.271	(285.7)
c-CuZrTi	298	190.7	95.55	47.59	127.3	0.334	0.374	(336.3)
g-CuHfTi	5	182.3	102.8	39.78	129.3	0.361	0.308	274.0
g-CuHfTi	298	177.5	102.7	37.38	127.6	0.367	0.293	(265.9)
c-CuHfTi	298	195.3	99.35	47.96	131.3	0.337	0.365	(298.5)

both BMGs, shear modulus C_{44} showed the largest temperature dependence of approximately 6%, while those of B and C_{11} are only 2% or 3%. Table I summarizes elastic constants and acoustic Debye temperature Θ_D of the BMGs at ambient and low temperatures. For comparison, we included elastic constants of the corresponding crystallized alloys obtained by heat treatment over their crystallization temperatures. The BMGs clearly show the unusually low C_{44}/B ratio or equivalently high Poisson's ratio ν. These tendencies also hold at low temperature so that the low C_{44}/B ratio is originated from intrinsic amorphous structure. We note here that thermodynamics constrains Poisson's ratio ν from -1 to 0.5. Here, the upper limit represents an instability criterion of solid (Born instability). Thus, high Poisson's ratio represents that the BMGs keep liquidlike elastic properties even in a deep glassy state $T \ll T_g$.

B. Einstein temperature and Grüneisen parameter

In addition to low-temperature elastic constants, we also estimate the Einstein temperatures for respective phonon modes. According to Leibfried and Ludwig,[34] elastic constants satisfy the following relation: $C_{ij}=C(1-DE)$. Here, C and D are the constants and E represents an average energy of a harmonic oscillator. From the Einstein-type Helmholtz free energy F and thermodynamic relation $E=F-T(\partial F/\partial T)_V$, temperature dependence of elastic constants $C_{ij}(T)$ can be expressed in the following form:

$$C_{ij} = C_{ij}(0) - s/(e^{\Theta_E/T} - 1). \quad (1)$$

This is known as Varshni's equation.[35,36] Here, s is an adjustable parameter representing anharmonicity and Θ_E can be interpreted as the Einstein temperature. $C_{ij}(0)$ is zero-temperature elastic constant including harmonic and zero-point vibration terms. Note that Θ_E is different from its thermodynamic definition $(0.75\Theta_D)$ due to the electronic contributions to $C_{ij}(T)$ and irregularities in phonon density of state as suggested by Ledbetter.[36] However, the parameter includes significant physical importance as seen in the next paragraph. Adopting Eq. (1) to $C_{ij}(T)$ results, we can estimate Θ_E for respective phonon modes. Solid lines in Figs. 2 show least-squares-fitting results by Eq. (1) and obtained parameters for C_{11} and C_{44} are summarized in Table II. For comparison, parameters of quasi-isotropic elastic constants[37] of crystalline Cu are also included. The present BMGs showed notably small Θ_E of C_{44} compared with C_{11}. This intriguing feature of the BMGs is readily understood when comparing to the case of crystalline Cu (Table II; two Einstein temperatures have similar values). Note that this tendency does not change whether we carry out quasi-isotropic approximation or not.

Figure 3(a) shows temperature dependence of the second derivative of the elastic constants (d^2C_{ij}/dT^2) for the CuHfTi BMG calculated from Varshni's equation. As seen in the figure, all elastic constants show a continuous asymmetric peak between 20 and 60 K. As is well known, the elastic constants are almost unchanged when temperature approaches 0 K (this is due to the zero-point vibration effect), whereas they decrease linearly at the high-temperature side due to anharmonicity. These features make the second derivative, d^2C_{ij}/dT^2, virtually zero both at low- and high-temperature limits. Thus, the peak temperature T_P in Fig. 3(a) represents the starting temperature of elastic softening upon heating. Figure 3(b) plots the T_P and the Θ_E for the BMGs and crystalline Cu obtained from Varshni's equation. As is expected, they are correlated in a linear relation. Thus, the Einstein temperature determined by this method represents the peak temperature (starting temperature of elastic softening) in Fig. 3(a); $\Theta_E=4.5T_P$. Generally, the elastic softening temperature depends on phonon frequency and it becomes small if low frequency modes are dominant in the phonon density of state. Thus, the low Θ_E for C_{44} can be readily understood as the softening in transverse-mode acoustic phonon in the BMGs.

TABLE II. Fitting parameters of Eq. (1) obtained from elastic constants C_{11} and C_{44} of the BMGs (g-CuZrTi and g-CuHfTi) and crystalline Cu ($c-$Cu) after the *VRH* quasi-isotropic approximation.

		$C_{ij}(0)$	s	Θ_E
g-CuZrTi	C_{11}	179.0	4.70	183.0
	C_{44}	37.8	1.15	122.9
g-CuHfTi	C_{11}	181.3	3.72	147.3
	C_{44}	39.6	1.18	122.6
c-Cu	C_{11}^{VRH}	210.5	9.09	190.4
	C_{44}^{VRH}	51.4	3.76	196.5

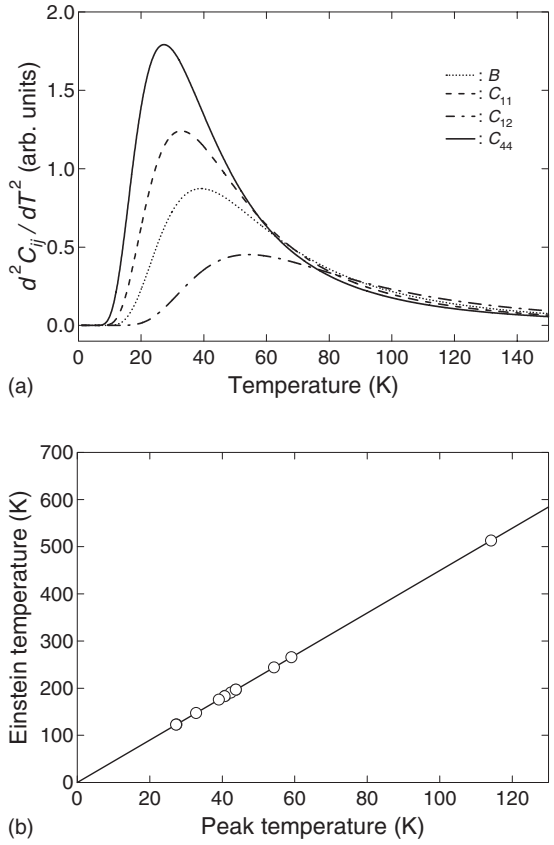

FIG. 3. (a) Temperature dependence of d^2C_{ij}/dT^2 for CuHfTi BMG calculated from Varshni's equation. Note that the data are normalized by $-s$. (b) A relationship between peak temperatures T_P and Einstein temperatures Θ_E for the BMGs and crystalline Cu.

We also evaluate zone-center-mode mean Grüneisen parameters from the $C_{ij}(T)$ results. At high-temperature limit, Ledbetter[38,36] derived the following relation between temperature derivative of bulk modulus and Grüneisen parameter γ:

$$dB/dT = -3k_B\gamma(\gamma+1)/V_a, \tag{2}$$

where k_B and V_a are the Boltzmann constant and the mean atomic volume, respectively. From the analysis, γ becomes 1.76 for CuZrTi and 1.70 for CuHfTi BMGs. These values are slightly smaller than that of crystalline Cu (2.0),[39] Pd-based BMG (2.59),[20] and Zr-based BMGs (2.0),[21] while they are almost usual in metallic systems.[39]

IV. MODEL CALCULATION

A. Inhomogeneous microstructure model

In the previous section, we showed that the Cu-based BMGs have low C_{44}/B ratio (or high ν), low Einstein temperature for transverse phonons, and usual Grüneisen parameter. The question to be solved here is how to understand these elastic and vibrational properties quantitatively. Density is one of the most essential parameters affecting the elastic and vibrational properties of solid since molar volume directly influences the phonon frequencies through anharmonicity. After crystallization, mass densities of the CuZrTi and the CuHfTi BMGs become 7614 and 9733 kg/m^3. Thus, the estimated volume change from crystallized to glassy material becomes almost identical in these two systems; 2.67% and 2.89% for CuZrTi and CuHfTi, and 2.78% in average. Within a framework of quasiharmonic thermodynamics, elastic features of the BMGs should be explained with the volume dilatation.

Inhomogeneous microstructure model[28] is based on the assumption that metallic glass consists of two elastic domains possessing different binding natures; strongly bonded regions (SBRs) are surrounded by a weakly bonded region (WBR) matrix.[40] Let us express the molar volume of BMG, equilibrium crystalline alloy, SBRs, and WBR by V_G, V_0, V_S, and V_W. Now, we have the following relation:

$$f_S V_S + f_W V_W = V_G, \tag{3}$$

where f_S and f_W represent volume fractions of SBRs and WBR; $f_S+f_W=1$. SBRs can be characterized as the region in which local density is close to crystalline state ($V_0=V_S$) such as short or medium range order (SRO or MRO) in glass. With the assumption, the mass conservation law constrains the f_S and f_W as

$$f_S = \frac{V_W/V_0 - V_G/V_0}{V_W/V_0 - 1}, \quad f_W = \frac{V_G/V_0 - 1}{V_W/V_0 - 1}, \tag{4}$$

where we used $V_G/V_0=1.0278$ which is determined from density difference between BMGs and corresponding crystallized alloys. Thus, the normalized molar volume V_W/V_0 of the WBRs uniquely determines volume fractions of the two elastic domains. Relationship between f_W and V_W/V_0 is shown in Fig. 4(a). Note that $f_W \to 1$ ($V_W/V_0=1.0278$) limit gives a homogeneous volume dilatation of the model.

Let us express the elastic constants of SBR and WBR in matrix notations by $\mathbf{C}_S$ and $\mathbf{C}_W$. As seen in the next section, molar volume influences the elastic constants through anharmonicity. Since V_S has been assumed to be V_0, only $\mathbf{C}_W$ depends on V_W/V_0 ($\mathbf{C}_S$ is constant). According to mean field micromechanics, macroscopic elastic constants of the inhomogeneous microstructure model $\bar{\mathbf{C}}$ become,[41–43]

$$\bar{\mathbf{C}} = [f_W\mathbf{C}_W + f_S\mathbf{C}_S\mathbf{A}][f_W\mathbf{I} + f_S\mathbf{A}]^{-1}, \tag{5}$$

where $\mathbf{I}$ denotes the unit matrix and $\mathbf{A}$ is strain intensity factor defined by

$$\mathbf{A} = [\mathbf{S}\mathbf{C}_W^{-1}(\mathbf{C}_S - \mathbf{C}_W) + \mathbf{I}]^{-1}. \tag{6}$$

In the equation, $\mathbf{S}$ is called the Eshelby tensor depending on $\mathbf{C}_W$ and the shape of the SBRs. To simplify the analysis, we assumed a spherical shape which is embedded in the WBR matrix.

B. Quasiharmonic thermodynamics

According to previous work by Tallon,[44,45] there are power-law relationships between C_{ij} and normalized molar volume of the system V/V_0,

$$C_{ij}(V) = C_{ij}^0(V/V_0)^{-g_{C_{ij}}}, \tag{7}$$

where

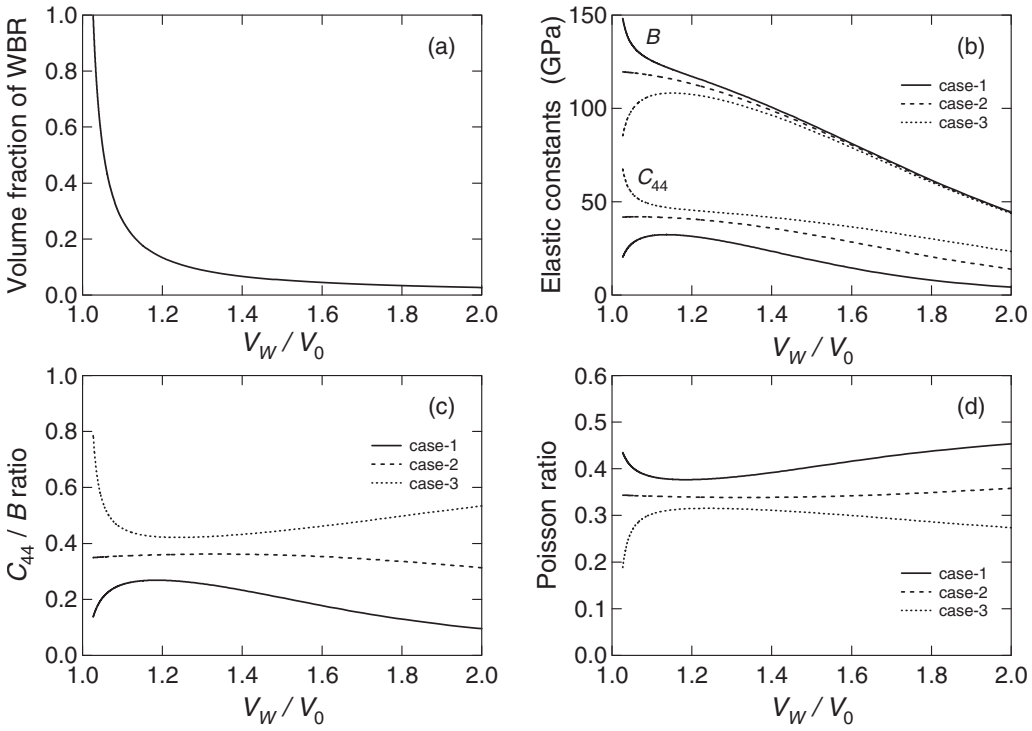

FIG. 4. (a) A relationship between the volume fraction of WBR and normalized molar volume of the region V_W/V_0. The limit $V_W/V_0 \rightarrow 1.0278$ represents the uniform volume dilatation of the model. (b)–(d) plot macroscopic elastic constants of the inhomogeneous microstructure model for three cases of shear moduli as a function of V_W/V_0. Elastic constants of BMGs obtained at 298 K show reasonable agreement with the case 1 results at $V_W/V_0 \approx 1.1$.

$$g_{C_{ij}} = (\partial \ln C_{ij}/\partial \ln V)_P. \tag{8}$$

This formulation is essentially equivalent to the quasiharmonic thermodynamics, namely, integration of Eq. (7) yields the well known Murnaghan EOS[46] and $g_{C_{ij}}$ is analogous to the acoustic Grüneisen parameter. Table III summarizes the experimentally determined parameters for crystalline Cu obtained at ambient temperature.[44] C' and C_{44} represent {110} ⟨110⟩-type and {100} ⟨100⟩-type shear resistance representing the lower and upper limits of shear modulus allowed in Cu. The superscript *VRH* stands for quasi-isotropic elastic constants obtained by the Voigt-Reuss-Hill approximation.[37] From Table III and Eqs. (7) and (8), one can uniquely determine elastic constants of Cu as a function of its molar volume.

Let us combine the quasiharmonic theory with our inhomogeneous microstructure model to examine whether the model supports present experimental results obtained at 298 K or not. In the BMGs, Cu is the major constitutive element and its parameters in the quasiharmonic theory are well defined (see Table III). In a first approximation, we employed these parameters to calculate elastic constants of the model. As mentioned, SBRs express the locally ordered structures in a BMG (SRO and/or MRO). Thus, we use the C_{ij}^{VRH} of crystalline Cu for the elastic constants of this region $\mathbf{C}_S$. This treatment would be valid because the C_{ij}^{VRH} are very close to those of the corresponding crystalline states (see Tables I and III). Namely, elastic constants of fully crystallized state of the model ($V_G \rightarrow V_0$) agree with the experimental results. On the other hand, microstructure of the WBR and its molar volume V_W have not been clarified, and so we fail to define the elastic constants of this region unambiguously. To avoid the loss of generality in the present analysis, we examined the three cases of shear moduli, C' (case 1), C_{44}^{VRH} (case 2), and C_{44} (case 3), for C_W, in which longitudinal modulus has been fixed to C_{11}^{VRH}. In the absence of volume dilatation, Poisson's ratios of the three cases become 0.43, 0.34, and 0.18. Thus, the three models present how the macroscopic elastic constants $\bar{\mathbf{C}}$ will be affected if the WBR changes its binding nature from a liquid like (case 1) into a solidlike (case 3) one.

TABLE III. Room temperature elastic constants C_{ij} of crystalline Cu and their anharmonicity $g_{C_{ij}}$ reported by Tallon. (Ref. 44) The superscript *VRH* represents the quasi-isotropic approximation by the Voigt-Reuss-Hill scheme.

	C_{11}	C_{44}	C_{12}	C'	C_{11}^{VRH}	C_{44}^{VRH}
C_{ij}^0	176.2	81.77	124.94	25.63	210.6	51.45
$g_{C_{ij}}$	6.945	7.17	6.327	8.97	6.945	7.845

V. RESULTS AND DISCUSSION

By inserting $\mathbf{C}_S$ and $\mathbf{C}_W(V_W/V_0)$ into Eqs. (5) and (6), we obtain macroscopic elastic constants of the inhomogeneous microstructure model as a function of V_W/V_0. From quanti-

tative comparison between the experimental and the theoretical elastic constants, we can justify the present inhomogeneous microstructure model without ambiguity. Figures 4(b)–4(d) plot macroscopic bulk modulus B, shear modulus C_{44}, shear to bulk modulus ratio C_{44}/B, and Poisson's ratio ν of the model as a function of V_W/V_0. In these figures, three curves represent the three cases of WBR (cases 1–3). The calculated elastic constants show rather insensitive V_W/V_0 dependences; C_{44}, C_{44}/B, and ν of the experimental results fall between the theoretical limits in a wide range of V_W/V_0. On the other hand, bulk modulus B for case 1 is across the experimental results around $V_W/V_0 \approx 1.1$. At this point, C_{44}, C_{44}/B, and ν show excellent agreement with the case 1 results consistently. Note that the present EMAR measurements provide sufficiently accurate elastic constants so that the measurement errors hardly affect the V_W/V_0 value. In addition, this normalized molar volume is reasonable because it does not exceed the topological instability limit ($V/V_0=1.128$) addressed by Egami.[47] Furthermore, the present analysis does not include ambiguous parameters to fit the experimental results except for V_W/V_0. Thus, full agreement of elastic constants at the same V_W/V_0 value makes the present model creditable within the quasiharmonic theory.

Let us discuss how characteristic features of the BMGs are explained from the model. (i) In Fig. 4(a), $V_W/V_0 \approx 1.1$ yields the volume fraction of WBR $f_W \approx 20\%$ which is almost consistent with the percolation threshold concentration.[48] (ii) The bulk moduli of WBR and SBR become 93.7 and 142.0 GPa, giving their ratio as 2/3. Generally, bulk modulus is proportional to the melting point T_m; the WBR behaves like a liquid phase around $2/3T_m$. The feature and results in (i) support the empirical relationship between T_g and T_m: $T_g \approx 2/3T_m$. Namely, WBR percolates through the system and macroscopic flow takes place when temperature approaches T_g. (iii) This microscopic perspective for glass transition qualitatively agrees with the free volume model.[49] (iv) Poisson's ratio of WBR becomes ~ 0.44 which is close to the upper limit of thermodynamics ($\nu = 0.5$), suggesting that the WBR has liquidlike behavior. This nature and the relatively large volume fraction of WBR ($f_W \approx 20\%$) would decrease transverse phonon frequency and account for the low Einstein temperature in C_{44}. (v) The present analysis employed the $g_{C_{ij}}$ reported for crystalline Cu so that the Grüneisen parameter of the BMGs should be comparable with it. This tendency has been confirmed from the present results as shown in Sec. III B. (vi) The present BMGs are in as-quenched states so that the volume fraction of WBR ($f_W \approx 20\%$) would provide an upper limit for the systems. Generally, structural relaxation by heat treatment increases macroscopic density and enhances the elastic stiffening due to the annihilation of free volume. However, glass transition temperature T_g is almost unchanged by the relaxation. According to the present model, the decrease in volume fraction of WBR readily explains this feature; a simple decrease in f_W gives an increase in density and macroscopic elastic constants with keeping its elastic constants and estimated melting point. (vii) The present analysis gives full agreement of experimental elastic constants for case 1 (C'-type shear modulus), while disagreements become significant if we apply a solidlike elastic constants for WBR (case 3). In the actual BMGs, variety of shear bonding would exist depending on its local structure. Among them, the present study suggests that the C'-type bonded regions act as the WBR. Generally, the C' shear modulus in fcc crystals is known to be unstable around their melting points.[50] The microscopic perspective on melting is therefore close to the present interpretation of glass transition.

Wang and co-workers[12,16] proposed an empirical relation between elastic constants of BMGs M with that of constitutive elements for Ce-based and Nd-based BMGs, $M^{-1} = \Sigma f_i M_i^{-1}$, where M_i and f_i denote elastic constants and atomic fraction of element i. Using the equation, we calculated C_{44}/B ratio for the present BMGs. However, disagreement reaches 38%. Recently, Zhang and Greer[51] proposed similar equations which consider atomic volumes in a glassy solid. The model provides a modified result, while inconsistency is still significant (about 33%). Thus, a simple density difference model fails to explain elastic constants of the present BMGs. The modification is, however, quite suggestive, namely, density difference between glass and corresponding crystals should be considered. The present inhomogeneous microstructure model deals it with a different way; density is nonuniform in a glass structure. As a result, notably low density in WBR ($V_W/V_0 \sim 1.1$) is acceptable with keeping the macroscopic density difference to only 2.78%. This extension also permits us to examine the three types of shear resistance (cases 1–3) where all of them are allowed in the actual crystalline Cu. Anharmonicities of elastic constants have also been included within a framework of the quasiharmonic thermodynamics. In the present model, disagreement of C_{44}/B ratio at $V_W/V_0=1.1$ ($f_W \approx 20\%$) becomes only -6% for CuZrTi BMG and that of CuHfTi is also fair (-13%). Since the present analysis does not include any ambiguous parameters, full agreement of elastic constants and reasonable interpretations of (i)–(vii) support the microstructural inhomogeneity in the present BMGs.

VI. CONCLUSION

In summary, we have studied temperature dependence of elastic constants $C_{ij}(T)$, vibrational properties Θ_D and Θ_E, and anharmonicity γ of Cu-based BMGs using electromagnetic acoustic resonance in deep glassy state at $T \ll T_g$. The BMGs showed low C_{44}/B ratio or equivalently high ν at ambient and low temperatures due to their intrinsic amorphous structures. Analysis for $C_{ij}(T)$ based on the Einstein-type oscillator model suggests that low frequency modes are dominant in transverse acoustic phonons. On the other hand, Grüneisen parameters become almost identical with that of crystalline Cu. Using mean field micromechanics, we demonstrated that inhomogeneous microstructure model successively explains the elastic constants as well as characteristic features of the BMGs within a framework of the quasiharmonic thermodynamics. These results suggest that microstructural inhomogeneity will play dominant role to illuminate the underlying physics that remain unsolved in BMGs.

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