Einstein oscillator in highly-random-packed bulk metallic glass

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Metallic glasses have often been regarded as ideal model systems of dense random packing with strong interaction among their components. Here we report direct evidence for the presence of the Einstein oscillator with an Einstein temperature θ_E of 74 K, which induces the boson peak at 4.9 meV in bulk metallic glass $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$. The presence of an Einstein oscillator suggests the existence of the vibrations of loose atoms in an independent localized harmonic mode in the highly random packed metallic glasses. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1849420]

Localized harmonic vibrational modes (Einstein oscillators) are uncommon in solids because of strong interatomic coupling. In metallic alloys, localized modes are exceedingly rare due to the close-packed microstructure. Filled skutterudite antimonides,[1,2] $Al_{10}V$,[3] LaB_6[4] intermetallic compounds and some metallic nanocrystalline materials[5] are observed to have the Einstein oscillators using specific heat, electric resistance, and inelastic neutron scattering measurements. In metallic compounds with the oversized cage structure or large voids or enough large free volume, some atoms or metallic ions are weakly bound and occupy the oversized cages or voids, and the vibrations of these loose "rattler" atoms are regarded to result in the independent localized harmonic modes that are important for understanding the unique physical properties of these materials.[1]

The low-energy vibrational spectra of many glasses deviate in a characteristic way from Debye's plane-wave density of states, the excess modes being designated as the "boson peak," which is observed mainly in nonmetallic glasses such as polymeric and ceramic glasses.[6–8] Recently, Meyer *et al.*[9,10] reported a pronounced boson peak in the vibrational spectra measured by the coherent neutron scattering for some metallic glasses, and the peak position shows no dispersion in wave numbers q, while intensities are strongly correlated with the static structure factor, indicating that the boson peak is related to the intrinsic properties of the metallic glasses. However, so far, no complete account is available for the origin of the excess vibrational density of states (VDOS) found in glasses with respect to the Debye behavior of the corresponding crystals. Various interpretations have been offered for the origin of the boson peak.[11–14] The question of whether these features are rooted in some specificity of the static structural disorder is highly debated, and no clear picture relating the glassy structure to the dynamics has been accepted. Therefore, it will be interesting to find how widespread such findings might turn out to be in the metallic glasses, and what sort of modes are involved in the boson peak.[15]

In this letter, we report the observation of the Einstein oscillator in a bulk metallic glass (BMG) $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (vit4) by measuring the specific heat at low temperatures. The VDOS, derived from the specific heat, shows that vit4 has an excess peak that corresponds to the boson peak observed by inelastic neutron scattering. Our results provide direct experimental evidence in BMG for the presence of an Einstein oscillator that induces the boson peak.

Vit4 was chosen as a model system because it is a representative and extensively studied BMG with excellent glass-forming ability and a highly random packed microstructure.[16–18] The BMG specimen was prepared by melting the pure elements and then produced by suction casting the melt into a copper mold under a pure argon atmosphere; the details of the synthesis were described in Refs. 17 and 18. The specific heat measurement of the sample with mass of 22.23 mg was carried out with the heat capacity option of a commercial Physical Properties Measurement System (Quantum Design Inc.). The relative error of the specific heat measurement is less than 2%.

The measured specific heat C_p of vit4 from 2 to 52 K is shown as C_p/T^3 vs T in Fig. 1(a). The Fig. 1(b) presents C_p/T vs T^2 plot in the temperature range of 2–15 K. In the temperature range $27 < T^2 < 227$ K^2, the data are well fitted in a polynomial form $C_p/T = \gamma + \beta T^2$ with $\gamma = 2.85$ mJ mol^{-1} K^{-2} and $\beta = 111.5$ μJ mol^{-1} K^{-4}, and just like other BMGs,[19] in the lower temperature range $4 < T^2 < 19$ K^2, the data are deviated from the linear behavior and also well fitted in the same polynomial form with $\gamma = 3.86$ mJ mol^{-1} K^{-2} and $\beta = 69.2$ μJ mol^{-1} K^{-4}. The deviation in the BMG could be ascribed to the glassy-state effect.[19] Usually the soft potential model[20,21] is used to explain the specific heat of glasses above 2 K. But from the results in Figs. 1(a) and 1(b), we see that there is no obvious hump in the C_p/T^3 vs T plot[20] and that the specific heat in the wide low-temperature range can be well fitted by $C_p/T = \gamma + \beta T^2$ without higher powers of T.[21] So the soft potential model fails to explain the result. By the Debye model $C_D = n_D \cdot 3R(T/\theta_D)^3 \int_0^{\theta_D/T} \xi^4 e^{\xi}/(e^{\xi}-1)^2 d\xi$, where θ_D is Debye temperature, n_D is a constant and stands for the Debye oscillator strength per mole and R is the gas constant. When the electrons' contribution to the specific heat γT ($\gamma = 2.85$ mJ mol^{-1} K^{-2}) is subtracted, the specific heat in the temperature ranges from 2 to 10 K and 35 to 52 K is least-squares fitted with $\theta_D = 240$ K and $n_D = 1.87$ [see Fig. 1(c)]. The low-temperature specific heat data around 20 K are larger than the fitted result. So the Debye model, applied in

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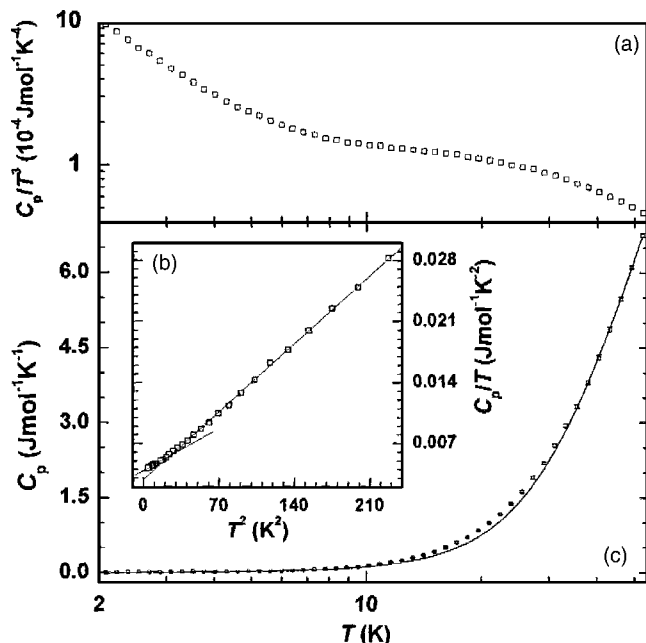a)Author to whom correspondence should be addressed; electronic mail: whw@aphy.iphy.ac.cn

FIG. 1. The specific heat C_p of vit4 in the temperature range from 2 to 52 K. (a) Specific heat plotted as C_p/T^3 vs T. (b) The specific heat, shown as C_p/T vs T^2. The solid lines are the results of the fitting specific heat between 2 and 15 K using the expression: $C_p/T = \gamma + \beta T^2$. (c) The specific heat is least-squares fitted by the Debye model.

the simplest way, cannot quantitatively explain the experimental results enough.

We find that an addition of the quantized Einstein oscillator is required to model the specific heat of the BMG. As illustrated in Fig. 2, a model calculation including the contributions of one Debye mode and one Einstein mode leads to an adequate description of the experimental data. The solid line through the specific heat data in Fig. 2 represents a fit to the equation

$$C_p = \gamma T + C_D + n_E \cdot C_E, \qquad (1)$$

where γT, shown in Fig. 2 by the dash-dotted line, is the contribution of electrons ($\gamma = 2.85$ mJ mol^{-1} K^{-2}); C_D, shown in the dashed line, represents contribution of the Debye
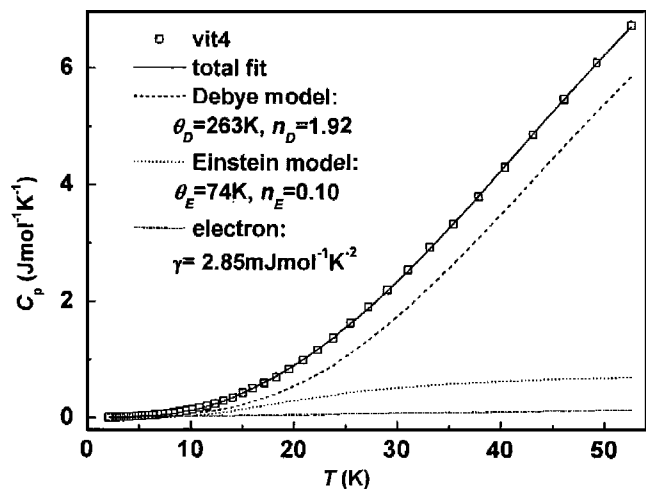

FIG. 2. The fitting results (the solid line) of the specific heat of vit4 between 2 and 52 K. The dashed and dotted lines represent contributions from the Debye mode and Einstein mode, respectively; the dash-dotted line is the contribution of electrons.
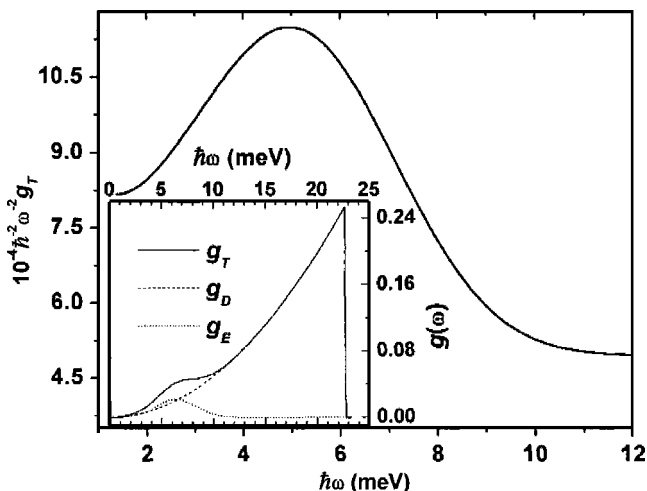

FIG. 3. The derived VDOS of vit4. The peak at about 4.9 meV is boson peak. The inset shows the total VDOS g_T (the solid line), and the VDOS contributed from the Debye g_D (the dashed line) and Einstein g_E (the dotted line) modes, respectively.

mode with $\theta_D = 263$ K and $n_D = 1.92$; C_E, and the dotted line in Fig. 2, is the contribution of the Einstein mode: $C_E = R(\theta_E/T)^2 e^{\theta_E/T}/(e^{\theta_E/T}-1)^2$, with an Einstein temperature $\theta_E = 74$ K and the constant $n_E = 0.10$ that stands for the Einstein oscillator strength per mole. The fact that one Einstein mode is required to model the data indicates the presence of the localized harmonic vibration mode in the BMG.[1–6]

The VDOS of vit4 can be derived from the specific heat. We suppose the Einstein mode's contribution to the VDOS has a Gaussian distribution:[2] $g_E = n_E/(\sigma\sqrt{2\pi}) \exp[-(T-\theta_E)^2/2\sigma^2]$, where σ is the width of Gaussian distribution (we postulate $\sigma = \theta_E/3.4$). Figure 3 shows the derived total VDOS $g_T (=g_D + g_E)$ (the solid line) in the units of oscillators per mole. The Debye mode's ω^2 contribution g_D (the dashed line) and the Einstein mode's contribution g_E (the dotted line) to the VDOS are also exhibited in the inset of Fig. 3. Clearly the Einstein mode induces a peak at about 4.9 meV, and the maximum of the VDOS is at about 22.7 meV, and both these observation are in quantitative agreement with the results of coherent neutron scattering:[9] the VDOS with the first maximum at about 20 meV also shows a pronounced boson peak at about 5 meV. However, the BMG only possesses a total oscillator strength $n_T(=n_D + n_E)$ of 2.02 in the units of oscillators per mole, and the value is far lower than the theory value 3, which is expected from quantum statistics in general solids. Following the neutron scattering results,[9] the Be atoms in the BMG vibrate with the energy at about 50 meV (corresponding to 580 K), so the Be atom contribution to the low-temperature specific heat is very little. If we add the contribution from the Be atoms to the VDOS, the total oscillator strength per mole is about 2.85, which trends to the theory value 3. The neutron scattering observations further confirm the results of our analysis.

There are many opinions as to the origin of the boson peak. Presently two hypotheses prevail: the localized vibrational modes and the collective propagating modes. The collective propagating modes persist at the high frequency.[7] The boson peak in other glasses, such as glycerol, is induced by the collective propagating mode because the wave number q-independent feature is absent at the energy of the boson peak.[7] In vit4, the peak in the VDOS (about 4.9 meV) almost

has the same energy as the boson peak (about 5 meV) determined by neutron scattering; and the energy of the boson peak shows the q-independent feature in the results of the neutron scattering.[9] The observations and agreement rather support a picture in which the boson peak in the metallic glasses is ascribed to localized vibrations that show no more anharmonicity than any other phonon modes.[12]

We have measured the specific heat at low temperatures for various typical BMGs currently available. The results show that the addition of the quantized Einstein oscillator is necessary to provide a good fit to the specific heat data of all these BMGs.[22] The central problem raised by our experimental results is how the Einstein mode correlates with the microstructural features of the BMGs. It is difficult to visualize the existence of the Einstein oscillator in the highly-random-packed metallic glass because of the strong interaction between the constituent atoms. However, more and more evidence has been found that the local structures of BMGs contain a significant degree of oversized icosahedral clusters,[23,24] which might contain loose or weakly bound atoms inside. Vit4 consists of five components with markedly different atomic sizes. The relative difference in Be (0.112 nm) and Zr (0.160 nm) atoms is 30%. The smaller atoms could act as loose or weakly bound atoms in the oversized cages or voids. Actually, the components show different diffusion behaviors in the glass. Tracer diffusion measurements in several BMGs have consistently demonstrated that large atoms such as Zr are slow, with diffusion constants that are orders of magnitude smaller than that of smaller atoms such as Ni (0.162 nm). Ni atoms remain mobile even at temperatures slightly below T_g, where the viscosity increased by several orders of magnitude.[25] The vibrations of the loose atoms show harmonic Einstein modes in the BMG. In the theoretical view, among various theories, the mode-coupling theory (MCT)[26] and the free volume theory[27] are two successful theories that can predict a qualitative change in microscopic dynamics and glass transition in various supercooled liquids. The essence of the MCT deals with the cage effect; that is, in a liquid of densely packed atoms, an atom is temporarily trapped inside the cage formed by neighboring atoms and undergoes vibrations and rattling before escaping the cage.[26] MCT predicts a two-step relaxation process, with α relaxation responsible for viscous flow and a faster β relaxation that can be visualized as a rattling of the atoms in the transient cages. Meyer *et al.*[9,10] observed such a fast β relaxation in the vit4 liquid, in full accord with MCT, and some metallic glasses showed stronger harmonic behavior than most crystalline solids. The free volume theory also involves the cage effect.[27] The BMGs, which have slow kinetics and are prepared by quick quenching from the liquid state, to some extent can inherit liquid structure and contain a large number of cage structure and free volumes. The atoms sitting in the oversized cage or in sufficiently large free volumes are loose and can vibrate in independent harmonic modes. The assumption is confirmed to some extent by Angell,[15] who found a much stronger boson peak in hyperquenched glasses.

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