Boson peak in Sm-Al-Co ternary metallic glasses and its possible structural origin*

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The low temperature specific heat of Sm-Al-Co ternary metallic glasses is investigated and a clear anomaly associated with the Boson peak is identified. While this anomaly depends slightly on the chemical composition, it has no dependence on external magnetic field. To figure out the mechanism of the Boson peak, we interpret the data within various model frameworks. Unlike earlier work, our study shows that this Boson peak is mainly ascribed to an additional T^2 term of the specific heat, which may originate from the quasi-two-dimensional and short-range ordered structure units possibly existing in the metallic glasses.

Keywords: metallic glasses, Boson peak, specific heat
PACC: 7125M, 6370, 6500

1. Introduction

The short range lattice configuration and its dynamics of relaxation in structurally disordered matters represent one of the most intriguing issues in the physics of disordered matters. A comprehensive understanding of the microstructures associated with their fascinating properties has been the key to the applications of these materials. One of the general and intriguing features of glassy materials is the Boson peak (BP), which is observable in the inelastic photon (Raman, x-ray) and neutron scattering spectrum in a THz frequency range, named after the Boson–Einstein distribution.[1−6] It is exactly the presence of an excess of states over the density of states (DOS), $g_{\rm D}\ (\omega)$, which contributes to the peak observed in a plot of $g(\omega)/\omega^2$ against ω, where $g(\omega)$ is the DOS and ω is the frequency.[7] The BP has been argued to reflect the scattering from some short-range ordered structure units with the lattice phonon spectrum satisfying the Boson–Einstein distribution. Therefore, the BP may allow for an opportunity to investigate some microstructural features which may not be accessible to other approaches. However, no details of the physical origin of the BP are available, or in other words, conventional explanations of the origins remain controversial.[8−12]

The BP can also be a feature associated with the thermal property of glassy materials. For typical crystalline matters, it is usually believed that the specific heat C_P consists of two terms. One is the electronic term $C_{\rm F}$ and the other is the lattice vibration (phonon) term $C_{\rm D}$. At low temperature (T), $C_{\rm F} = \gamma T$ is believed to hold, while $C_{\rm D} = bT^3$ is argued within the framework of the Debye theory as long as T is far below the Debye temperature $\theta_{\rm D}$. For typical glasses, at $T < 1.0$ K, C_P depends approximately linearly on T,[13] due to the existence of low-energy excitations which are commonly interpreted as a two-level system arising from tunnelling of atoms or groups of atoms between two nearly degenerate local energy minima.[14] At $T > 1.0$ K, the term $C_{\rm D}$ should be dominant. However, it was observed that for some glassy materials, even at $T \gg 1.0$ K, C_P still deviates from T^3 dependence, presenting a broad maximum in C_P/T^3 as a function of T.[15] This maximum as an anomaly can be ascribed to the presence of the BP. Therefore, it is possible to approach the BP by carefully investigating C_P at low T.

Nevertheless, a substantial effort has been made to comprehend the underlying physics of glassy materials. Currently, three different theoretical models, i.e.

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the mode-coupling model,[8,9] the soft-mode-dynamics (SMD) model,[10] and the Euclidean random matrices approach,[11] were proposed for describing the vibration dynamic anomalies, as well as the associated thermal anomaly,[12] in glassy matters under consideration. None of these theories has yet fully described every aspect of the physical origin of the BP. The previous investigations on the BP focused on traditional glass SiO_2 or polymeric/network glasses. It has been addressed that the intra-molecular, reorientational and translational motions of molecules in normal glasses all may contribute to the BP, making a detailed comprehension challenging. In the present work, we would like to address bulk metallic glasses in which the existence of short/local atomic order is usually believed to exist. Bulk metallic glasses offer relatively simple atomic interactions with respect to polymeric glasses or quartz glass, and thus those complicated degrees of freedom of motions mentioned above can be ignored. Due to this, one may possibly correlate the BP feature in specific heat with some microstructural essence of metallic glasses, which is our main motivation in the present study.

2. Experiment

We report on our delicate experiment of the low-T C_P on ternary Sm-Al-Co metallic glasses, and our primary motivation is to investigate the possible anomaly and explore its microstructure origin. The samples in our study were $Sm_{50}Al_{25}Co_{25}$, $Sm_{52}Al_{24}Co_{24}$, and $Sm_{54}Al_{23}Co_{23}$, so that we could investigate the composition dependence of the BP. We also investigated the magnetic field dependence. The ingot samples were prepared by arc-melting the mixture of high purity constituent elements under argon atmosphere. The details of the sample synthesis were given previously, and conventional structural characterizations demonstrated that the samples were 'homogeneously' amorphous without additional particulates.[16,17] The Co content of these samples was denoted by $y = 23$, 24, and 25, separately. The samples for measurement were shaped into rods of 3 mm in diameter. The experiment was performed by using the thermal relaxation method with a Quantum Design PPMS (Quantum Design Inc.). The latest improved measurement puck for specific heat from Quantum Design, in which the field dependence of the thermometer sensor on chip and the thermal conductance of thermal linking wires could be calibrated, was used for the data collection. This puck was demonstrated to be very successful in collecting high-precision data for a number of matters.[18]

3. Results and discussion

Figure 1(a) presents the measured curves for C_P versus T from 2 K to 30 K for the three samples. A first look at the data shows that C_P decays down to zero as $T \to 0$ K. No significant dependence of C_P on y is detected. We employ the formula $C_p = \gamma T + bT^3$ to fit the data.[19] A best fitting gives coefficients γ and b : $\gamma = 0.3$, 0.32, and 0.34 mJ/g·K^2 and $b = 7.2813$, 7.1161, and 6.99867 μJ/g·K^4, respectively, for $y = 23$, 24, and 25. Over the whole T-range, the fitting seems to be highly reliable, indicating that the specific heat is indeed contributed from the electronic and lattice vibrations separately.

Nevertheless, further and careful analysis of the data does show a clear anomaly of $C_P(T)$ in low T ranges. If the formula $C_p = \gamma T + bT^3$ is a sound description in physics, one will have $(C_P - \gamma T)/T^3 = b$, a constant or monotonically dependent on T.[20] Using the fitted coefficient γ, we plot the curves for term $(C_P - \gamma T)/T^3$ against T for the three samples. A clear and broad peak pattern instead of either a constant or a monotonically T-dependent term is observed. The results are also presented in Fig. 1(a). Clearly, the broad peak appearing at $T \approx 7$ K represents a specific heat anomaly, i.e. the BP as addressed previously.

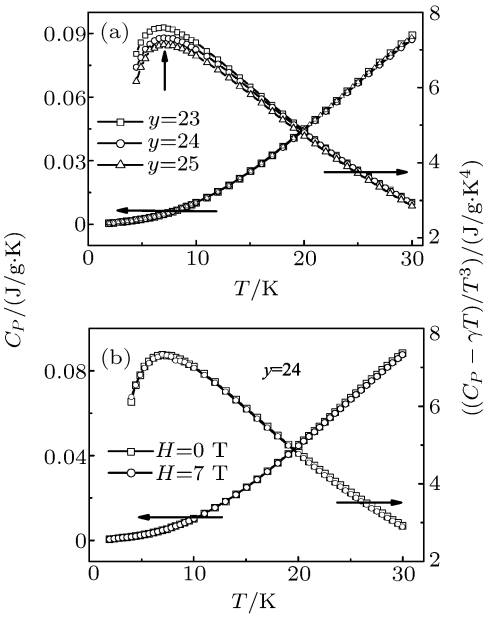


Fig. 1. Measured curves for C_P and evaluated $(C_P - \gamma T)/T^3$ versus T under $H = 0$ for $y = 23$, 24, 25, respectively (a), and under $H = 0$ and 7 T for $y = 24$ (b).

To understand the origin of the BP, we need to exclude the effect of composition y and magnetic field H as well as other possible factors. Although the peak position (height and location) depends somehow on y, no significant correlation of the peak with y is identified. We also measure the values of $C_P(T)$ under different values of H. The data for $y = 24$ under $H = 0$ and 7 T are plotted in Fig. 1(b). No dependence of C_P on H is identified within the measuring uncertainties, indicating that the BP has little to do with spin ingredient, if any, and chemical composition. Furthermore, the BP can not be ascribed to the electronic contribution, since $C_{\rm F}$ is remarkable only at $T < 1$ K, which can not be responsible for the BP appearing at $T \approx 7$ K. The anomaly must come from Debye lattice vibration associated with some microstructural objects except the conventional T^3 term. Subsequently, we consider the microstructural origin.

In fact, the BP effect in metallic glasses was recently addressed[1] and the Debye–Einstein coupling theory was used to explain the BP effect, where C_P is described by $C_P = \gamma T + C_{\rm D} + n_{\rm E} C_{\rm E}$, where $C_{\rm E}$ is the Einstein term $C_{\rm E} = R\,(\theta_{\rm E}/T)^2 \left[{\rm e}^{\theta_{\rm E}/T}/\left({\rm e}^{\theta_{\rm E}/T} - 1\right)^2\right]$ and $n_{\rm E}$ the coefficient scaling the Einstein high energy excitation.[1] We note that the Einstein specific heat model usually works well for describing the specific heat at high T since it does not account for the low-energy excitation of phonons, while the Debye model usually works well as $T \ll \theta_{\rm D}$. In this sense, the coexistence of the Einstein excitation and Debye excitation may not be always reasonable since they are two different approximations. Indeed, the Debye–Einstein coupling theory fits the values of C_P anomaly well at low T, and it was claimed that the BP originated from the excitation of those loose atoms in metallic glasses.[1]

Nevertheless, one may argue that each of those loose atoms may not have identical Einstein mode and thus the assumption of a single Einstein frequency of vibration seems questionable. Given the different Einstein frequencies of these loose atoms, an imposition of them in fact becomes equivalent to the Debye model. Here shown in Fig. 2 are the results including an additional Einstein mode in detail. Line IV in Fig. 2(a) represents the fitting by using $C_P = \gamma T + C_{\rm D} + n_{\rm E} C_{\rm E}$, and line III in Fig. 2(b) represents the contribution of the Einstein term while the black circle dots show the sum of both the Einstein and Debye terms. Compared with the experimental data, the fitting does have a significant difference from the experimental data, from which we can actually see that the Einstein mode could not explain the origin of BP satisfactorily. Therefore, one needs to search for a new explanation.

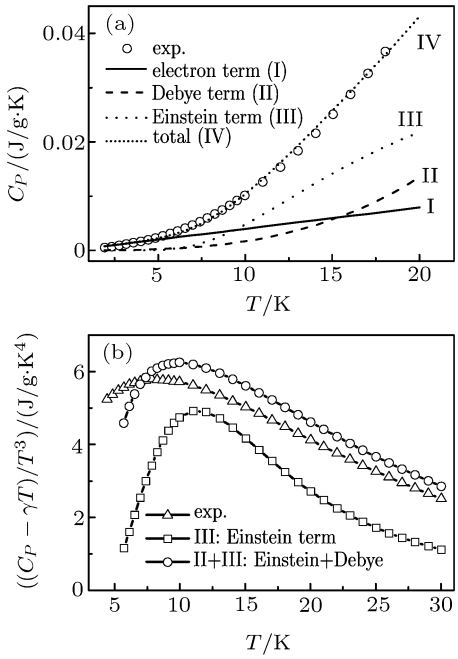


Fig. 2. Electronic term (I), Debye term (II), Einstein term (III), and sum of these terms (IV), each as a function of T, obtained from the best fitting (a), and these terms are presented in the form of $(C_P - \gamma T)/T^3$ vs. T, $y = 23$ (b). The measured data are presented for comparison.

A tentative extension of $C_P = \gamma T + bT^3$ is to include an additional term αT^2 so that the observed BP anomaly can be removed. The reason for including this term will be presented below. By this extension, $C_P = \gamma T + \alpha T^2 + bT^3$ is used to fit the measured data, approved by the high fitting reliability. The fitting produces $\gamma = 0.19$, 0.24, and 0.24 mJ/g·K^2, $\alpha = 0.03$ mJ/g·K^2, and $b = 4.8406$, 5.2513, and 4.7845 μJ/g·K^4 for $y = 23$, 24, 25, respectively. Given these fitted parameters, one can check whether the BP effect exists. We plot the curves for terms $(C_P - \gamma T)/T^3$ and $(C_P - \gamma T - \alpha T^2)/T^3$ each against T, separately, and the results for $y = 23$ are shown in Fig. 3(a). It is seen that with respect to the remarkable BP shown in Fig. 3(a), no more peak pattern is available and the evaluated data are smooth without any anomaly. Similar behaviours are obtained from samples $y = 24$ and 25, separately. This indicates that the BP is successfully suppressed by including the αT^2 term. What should be mentioned here is that $(C_P - \gamma T)/T^3 = (\alpha/T + b)$ allows term $(C_P - \gamma T)/T^3$ to be a linear function of $1/T$ as demonstrated in Fig. 3(a). Also, relation $(C_P - \gamma T - \alpha T^2)/T^3 = b$ does work well for the present systems, although the

evaluated parameter b again shows a weak T dependence, a well known phenomenon.[20]

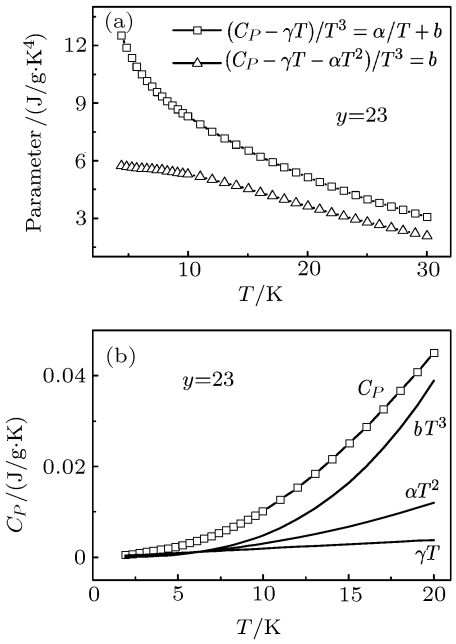


Fig. 3. Evaluated terms $(C_P-\gamma T)/T^3$ and $(C_P-\gamma T-\alpha T^2)/T^3$ each as a function of T for $y=23$ (a), and measured C_P and its three components γT, αT^2 and bT^3 each as a function of T (b).

Considering the Debye theory on C_P, it is easy to learn that two-dimensional (2D) ordered structures will contribute to C_P proportionally to T^2 (αT^2), at low $T \ll \theta_{\rm D}$. Given a relatively low density of these 2D structures, one may assume that they are independent of each other and no interaction between them is significant. Therefore, one has the specific heat $C_P=\gamma T+\alpha T^2+bT^3$. We use this formula to fit the measured data for $y=23$ (similar to the results for $y=24$ and 25), and the evaluated γT, αT^2 and bT^3 terms each as a function of T are presented in Fig. 3(b). The linear T term is quite weak compared with the T^2 and the T^3 terms. What impressed us is that the T^2 term is remarkable and its ratio to the T^3 term is about 0.3, indicating that the short-range 2D ordered structures may not be negligible. Our results reveal that the BP seems to come mainly from the short-range 2D ordered structures.

To provide more evidence to support the above argument, we evaluate $g(\omega)$ from the C_P data, noting that no experimental DOS data for ternary Sm-Al-Co metallic glasses are available. Details of the evaluation procedure can be found in Ref. [21], yielding the following expression for $g(\omega)$, given $C_P=\gamma T+\alpha T^2+bT^3$:

$$g(\omega)=-\frac{\hbar}{10rk_{\rm B}^2}\gamma+\frac{2\hbar^2\omega}{45rk_{\rm B}^3}\alpha+\frac{3\hbar^3\omega^2}{80rk_{\rm B}^4}b, \qquad (1)$$

where $\hbar$ is the Planck constant, $k_{\rm B}$ the Boltzmann constant, and r the number of atoms in a unit cell which is taken to be 3, i.e. $r=3$, and does not change the conclusion above. A linear density of states associated with the αT^2 term is generated. Substituting the fitted data for parameters γ, α, and b into expression (1), we obtain the curves of $g(\omega)/\omega^2$ versus ω for the three samples as shown in Fig. 4. It is seen that $g(\omega)/\omega^2$ for all the three samples does show the BP feature. Furthermore, an exclusion of the T^2 term in C_P, i.e. $\alpha=0$, leads to the disappearance of the BP in $g(\omega)/\omega^2$ as a function of ω as indicated by expression (1). This demonstrates that the BP is contributed mainly from the T^2 term, i.e. from the short-range 2D ordered structure units.

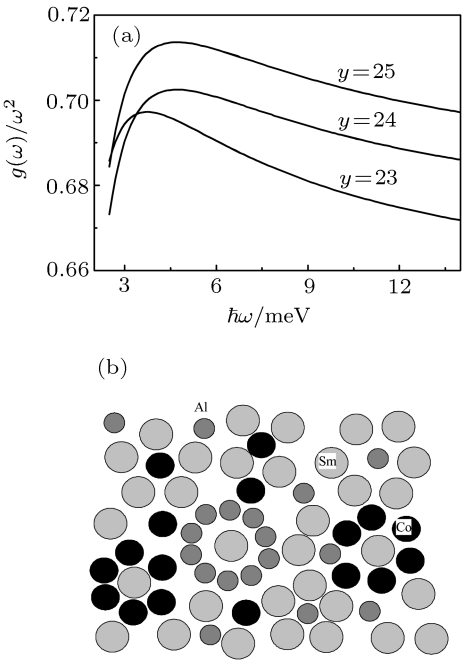


Fig. 4. (a) Curves for evaluated DOS, $g(\omega)$, in the form of $g(\omega)/\omega^2$, as a function of energy $\hbar\omega$ for $y=23$, 24, and 25, separately, and (b) schematic of the possible short-range polygon structure units in the present samples.

What should be mentioned here is that in an amorphous material there can hardly exist 2D structures which produce a linear density of states. In order to produce such a contribution there must exist large 2D sheets of material in which extended plane waves can propagate, which are rarely scattered. In the metallic glass we study here, the low-frequency excitations are mainly 3D sound waves. The structural features on the atomic scale and on the mesoscopic scale

lead to the scattering of these 3D waves, which should be the origin of the BP. However, the contribution of 2D ordered structure units to C_P in the form of αT^2 is also possible, although it has never been probed. A typical example is graphite which exhibits 2D layer structure. In fact, well defined T^2 dependence of C_P at $T < 58$ K for graphite was demonstrated.[22] For glassy materials, especially metallic glasses, the existence of short-range atomic-ordered structures, the so-called Bernal structures, embedded in the atomic-disordered matrix has been repeatedly revealed by a number of experiments.[23] In fact, the Bernal structure often appears in disordered systems with inhomogeneous interactions.[24] Such an atomic configuration usually favours short-range polyhedral structure units. Surely, the 3D structure units are dominant. However, it was argued that when T approached a very low value, the secondary bonds between atom-pairs became weak with respect to the primary bonds due to spatially inhomogeneous interactions, thus favouring the formation of 2D or even 1D short-ordered structures besides the 3D structures. The internal Debye vibration of these structures must also make a contribution to C_P.

Here a model is schematically shown in Fig. 4(b). No crystalline phase can be found in metallic glasses, implying that the whole atomic configuration is a disordered state. Nevertheless, we may find the imperfect ordered packing of nano-ordered clusters with a size of 1–2 nm,[25] meaning that it is all short-ordered. A lot of polygons are shown to form the configuration, indicating that it is ordered at the atomic level. When the liquid state evolves into the glass state during the cooling, these short-ordered clusters can be retained, generating the short-range 1D, 2D, and mostly 3D structure sheets,[26] although the 1D and the 2D sheets occupy only a very low volume fraction in the sample separately.

4. Conclusion

We investigate the low-T specific heat of ternary Sm-Al-Co metallic glasses and the associated BP effect. We observe the remarked BP anomaly at $T \approx 7$ K and this anomaly has no dependence on chemical composition and spin ingredient. We correlate this anomaly mainly with the possible short-range 2D ordered structures. This work may give insight into our understanding of the short-range ordered structures in metallic glass materials, and we appeal for microscopic evidence with this prediction.

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