

Pronounced slow β -relaxation in La-based bulk metallic glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2011 J. Phys.: Condens. Matter 23 142202

(<http://iopscience.iop.org/0953-8984/23/14/142202>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 159.226.37.41

The article was downloaded on 19/03/2011 at 02:29

Please note that [terms and conditions apply](#).

FAST TRACK COMMUNICATION

Pronounced slow β -relaxation in La-based bulk metallic glasses

Z Wang, H B Yu, P Wen, H Y Bai and W H Wang¹Institute of Physics, Chinese Academy of Sciences, Beijing 100190,
People's Republic of ChinaE-mail: whw@aphy.iphy.ac.cn

Received 27 January 2011, in final form 12 February 2011

Published 18 March 2011

Online at stacks.iop.org/JPhysCM/23/142202**Abstract**

Most metallic glasses (MGs) exhibit weak evidence of slow β -relaxation in their dynamic mechanical spectroscopy spectra. In contrast to other MGs, the La-based MGs we report here show a distinct slow β -relaxation peak in the mechanical relaxation measurements. We find that the slow β -relaxation behavior can be tuned by modification of the chemical composition and fragility. The structural origin of the slow β -relaxation and correlation between β -relaxation and α -relaxation in the MGs are also discussed. MGs with pronounced slow β -relaxation and tunable properties might provide a model system to investigate some long-standing issues in the glass field.

(Some figures in this article are in colour only in the electronic version)

The study of slow β or Johari–Goldstein relaxation in supercooled liquids and glasses has attracted considerable attention for its importance in understanding the nature of glass [1–5]. Plenty of work on the second relaxation has been done in non-metallic glasses like glassy polymers [6, 7]. Due to the complex intramolecular effects in polymer glasses, it is difficult to correlate the static structural features with the relaxation process in these kinds of glasses, and the structural origin of slow β -relaxation is still a controversial issue [8, 9]. In contrast, metallic glasses (MGs) are regarded as simple glasses because their structure is close to the dense random packing of spheres [10]. Previous work on the slow β -relaxation mode in supercooled liquids suggested that the degree of coupling between α - and slow β -relaxations correlates with the fragility of the glass-forming liquids [11, 12], and the distinct slow β peak often exists in very fragile glass formers and no pronounced slow β -relaxation should be observed in ‘strong’ metallic supercooled liquids. The results seem to coincide with this prediction [8]. Even though the slow β -relaxation has been identified in MGs both in experiments and simulations [13–17], only a slow β -relaxation shoulder or excess wing has been observed on the

high-frequency flank of the α -relaxation so far. The MGs with pronounced slow β -relaxation in their spectrum of dynamic mechanical spectroscopy are highly desired, because they are ideal systems for studying the β -relaxation peak change with applied conditions which can provide insight into some related fundamental issues in the glasses.

On the other hand, the slow β -relaxation is also inferred to closely correlate with the plastic deformation in MGs [18]. It is found that the activation of shear transformation zones (STZs, which is the basic unit of plastic deformation in glassy material) and β -relaxations in MGs are nearly equivalent. Therefore, an MG with a distinct β -relaxation peak would be very useful for studying the underlying physics of the relaxation and plastic mechanism of MGs.

In this letter, we report the formation of a series of La-based MG systems showing a pronounced slow β -relaxation peak in its spectrum from a dynamic mechanical analyzer (DMA). The effects of the composition and fragility on the evolution of the slow β -relaxation are investigated. We accurately determine the activation energy of the slow β -relaxation in the MGs which further confirms the relationship between slow β -relaxation and plastic deformation. We also discuss the structural origin of the slow β -relaxation and the correlation between β - and α -relaxations in the MGs.

¹ Author to whom any correspondence should be addressed.

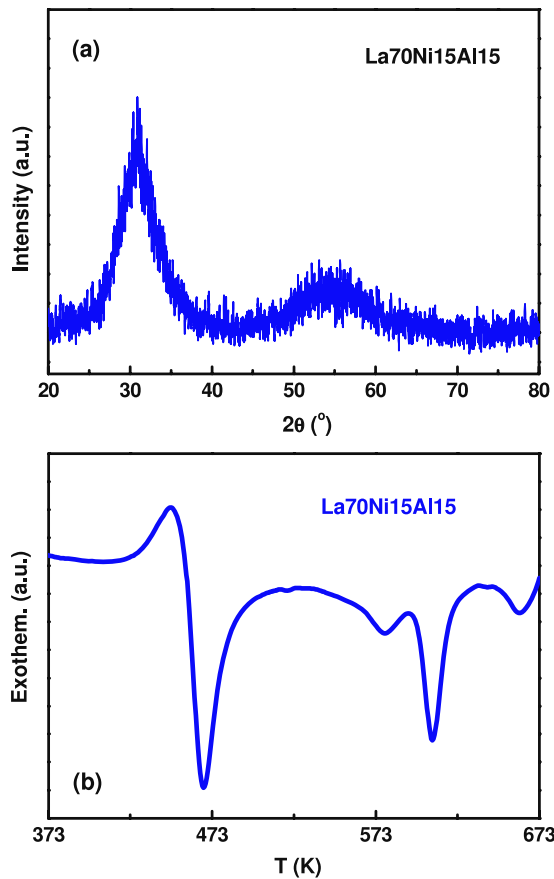


Figure 1. (a) The XRD pattern and (b) the DSC curve of $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$ alloys.

La-based bulk MGs were prepared by the water-cooled copper mold cast method, and amorphous ribbons were obtained by the melt spinning technique. The glassy nature was identified by x-ray diffraction (XRD) using a MAC M03 diffractometer with a $\text{Cu K}\alpha$ radiation source, and differential scanning calorimetry (DSC) was performed under a purified argon atmosphere in a Perkin-Elmer DSC-7. Dynamic mechanical measurements were performed using a TA DMA Q800 by the single-cantilever bending method for rod samples and the film tensile method for ribbons in a nitrogen-flushed atmosphere. The storage modulus E' and loss modulus E'' were measured by the temperature ramp mode at a heating rate of 3 K min^{-1} .

Figure 1(a) shows the XRD pattern of a typical $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$ MG with diameter of 2 mm. The broad diffraction peak without distinct sharp crystalline peaks in the XRD pattern indicates the amorphous nature of the alloy. The DSC trace of the same sample focusing on the glass transition and crystallization behavior is shown in figure 1(b). The glass transition temperature T_g of the MG is 441 K, while the crystallization temperature T_x is 457 K. The distinct glass transition and sharp crystallization behaviors further confirm the glassy structure of the alloy.

Figure 2(a) shows the temperature dependence of the storage modulus E' and loss modulus E'' of a $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$ MG measured at 1 Hz. Remarkably, the E'' curve shows

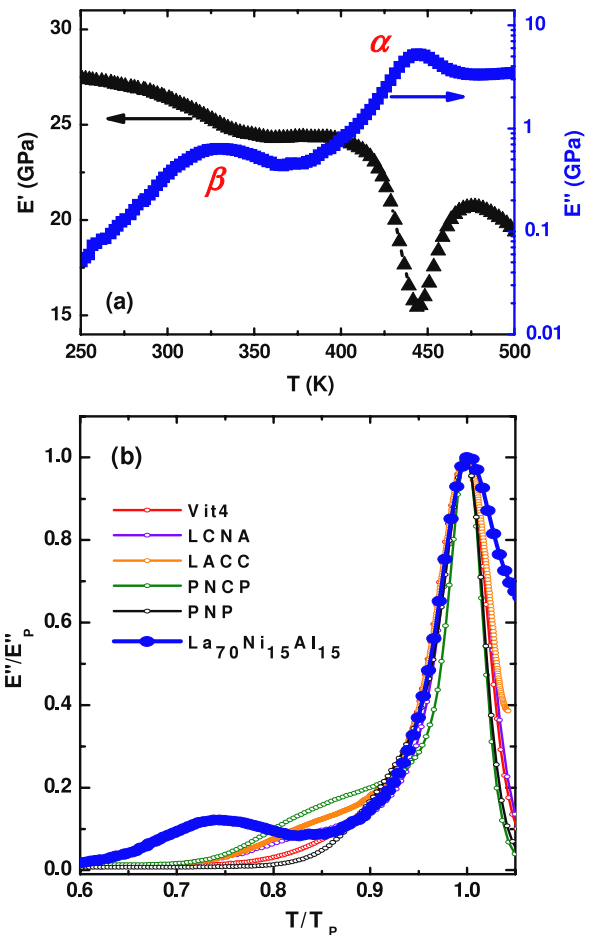


Figure 2. (a) The T dependence of the storage modulus E' (left) and the loss modulus E'' (right) of $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$ measured at 1 Hz. (b) The T dependence of the loss modulus E''/E_p measured at 1 Hz on different MGs ($\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ (Vit4), $\text{La}_{57.5}(\text{Cu}_{50}\text{Ni}_{50})_{25}\text{Al}_{17.5}$ (LCNA), $\text{La}_{68}\text{Al}_{10}\text{Cu}_{20}\text{Co}_2$ (LACC), $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ (PNCP), $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ (PNP), and $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$). T was normalized to T_p for comparison.

two distinct peaks: an α -relaxation peak of E'' at $443 \pm 5 \text{ K}$ and an obviously slow β -relaxation peak at $330 \pm 5 \text{ K}$. Both the α -relaxation and the slow β -relaxation peaks have a corresponding drop in E' curve. Previously, the MGs always showed excess wing or shoulder instead of a well-defined peak in the E'' curves. Figure 2(b) contrasts the slow β -relaxation peak (all measured at 1 Hz) for six different typical bulk MGs with markedly different properties including $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ (Vit4), $\text{La}_{57.5}(\text{Cu}_{50}\text{Ni}_{50})_{25}\text{Al}_{17.5}$ (LCNA), $\text{La}_{68}\text{Al}_{10}\text{Cu}_{20}\text{Co}_2$ (LACC), $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ (PNCP), $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ (PNP), and $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$ MGs [16]. In figure 2(b), the E'' is scaled with the loss modulus at the α -relaxation peak E_p'' of these systems and temperature (T) is also scaled by the α -relaxation peak temperature T_p . The comparison clearly shows that the $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$ has a pronounced slow β -relaxation peak among these typical MGs. Based on this unique relaxation behavior, we can identify the key factors of the slow β -relaxation in MGs.

Through adjusting the composition ratio or replacing the element, we try to find the link between the microstructural

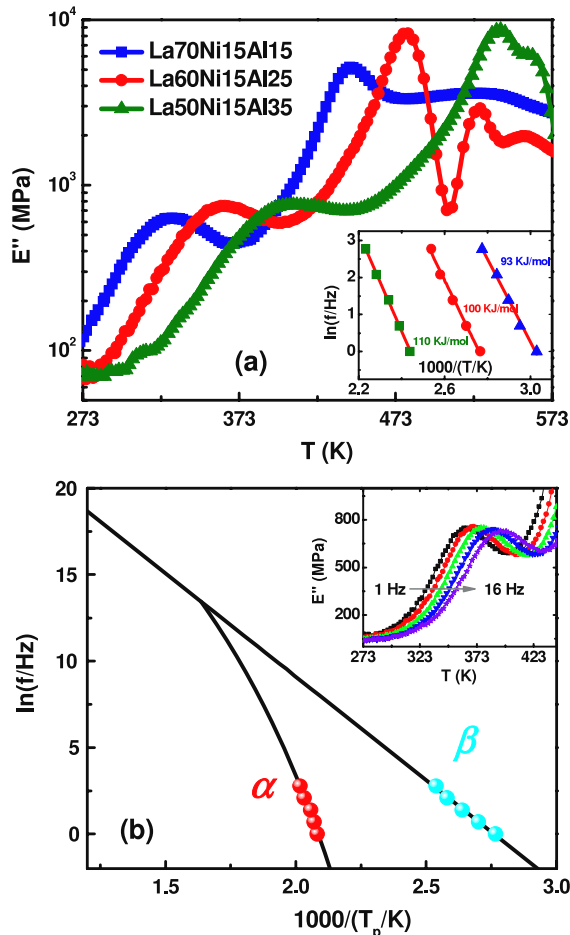


Figure 3. (a) The T dependence of the loss modulus E'' of La₇₀Ni₁₅Al₁₅, La₆₀Ni₁₅Al₂₅, and La₅₀Ni₁₅Al₃₅ measured at 1 Hz. The inset shows the plots of $\ln(f)$ versus $1000/T_{\beta p}$, where $T_{\beta p}$ is the peak temperature of the slow β -relaxation peak. The activation energy E_{β} can be determined from the plot. (b) The T dependence of the peak frequency of La₆₀Ni₁₅Al₂₅; the red and blue dots represent α - and slow β -relaxations, respectively. The inset plots are the T dependence of the loss modulus slow β -relaxation peak measured at 1–16 Hz.

characteristics and the relaxation scenario in relatively simple MG systems that have no complex intramolecular effects in glassy polymers. The La–Ni–Al system has a wide composition range, and we can adjust the composition ratio of La and Al. The reduced loss moduli E'' of three typical compositions in the temperature domain measured at 1 Hz are shown in figure 3(a). The values of T_p ($T_{\beta p}$, the β -relaxation peak temperature) are 443 ± 5 K (330 ± 3 K) for La₇₀Ni₁₅Al₁₅, 480 ± 5 K (361 ± 3 K) for La₆₀Ni₁₅Al₂₅, and 540 ± 5 K (410 ± 3 K) for La₅₀Ni₁₅Al₃₅, respectively. Both T_p and $T_{\beta p}$ shift to higher temperature with increasing Al content in the alloys. The α -relaxation peak is related to the dynamics of the metallic supercooled liquid and the temperature corresponding to the α -peak is always a little higher than T_g [15]. Thus, with the Al–La ratio increase, the values of T_p shift to higher temperature as T_g increases. The β -relaxation is Arrhenius type, and its activation energy E_{β} can be determined from the frequency dependent peak temperature (Arrhenius plot). As

shown in the inset of figure 3(a), the E_{β} of the three typical La-based bulk MGs are 93, 100, and 110 kJ mol⁻¹, respectively. The obtained values of E_{β} fit well the empirical relationship of $E_{\beta} \approx 26RT_g$ obtained through other methods [17, 18], which confirms the proposal of the ‘ β -relaxation to α -relaxation’ self-similar organization [19]. The result indicates that more Al addition makes the activation of the β -relaxation more difficult. According to the current view on the structural origin of the β -relaxation, the slow β -relaxation may originate from the density differences resulting from loose-packing regions in the glassy matrix. Replacing the La atoms with the smaller Al atoms, the MG becomes more densely packed, some excess volume vanishes in the original loose-packing regions, and the slow β -relaxation becomes more difficult to activate. From figure 3(a), one can see that the slow β -relaxation peak is gradually merging into the α -relaxation with increasing Al content.

The fragility of La₅₀Ni₁₅Al₃₅, La₆₀Ni₁₅Al₂₅, and La₇₀Ni₁₅Al₁₅ MGs determined by DSC and DMA according to the method in [16, 20] are 48 ± 5 , 43 ± 5 , and 31 ± 5 , respectively. The pronounced slow β -relaxation peak in the intermediate strong La-based MG system may indicate that the microstructural origin of the MG system differs from that of other glasses such as polymer. The relationship between the fragility and slow β -relaxation behavior in the La–Ni–Al alloy is incompatible with the previous empirical rule, which suggests that the glass with larger fragility has more obvious slow β -relaxation behavior. On the other hand, with the increase of fragility, the degree of coupling between the two relaxation modes becomes weakened, which is embodied in the increase of ΔT ($=T_p - T_{\beta p}$) as the atom ratio of La changes from 70 to 50. The effect of decoupling between α - and slow β -relaxation is reduced by the broadening of the distribution of the α -relaxation. To intuitively show the coupling between the two relaxations, figure 3(b) plots the value of frequency versus the loss peak temperature for La₆₀Ni₁₅Al₂₅ MG. The α -relaxation is described well by the Vogel–Fulcher–Tammann (VFT) equation: $f = f_0 \exp[-B/(T_p - T_0)]$. The values of f_0 , B , and T_0 are 1.1×10^{13} Hz, 4874.5 K, and $316(\pm 10)$ K, respectively. The relationship between frequency and $T_{\beta p}$ for the slow β -relaxation has the form of the Arrhenius process: $f = 2.2 \times 10^{14} \exp(-99435/RT_{\beta p})$. Below the crossover temperature $610(\pm 30)$ K, the slow β -relaxation starts to decouple from the α -relaxation.

It is interesting to note that the chemical species play an important role in the relaxation behavior. When the nickel in La₇₀Ni₁₅Al₁₅ alloy is replaced by elements with similar atom volume such as cobalt and copper, the mechanical relaxation behavior (measured at 2 Hz) can be markedly changed as shown in figure 4. Due to the limits of the glass-forming ability of these alloys, MG ribbons were used in the tensile mode of the DMA. The La₇₀Co₁₅Al₁₅ and La₇₀Ni₁₅Al₁₅ show similar slow β -relaxation behavior with a slight change of peak temperature and intensity. However, the substitution of copper for nickel leads to the disappearance of the slow β -relaxation peak, and the La–Cu–Al MG only shows a shoulder in the DMA spectrum. The origin of the slow β -relaxation could be attributed to the intrinsic heterogeneity of

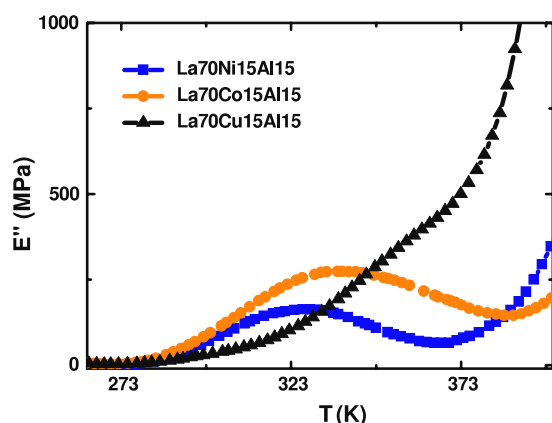


Figure 4. The T dependence of the loss modulus E'' of $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$, $\text{La}_{70}\text{Co}_{15}\text{Al}_{15}$, and $\text{La}_{70}\text{Cu}_{15}\text{Al}_{15}$ measured at 2 Hz.

metallic supercooled liquids and glasses. The MGs are usually structurally inhomogeneous and contain dense-packing regions with solid-like behavior such as strong bonding, fewer free volumes, high viscosity and higher elastic moduli, and loose-packing regions with liquid-like behaviors including weakly bonded atoms, low viscosity, rich free volume, and lower elastic moduli. Structural heterogeneity has been detected or confirmed in many bulk MG systems by various experimental methods and simulation [20–24]. The translational diffusion of the atoms in the loose-packing regions represents the slow β -relaxation [25]. This significant change of the slow β -relaxation scenario induced by replacement of Ni with Cu may indicate the component change in the alloy leading to reorganization of the microstructure. Ni and Co tend to combine with Al to form loose-packing regions, but Cu does not. This is due to the enthalpy of mixing of Cu and Al being -1 kJ mol^{-1} , which is much larger than the values of Ni and Al or Co and Al (-22 and -19 kJ mol^{-1} , respectively). The change of composition ratio or elements will change the proportion and structure of loose-packing regions, which affect the relaxation mode.

As a simple ternary MG system with a pronounced β -relaxation peak, La–Ni–Al alloy can be used as a model system for studying some of the long-standing puzzles in the field of glass transition and plastic deformation mechanisms in MGs. For example, these La-based alloys are model systems for confirming whether the slow β -relaxation and STZs are directly related and for studying how the β -relaxation affects the mechanical properties in MGs. Since ^{27}Al is a quadrupolar nucleus, the local structural change can be investigated in the La–Ni–Al MG systems by means of ^{27}Al nuclear magnetic resonance [26], and the structural origin of the slow β -relaxation could be deeply understood. Further work on this topic is in progress.

In conclusion, a pronounced β -relaxation peak is observed by DMA measurement in the La-based bulk MGs. The second relaxation is found to be sensitive to the composition and

components. The MGs provide a model system for studying controversial issues in glasses such as the structural origin of the slow β -relaxation, the decoupling between β - and α -relaxations in metallic supercooled liquids, and the correlation between β -relaxation and mechanical properties.

We are grateful to D Q Zhao and M X Pan for valuable discussions and experimental assistance. Financial support is from the NSF of China (Nos 50731008 & 50921091) and MOST 973 (Nos 2007CB613904 & 2010CB731600).

References

- [1] Johari G P and Goldstein M 1970 *J. Chem. Phys.* **53** 2372
- [2] Gotze W and Sjogren L 1992 *Rep. Prog. Phys.* **55** 241
- [3] Angell C A, Ngai K L, McKenna G B, McMillan P F and Martin S W 2000 *J. Appl. Phys.* **88** 3113
- [4] Lunkenheimer P, Schneider U, Brand R and Loidl A 2000 *Contemp. Phys.* **41** 15
- [5] Ngai K L, Lunkenheimer P, Leon C, Schneider U, Brand R and Loidl A 2001 *J. Chem. Phys.* **115** 1405
- [6] Frick B and Richter D 1995 *Science* **267** 1939
- [7] Lunkenheimer P, Pimenov A, Dressel M, Goncharov Y G, Bohmer R and Loidl A 1996 *Phys. Rev. Lett.* **77** 318
- [8] Tanaka H 2004 *Phys. Rev. E* **69** 021502
- [9] Ngai K L 2004 *Phys. Rev. E* **70** 063501
- [10] Wang W H 2006 *J. Appl. Phys.* **99** 093506
- [11] Doss A, Paluch M, Sillescu H and Hinze G 2002 *Phys. Rev. Lett.* **88** 095701
- [12] Zhao Z F, Wen P, Shek C H and Wang W H 2010 *J. Non-Cryst. Solids* **356** 1198
- [13] Okumura H, Chen H S, Inoue A and Masumoto T 1991 *J. Non-Cryst. Solids* **130** 304
- [14] Wen P, Zhao D Q, Pan M X, Wang W H, Huang Y P and Guo M L 2004 *Appl. Phys. Lett.* **84** 2790
- [15] Zhao Z F, Wen P, Wang W H and Shek C H 2006 *Appl. Phys. Lett.* **89** 071920
- [16] Zhao Z F, Wen P, Shek C H and Wang W H 2007 *Phys. Rev. B* **75** 174201
- [17] Hu L and Yue Y Z 2008 *J. Phys. Chem. B* **112** 9053
- [18] Yu H B, Wang W H, Bai H Y, Wu Y and Chen M W 2010 *Phys. Rev. B* **81** 220201
- [19] Harmon J S, Demetriou M D, Johnson W L and Samwer K 2007 *Phys. Rev. Lett.* **99** 135502
- [20] Zhang B, Zhao D Q, Pan M X, Wang W H and Greer A L 2005 *Phys. Rev. Lett.* **94** 205502
- [21] Ichitsubo T, Matsubara E, Yamamoto T, Chen H S, Nishiyama N, Saida J and Anazawa K 2005 *Phys. Rev. Lett.* **95** 245501
- [22] Liu Y H, Wang G, Wang R J, Zhao D Q, Pan M X and Wang W H 2007 *Science* **315** 1385
- [23] Fujita T, Guan P F, Sheng H W, Inoue A, Sakurai T and Chen M W 2010 *Phys. Rev. B* **81** 140204
- [24] Tanaka H, Kawasaki T, Shintani H and Watanabe K 2010 *Nature Mater.* **9** 324
- [25] Ye J C, Lu J, Liu C T, Wang Q and Yang Y 2010 *Nature Mater.* **9** 619
- [26] Wen P, Zhao Z F, Pan M X and Wang W H 2010 *Phys. Status Solidi a* **207** 2693
- [27] Xi X K, Li L L, Zhang B, Wang W H and Wu Y 2007 *Phys. Rev. Lett.* **99** 095501