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Heavy-fermion behavior in cerium-based metallic glasses

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We report the observation of the heavy-fermion behavior in the cerium-based bulk metallic glasses with an inherent strong structural disorder. The heavy-fermion behavior in the glasses with 4*f* electrons shows unique features not found in crystalline materials. The distribution of the *f* levels due to structural disorder produces internal variation from the Kondo regime to the valence fluctuation regime, with the heavy-fermion behavior at the crossover. The glasses might provide a model system to investigate some longstanding issues with electron strong correlation in complex solids.

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The heavy-fermion (HF) behavior is observed in a number of crystalline alloys or compounds.[1] It occurs as a consequence of the competition between the local Kondo resonance and magnetic ordering.[2,3] It has also been recognized that the HF behavior is strongly affected by disorder due to alloying, lattice defects, etc. Dynamical mean-field theory shows that sufficient disorder can cause substantial modifications of the low-T physical properties of a HF system, resulting in a breakdown of conventional Fermi-liquid behavior.[4,5] Indeed, it has been shown experimentally that certain disordered HF systems, such as $UCu_{5-x}Pd_x$ (Refs. 6–8) or $U_{1-x}Th_xPd_2Al_3$,[9] exhibit non-Fermi-liquid (NFL) behavior at low temperatures. However, the disorder in these compounds is relatively weak; it is mainly due to the random substitution of constituent elements (or the Kondo and/or Anderson lattices), and there are few experimental studies or theories on the influence of structural disorder on the HF behavior. The interplay between disorder and strong correlations, especially in HF materials, remains one of the least understood topics of condensed-matter physics.

Bulk metallic glasses (BMGs) have been drawing increasing attention in recent years due to their scientific and engineering significance.[10] Very recently, a new class of rare-earth-based BMGs including Ce-based BMG with 4*f* electrons was developed.[11] The disorder in BMGs is strong compared with the Kondo and/or Anderson lattices[10] and can be tuned by the annealing-induced relaxation.[12–17] Similar valences and ionic radii of cerium and lanthanum allow gradual transition from the nonmagnetic state to magnetic state by alloying, without much change in the structure. The bulk form of the glass allows effective and accurate physical property measurements. In this Brief Report, the T dependence of specific heat C_p, susceptibility χ, and electrical resistivity ρ of the Ce-based glasses are studied. The results indicate that the glasses exhibit the structural disorder-driven HF behavior. The unique features of the HF glasses are described and the connection between the structural disorder and HF behavior is discussed.

A series of BMGs with the composition of $Ce_xLa_{65-x}Al_{10}Cu_{20}Co_5$ ($x=0$, 10, 20, and 65 at. %) were prepared by the process described in Ref. 11. The glassy structure was confirmed by x-ray diffraction and differential scanning calorimetry. To modify the degree of the disorder, isothermal annealing was performed under a high vacuum at 351 K (below the glass transition temperature T_g) to induce structural relaxation. Crystallized BMG was obtained by annealing the BMG at 573 K (above the crystallization temperature) for 12 h. The measurements of heat capacity C_p (error $<2\%$) were carried out with a physical property measurement system (PPMS 6000) down to 0.53 K and up to 5×10^4 Oe in a helium-3 system. The measurements of resistivity ρ, using a standard four-probe technique, were made down to 56 mK in an adiabatic demagnetization Cryostat IV. The dc magnetic susceptibility was measured using PPMS from 1.9 to 300 K after zero-field cooling.

The measured C_p of the $Ce_xLa_{65-x}Al_{10}Cu_{20}Co_5$ ($x=0$, 10, 20, and 65) BMGs is shown in Fig. 1(a). The C_p of the BMGs with Ce is larger than that of the nonmagnetic La-based BMG ($x=0$) below 10 K. The superconducting transition of the La-based BMG can be seen by the jump in C_p at 3.2 K and was confirmed by the ρ measurement (Fig. 3). Above 3.2 K, C_p is well fitted by $C_p/T=\gamma+\beta T^2$, with $\gamma=3.44(14)$ mJ/mol K^2, which is close to that of many other metallic glasses.[17,18] However, for the BMGs with the Ce content of $x=10$, 20, and 65, the C_p at low T follows: $C_p/T=\gamma+\beta T^2$, with $\gamma=17.4(6)$, 38.4(5), and 127.3(5) mJ/mol K^2, respectively. The large γ value is markedly different from that of other metallic glasses.[17,18] The 4*f*-electron contribution to the C_p of the BMGs, C_{el}, normalized to a mole of Ce, was obtained by subtracting the C_p of the La-based glass [Fig. 1(b)]. The $\gamma(T)$ ($=C_{el}/T$) shows a large value at low T in Fig. 1(c). The values of γ at

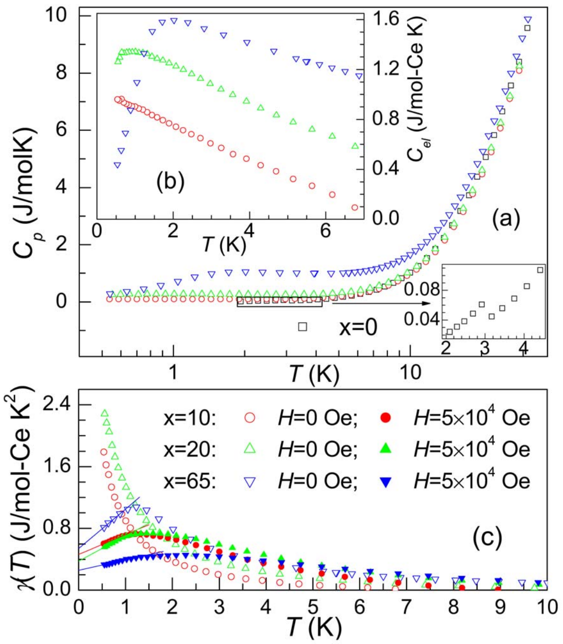

FIG. 1. (Color online) Specific heat C_p of the $Ce_xLa_{65-x}Al_{10}Cu_{20}Co_5$ BMGs ($x=0$, 10, 20, and 65). (a) C_p vs $\log_{10}(T)$ for the BMGs at $H=0$ Oe. (b) The 4f-electron specific heat C_{el} vs T of the BMGs at $H=0$ Oe. (c) The $\gamma(T)$ vs T of the BMGs at $H=0$ and 5×10^4 Oe (the solid lines are the linearly extrapolated results).

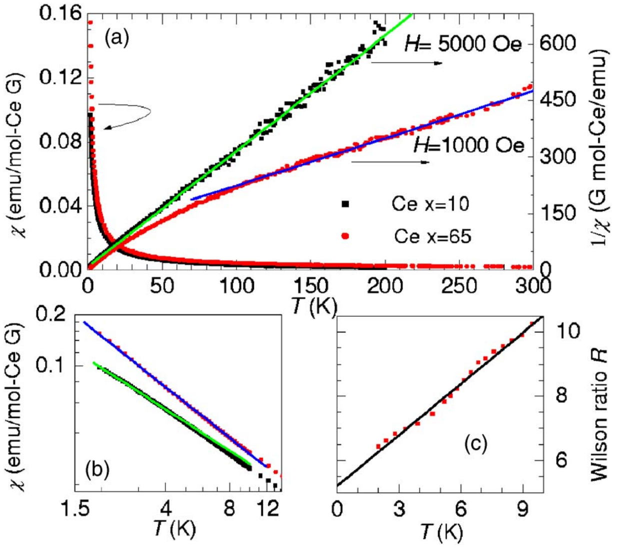

FIG. 2. (Color online) (a) The dc magnetic susceptibility χ for the $Ce_xLa_{1-x}Al_{10}Cu_{20}Co_5$ ($x=10$ and 65) BMGs. At high T, the χ exhibits the Curie-Weiss law (the solid line). (b) At low T, $\chi\propto T^{-1+\lambda}$ (the solid line). (c) The T-dependent Wilson ratio R of the BMG ($x=65$). The straight red line denotes the linear extrapolation.

0.53 K for the BMGs with $x=10$, 20, and 65 are 1789, 2282, and 811 mJ/mol Ce K^2, respectively. The presence of the enormous $\gamma(T)$ indicates that the BMGs behave as a HF alloy. A broad peak in C_{el}/T of the BMG ($x=65$), which is similar to that of the HF spin-glass compound URh_2Ge_2,[19] is observed around 1.2 K. The spin-glass-like effect at very low T in the heavy-fermion BMG is induced by the disordered arrangement of the localized moments in the high Ce-content glass. When the average distance between Ce atoms increases as the Ce content is decreased, the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction decreases markedly, and the BMGs with low Ce content show dominantly the HF behavior. The change of the low-T properties with Ce content (such as the increase in γ) is due to the competition between the Kondo effect and the RKKY interaction.

We measured the C_p of the glasses under the magnetic field of 5×10^4 Oe and linearly extrapolated the $\gamma(T)$ values to 0 K in Fig. 1(c). The extrapolated $\gamma(0\text{ K})$ values at $H=5\times10^4$ Oe are shown in Fig. 1(c). The $\gamma(0\text{ K})$ values of the glass ($x=65$) at 0 and 5×10^4 Oe are 540 and 258 mJ/mol Ce K^2, respectively. The glass ($x=10$) has the largest $\gamma(0\text{ K})$ (=464 mJ/mol Ce K^2) at 5×10^4 Oe. The large $\gamma(0\text{ K})$ remaining in the high magnetic field further confirms that the glasses are HF alloys, and the HF behavior can be tuned by the magnetic field.

The dc susceptibility χ of the Ce-based BMG ($x=10$ and 65) is shown in Fig. 2(a). In the glass with $x=65$, the Ce^{3+} moment obtained by the Curie-Weiss law, as shown in Fig. 2(a), is 2.53μ_B, which is very close to the free-ion value of 2.54μ_B. However, in the glass ($x=10$), the Ce^{3+} moment is only 1.61μ_B. The inverse χ decreases rapidly with decreasing T at low temperatures. As exhibited by the solid line in Fig. 2(b), the χ shows a behavior of $\chi\propto T^{1+\lambda}$ with $\lambda=0.0041(28)$ and 0.187(4) at low T for the $x=65$ and 10 glass, respectively, and is in agreement with the prediction of the Griffiths phase model, indicating that the HF systems show NFL behavior.[20,21]

The Wilson ratio R in HF systems is the relation between C_p and χ. $R=\frac{\pi^2 k_B^2 \chi T}{\mu_{\mathrm{eff}}^2 C_p}$, where k_B is the Boltzmann constant and g the Lande factor. The T-dependent R of the BMG ($x=65$) is shown in Fig. 2(c). R is about 5.2 at 0 K by the linear extrapolation and is much larger than the theoretically predicted value ($R=2$ in the spin-$\frac{1}{2}$ Kondo system[22,23]). Similarly, R is about 6.5 at 0 K for the $x=10$ glass. The large R value is also observed in other compounds such as CePtSi (Ref. 24) and $YbRh_2Si_2$.[25] Figure 3(a) shows T-dependent ρ of the BMGs ($x=65$, 20, 10, and 0). As in many other glassy alloys,[26] ρ of the BMGs exhibits a negative T coefficient in the high-temperature range. At low temperatures, ρ exhibits a minimum near 11 K, and then increases rapidly with decreasing T, which is markedly different from the behavior of other typical BMGs. With decreasing Ce content, the minimum of ρ moves to lower T and becomes less obvious. The ρ measurements of BMG ($x=65$) were extended to 56 mK in an adiabatic demagnetization cryostat [Fig. 3(b)]. The ρ of the glass ($x=65$) follows the ρ_0+AT^n behavior with $n=1.454(5)$ up to 56 mK, which deviates from the Fermi-liquid behavior ($n=2$).

The metastable state of metallic glasses can relax structurally to a more ordered state upon annealing below T_g.[12–17] The effect of structural disorder on the HF behavior of the BMG ($x=65$), characterized by the extrapolated $\gamma(0\text{ K})$ values of the annealed alloys, is shown in Fig. 4. The $\gamma(0\text{ K})$ value is sensitive to the degree of disorder in the glass and

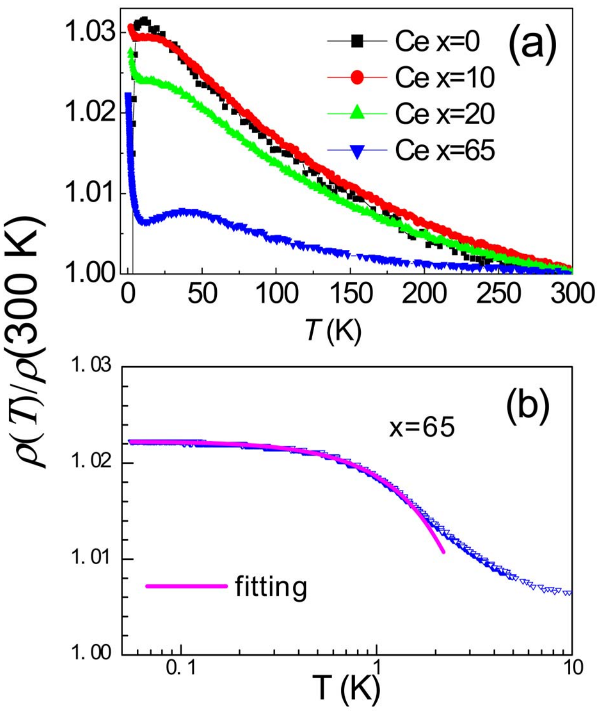

FIG. 3. (Color online) (a) The T-dependent ρ of the $\mathrm{Ce}_x\mathrm{La}_{65-x}\mathrm{Al}_{10}\mathrm{Cu}_{20}\mathrm{Co}_5$ ($x=0$, 10, 20, and 65) BMGs. (b) The T-dependent ρ of the BMG ($x=65$). The solid line denotes the fitting result of the BMG ($x=65$) by $\rho=\rho_0+AT^n$, with $n=1.454$.

decreases from 540 mJ/mol Ce K^2 for the as state to 431 mJ/mol Ce K^2 for the relaxed state (annealed for 90 h). The increase in the short- or medium-range ordering due to annealing below T_g results in the decrease in the $\gamma(0\text{ K})$ values. The degree of disorder is greatly diminished after crystallizing the alloy. The corresponding value of $\gamma(0\text{ K})$ of the crystallized state is much smaller than that of the glass state. Since the crystalline state is a mixture of several phases, it is not simple to explain the HF behavior in the crystalline state. The mixed crystalline phases themselves can have disorder especially in the boundaries between phases, which could be the reason for the HF behavior of the crystallized phases. Nevertheless, the experimental results suggest that the structural disorder enhances the HF behavior in the glass.

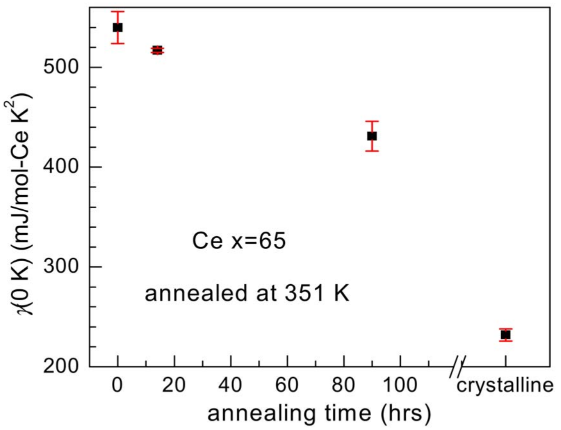

FIG. 4. (Color online) The linearly extrapolated $\gamma(0\text{ K})$ of the annealed $\mathrm{Ce}_{65}\mathrm{Al}_{10}\mathrm{Cu}_{20}\mathrm{Co}_5$ alloys ($H=0$ Oe).

It is widely recognized that the HF behavior occurs because of the competition between the Kondo resonance and magnetic ordering. The strength of the Kondo resonance depends on the energy levels of the f electrons. In a simple picture, the coupling constant Γ is given by $\Gamma = N(E_F)V^2/(E_f-E_F)$, where $N(E_F)$ is the Fermi density of states, V is the hopping matrix between the conduction band and the f level, E_f the energy of the f level, and E_F the Fermi energy.[2,3] The Kondo temperature is proportional to $\exp(-1/\Gamma)$.[2,3] In metallic glasses, the nearest-neighbor distance has a considerable distribution, as evidenced in the width of the pair-density function determined by x-ray or neutron scattering.[15] This variation results in the distribution in the local volume,[27] or atomic-level pressure,[28] which results in the distribution in the f levels, and thus the distribution of the local Γ factor. On the other hand, the magnetic interaction between the Ce spins on neighboring sites via the RKKY interaction is roughly proportional to Γ^2.[2,3] So when Γ is small, the RKKY interaction dominates, while when Γ is large the valence fluctuation destroys magnetic correlation. In the vicinity of the crossover at Γ_c, the HF behavior is observed.[2,3] Thus, when the f level of Ce is right at E_F, strong Kondo resonance overrides the RKKY interaction, while when it is far above or below E_F, the local Kondo resonance is weak and the RKKY interaction dominates. In other words, the distribution in the f level internally creates sites with valence fluctuation and the sites with well localized spin. The picture of distribution of f levels and wide range of Kondo resonances are very similar to the picture described by the Kondo disorder model described by Ref. 8.

Judging from the magnitude of the high-temperature magnetic moment, most of the f levels of the $x=65$ glass are below E_F, while some of the f levels of the $x=10$ glass are above E_F. This is consistent with the larger value of γ per Ce for the $x=10$ glass than for the $x=65$ glass, the spin-glass-like peak in χ of the $x=65$ glass, and the larger value of λ for the $x=10$ glass. Furthermore, structural relaxation will make the distribution of the f levels narrower.[16] For the $x=65$ glass, this means that most of the f levels will sink well below E_F and reduce the HF effect, as observed here. The relatively large values of the Wilson ratio can be explained by a large portion of the f levels that are well below E_F for all glasses. These f electrons are well localized and contribute much more to χ than to C_p.

In our view, the strong structural disorder that results in a wide distribution of the f levels of Ce is crucial in producing the observed complex HF behavior. The distributed f levels and the Fermi level within the band of f levels produces a wide range of strengths of the Kondo resonance and the coexistence of atomic sites in the valence fluctuation regime, the spin-glass sites dominated by the RKKY interaction, and the crossover sites that show the HF behavior. So far, the HF behavior is mainly observed in crystalline alloys with a low content of 4f-electron elements ($\leqslant 33$ at. %). In the Ce-based BMG, most of the 4f electrons are well above or below the Fermi level, with a relatively small fraction of them being close to the Fermi level and exhibiting the HF behavior. Because of this internal selection, this system is equivalent to the crystalline alloys with low f-electron concentration. While many experiments have shown that disorder is indeed a very important factor in bringing about the HF behavior, it has been difficult to determine experimentally the role of the structural disorder in the HF compounds. The results in the BMGs with a strong and tunable structural disorder demonstrate that the interplay between $4f$ electrons and conduction electrons can be tuned by the structural disorder. Along this idea, other HF alloys containing rare-earth elements might be developed.

In summary, we find that the bulk metallic glasses with an inherent and strong structural disorder showing the HF behavior and their HF behavior can be tuned by the composition, magnetic field, and structural relaxation. These HF glasses show NFL behavior and a large Wilson ratio. We propose that the intrinsic structural disorder is crucial to the HF behavior in the glass. The detailed theoretical understanding of the role of structural disorder in HF remains a challenge.

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